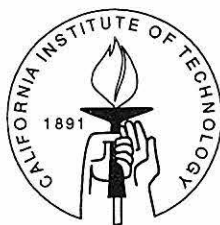


Surface Chemical Analysis Using Reflection Electron Energy Loss Spectrometry During Molecular Beam Epitaxy

Thesis by
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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy



Pasadena, California

1996

(Submitted June 28, 1995)

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Acknowledgements

My deepest gratitude goes to my advisor, Dr. Harry Atwater. His abundant enthusiasm for science and bottomless well of scientific ideas have been an inspiration. I gratefully acknowledge his constant support and encouragement which have seen me through graduate school; they were especially instrumental in times of frustration.

I am indebted to Dr. Channing Ahn for graciously spending copious amounts of time indoctrinating me to the fine art of electron energy loss spectrometry. His pedagogical manner and willingness to go one step beyond the call of duty in providing assistance in learning are greatly appreciated.

I thank Dr. Shouleh Nikzad for taking me under her wing when I first joined the Atwater group, for her scientific supervision, and for her companionship while she was here (she is now at JPL). I wish to thank her again for staying up all night with me while I was preparing for my first conference presentation, and for her continuing encouragement.

I wish to thank Gang He for being tremendously helpful in many ways. He provided me with his expertise in C++ programming, had useful comments and suggestions about virtually everything I asked him about in the lab, and most recently, spent unconventional hours of the day working with me on the MBE chamber. He always did all of these things happily and with a smile.

Numerous other people have provided me with friendship and technical assistance which have benefited me. These include Renato Camata, Imran Hashim, Ramana Murty, Hyun Joo, Masashi Fukazawa, Kyu Min, Kirill Shcheglov, Heather Frase, and Maggie Taylor. I thank Jimmy Yang for all the computer-related help, and Ruth Brain for her late-night companionship while we were both writing our theses. I also wish to acknowledge Torrey Lyons, Deepto Chakrabarty, Aaron Gillespie, Stephanie Leifer, and Aimee Smith, all of whom I have gathered inspiration from, in various forms.

I wish to acknowledge the untiring moral support remotely given to me (mostly electronically) by folks at the U. S. Naval Research Laboratory, to whom I have grown quite emotionally attached; these include Catherine Cotell, Paul Dorsey, Doug Chrisey, Jim Horwitz, and Ray Auyeung.

I thank Dale Capewell for his companionship and for his wisdom and strength and unbending integrity, which have moved me greatly in the last several years. I thank my parents for being encouraging and supportive throughout my graduate school years; in fact, throughout my entire life.

Abstract

This thesis demonstrates for the first time the versatility of a recently developed surface chemical analysis technique, reflection electron energy loss spectrometry (REELS) of RHEED electrons, for gleanng quantitative surface structural and compositional information *during* molecular beam epitaxial (MBE) growth. In REELS, a component of the scattered RHEED beam is allowed to pass through a small aperture in the RHEED screen and is energy analyzed. The energy losses of the incident electrons are characteristic of inner-shell core electron ionizations of the target material.

We have employed REELS to determine the chemical composition of $\text{Ge}_x\text{Si}_{1-x}$ alloys, by using empirical cross sections and by comparing the signal intensities of the Ge $L_{2,3}$ and Si $L_{2,3}$ core loss intensities. Compositional analysis by REELS was found to agree well with compositional determinations made by Rutherford backscattering spectrometry.

Fabrication of device-quality epitaxial semiconductors with no defects requires that the starting substrate be atomically clean. Thus it is desirable to directly determine *in situ* that a substrate surface is clean on the atomic level prior to epitaxial growth. We have performed REELS measurements of the carbon K edge on HF/ H_2O -dipped substrates prebaked at 200 °C for one hour and found that physisorbed hydrocarbons desorb from the surface during this prebake, rendering the surface clean and ready for growth. We have also performed the first time- dependent measurements on hydrocarbon desorption from the Si(100) surface during a low-temperature substrate cleaning.

The ability to determine local order structural and chemical information is useful in learning about the evolution of thin film microstructure. The REELS spectrum contains extended-edge energy loss fine structure (EXELFS) which can provide local order information in condensed matter. We have performed EXELFS analysis on thin monolayers of Sn adsorbed on hydrogen-terminated Si(100) and discovered a

(3×1) Sn-induced reconstruction of the Si surface. REELS EXELFS analysis of dilute SnGe alloys has provided insight on the local surface structure of this material, which, combined with long-range structure information, demonstrate the ability for surface structure determination of reconstructions and adsorbed films.

Lastly, we have successfully designed and demonstrated the viability of a parallel-detection REELS spectrometer, which is capable of very high data rate, high dynamic range, superior sensitivity, and resistance to mechanical and electromagnetic noise, while affording data acquisition times 50 times to several thousand times smaller than has previously been achieved with serial-detection REELS. Parallel REELS has great potential to be a novel diagnostic tool for real-time monitoring of complex dynamic processes in the MBE environment.

List of Publications

1. "Real-Time *In Situ* Analysis of $\text{Ge}_x\text{Si}_{1-x}$ Alloy Composition Using Parallel-Detection Reflection Electron Energy Loss Spectrometry (PREELS)," S. S. Wong, C. C. Ahn, Gang He and H. A. Atwater, to be submitted to *Appl. Phys. Lett.*
2. "Analysis of Surface Roughness of Silicon(001) Surfaces by Reflection Electron Energy Loss Spectroscopy," H. N. Frase, S. S. Wong, C. C. Ahn and H. A. Atwater, to be submitted to *Appl. Phys. Lett.*
3. "Local Order Measurement on SnGe Alloys and Monolayer Sn Films on Si With Reflection Electron Energy Loss Spectrometry," S. S. Wong, G. He, S. Nikzad, C. C. Ahn, and H. A. Atwater, *J. Vac. Sci. Technol. A* **13**(2), 216 (1995).
4. "Analysis of Surface Roughness of Silicon (001) Surfaces by Reflection Electron Energy Loss Spectroscopy," H. N. Frase, S. S. Wong, C. C. Ahn and H. A. Atwater; submitted to *J. Vac. Sci. Technol.*
5. "Analysis of Monolayer Films During Molecular Beam Epitaxy by Reflection Electron Energy Loss Spectroscopy," H. A. Atwater, S. S. Wong, C. C. Ahn, S. Nikzad and H. N. Frase, *Surf. Sci.* **298**, 273-283 (1993).
6. "*In Situ* Reflection Electron Energy Loss Spectroscopy Measurements of Low Temperature Surface Cleaning for Si Molecular Beam Epitaxy," S. Nikzad, S. S. Wong, C. C. Ahn, A. L. Smith and H. A. Atwater, *Appl. Phys. Lett.* **63**(10), 1414 (1993).
7. "*In Situ* Analysis of Surface Contaminant Desorption During Low-Temperature Silicon Substrate Cleaning Using Reflection Electron Energy Loss Spectrometry," S. S. Wong, S. Nikzad, C. C. Ahn, A. L. Smith and H. A. Atwater, *Mat. Res. Soc. Symp. Proc.* **259**, 449-454 (1992).

Contents

Acknowledgements	iii
Abstract	v
List of Publications	vii
1 Introduction	1
1.1 Beam-solid interactions	1
1.2 Theory of high-energy scattering	2
1.2.1 Differential cross section in first Born approximation	2
1.2.2 Generalized oscillator strength and relation to photoabsorption	5
1.2.3 The case of ionization	7
1.2.4 Some considerations	7
1.3 Molecular beam epitaxy and <i>in situ</i> characterization with RHEED	10
1.3.1 Fundamentals of MBE	10
1.3.2 Reflection high energy electron diffraction (RHEED)	13
2 Reflection Electron Energy Loss Spectrometry (REELS)	21
2.1 Overview of technique	21
2.2 REELS instrumentation	23
2.3 Obtaining and interpreting a REELS spectrum	26
2.3.1 Partial cross sections	26
2.3.2 Empirical cross sections	26
2.3.3 Hydrogenic vs. Hartree-Slater cross sections	27
2.3.4 The REELS spectrum	27
2.4 Other analysis techniques used	31
2.4.1 X-ray photoelectron spectroscopy (XPS)	31

2.4.2	Rutherford backscattering spectrometry (RBS)	34
2.5	Still other analytical techniques	34
2.5.1	Auger electron spectroscopy (AES)	34
2.5.2	Secondary ion mass spectrometry (SIMS)	35
2.5.3	Ellipsometry	36
2.6	REELS analysis of $\text{Ge}_x\text{Si}_{1-x}$ alloys	36
2.6.1	Background investigations	38
2.6.2	A new twist	38
2.6.3	Discussion	41
2.7	Summary	43
3	Surface Contaminant Detection and Time-Dependent Measurements of Hydrocarbon Desorption	47
3.1	Introduction	47
3.2	Background	49
3.2.1	Silicon bonds with common elements	49
3.2.2	Hydrogen termination of the Si surface	49
3.3	Experimental	50
3.3.1	Surface preparation methods	50
3.3.2	Empirical cross sections	52
3.3.3	Results	54
3.4	Discussion	62
3.5	Summary	65
4	Investigation of Short-Range Surface Order With REELS EXELFS	68
4.1	Introduction	68
4.2	Overview of EXELFS	69
4.2.1	Qualitative description	69
4.2.2	Quantitative description	72
4.2.3	Data processing	75
4.2.4	Problems and their resolutions	77

4.3	Monolayer Sn films on Si(100)	81
4.4	SnGe alloys	88
4.5	Summary	92
5	High-speed parallel-detection REELS and real time <i>in situ</i> monitoring	97
5.1	Introduction	97
5.2	Instrumentation	99
5.2.1	Overview	99
5.2.2	Magnetic quadrupole lenses	99
5.2.3	Phosphor screen	103
5.2.4	Optical lens	104
5.2.5	CCD array detector	104
5.3	Parallel REELS data processing	105
5.4	Overall energy resolution of parallel REELS	106
5.5	Real-time monitoring of the SiGe heterostructure system	107
5.5.1	Experimental	107
5.5.2	Discussion	111
	Appendix A. Details of the serial REELS instrumentation	114
	Appendix B. Source code for EXELFS analysis with relaxed knot constraints	136

List of Figures

1.1	Beam-solid interactions	2
1.2	Schematic diagram illustrating the main scattering parameters.	3
1.3	Variation of q_{min} for different primary energies E_p vs. energy loss	9
1.4	Schematic of typical MBE system	11
1.5	Reciprocal space for a 2-dimensional surface net	15
1.6	Intersection of Ewald sphere in LEED and RHEED	16
1.7	RHEED patterns of the unreconstructed (1×1) and (2×1) Si(100) surface	17
2.1	Photograph of REELS system	22
2.2	Schematic of REELS system.	23
2.3	Schematic of double rocking configuration	24
2.4	Photograph of RHEED beam scattering from sample at grazing incidence and the resulting RHEED pattern	25
2.5	Hydrogenic cross sections for Si K , C K and O K	28
2.6	Typical REELS spectrum	29
2.7	Illustration of the low loss region of a REELS spectrum for shallow and steep incidence of the RHEED beam	30
2.8	Typical transmission EELS spectrum	30
2.9	Schematic of the physical mechanisms behind the techniques of XPS and AES	32
2.10	Schematic of XPS instrumentation	33
2.11	Illustration of typical ellipsometry setup	37
2.12	REELS core loss intensities of Ge $L_{2,3}$ and Si K for various alloy compositions	39
2.13	Calculated ionization cross sections for Ge $L_{2,3}$ and Si $L_{2,3}$	39

2.14	Schematic of representative $\text{Ge}_x\text{Si}_{1-x}$ alloys studied	40
2.15	Typical background-subtracted Si $L_{2,3}$ and Ge $L_{2,3}$ core loss intensities	41
3.1	Hydrogen termination of the Si(100) surface	51
3.2	Si(100) surface preparation methods	52
3.3	Hydrogenic ionization cross sections for Si $L_{2,3}$, C K and O K	53
3.4	REELS spectra from C and O reference samples	55
3.5	REELS data from HF/ H_2O -dipped Si(100)	57
3.6	Second difference of C K intensities at various temperatures	59
3.7	Carbon coverage on Si substrate vs. position	61
3.8	Time-dependent C coverage on Si surface at 115 °C	62
3.9	Time-dependent C coverage on Si surface at 175 and 150 °C	63
4.1	Schematic of fine structure features in typical absorption spectrum	70
4.2	Schematic of backscattering of electron waves	71
4.3	Example of polynomial spline fit to core loss data	76
4.4	Multiple scattering processes in the forward direction	80
4.5	RHEED pattern from the Si(100) (3×1) surface	81
4.6	Sn $M_{4,5}$ intensity and $\chi(k)$ from 1.9 ML Sn/Si(100)	84
4.7	EXELFS obtained from Si $L_{2,3}$ intensity from Si(100)	85
4.8	RDF of 1.9 ML Sn/Si(100) and comparison with Si(100)	86
4.9	RDF derived from Si K edge obtained by transmission EXELFS	87
4.10	Schematic of 1.9 ML Sn/Si(100) surface structure	88
4.11	Surface phase diagram of Sn/H-terminated Si(100)	89
4.12	EXELFS obtained from Sn $M_{4,5}$ intensity from dilute SnGe alloys	90
4.13	RDF of $\text{Sn}_{0.2}\text{Ge}_{0.8}$ and $\text{Sn}_{0.01}\text{Ge}_{0.99}$	91
4.14	Schematic of structure of dilute SnGe alloy	92
4.15	Expected and observed neighbor distances for Sn, Ge and SnGe	93
5.1	Schematic diagram of the parallel REELS assembly	100
5.2	Photograph of the parallel REELS instrumentation	101

5.3	Photograph of magnetic lens system employed in the parallel REELS assembly	102
5.4	Schematic of the action of the quadrupole lenses	103
5.5	Schematic of CCD chip and method of data transfer	105
5.6	Schematic diagram of the superlattice studied with parallel-detection REELS	108
5.7	Photograph of RHEED pattern during $\text{Ge}_x\text{Si}_{1-x}$ heterostructure growth	109
5.8	Photograph of electron dispersion imaged by parallel REELS	109
5.9	Background-subtracted Ge $L_{2,3}$ core loss intensities for several $\text{Ge}_x\text{Si}_{1-x}$ alloys, measured with PREELS with 2 sec and 20 sec data acquisition times	110

List of Tables

2.1	Comparison of REELS composition analysis results with results obtained by RBS	42
2.2	Comparison of REELS with more widely used materials analysis techniques	44
3.1	Surface carbon concentrations found by REELS	56

Chapter 1 Introduction

1.1 Beam-solid interactions

Collimated, highly monoenergetic beams of particles or electromagnetic radiation are widely used to probe target materials in order to glean information about the target. Scattering of such a beam of x rays or electrons provides crystallographic structure analysis of atomically-ordered materials. The experiment on alpha-particle scattering from a gold foil by Geiger and Marsden (1909) led Rutherford in 1911 to deduce that the frequent occurrence of large-angle scatters must be due to the presence of a very concentrated region of positive charge, or the nucleus, of the gold atoms. In the regime of high-energy particle physics, beams of electrons and protons are used in deep inelastic scattering investigations of nucleon structure.

When a beam of particles or radiation impinges upon a sample of target material in a condensed phase, the scattering events that occur may take various pathways (see Figure 1.1). Possible outcomes include: transmission of incident beam with no energy loss or deviation from original trajectory; elastic scattering of transmitted beam; sample heating due to transfer of energy from the incident beam to the sample during inelastic scattering; and x-ray emission resulting from decay of excited states. Beam diffraction can occur if the target is crystalline. In addition, electrons may be ejected as a result of atomic ionization by the incident beam. The distribution of ejected electrons with respect to their kinetic energy and ejection angle yields a wealth of information about the target material. This is the basis for x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), two conventional surface chemical analysis tools which are currently widely used and will be discussed at greater length in Chapter 2. Finally, analysis of the outcoming primary probe beam also yields a veritable storehouse of data about the target material, as will be demonstrated for *in situ* reflection electron energy loss spectrometry (REELS), a spectroscopic analysis

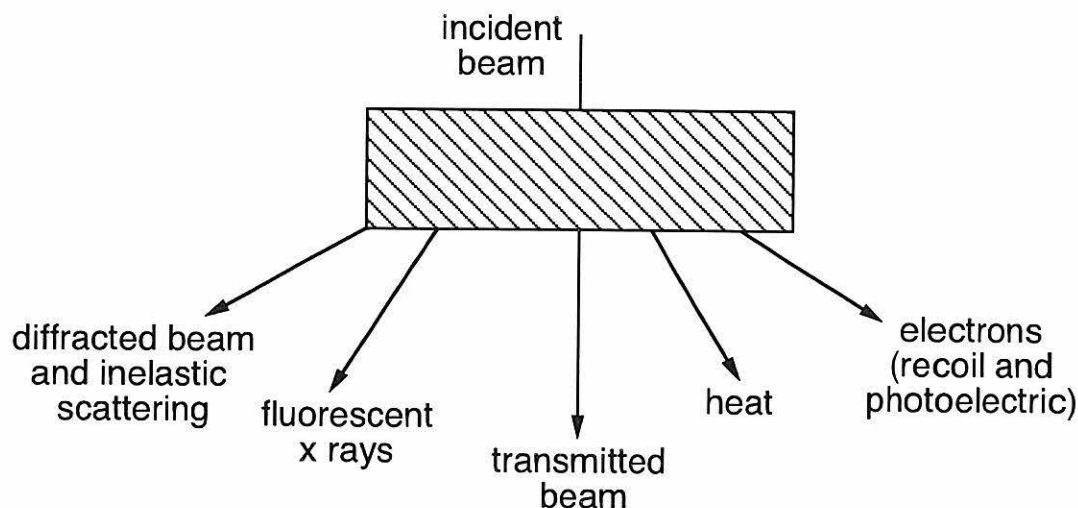


Figure 1.1: Various beam-solid interactions may take place when an energetic beam is incident upon a target sample, with a number of possible results.

applied in this thesis to the case of a strongly forward scattered electron beam at ~ 30 keV energies, on Group IV semiconductor thin films deposited by molecular beam epitaxy.

1.2 Theory of high-energy scattering

1.2.1 Differential cross section in first Born approximation

Important in any investigations of scattering is the concept of a differential scattering cross section. The differential scattering cross section, $d\sigma/d\Omega$ (where $d\Omega$ is the solid angle element, e.g., $\sin\theta d\theta d\phi$ in spherical coordinates) of a target atom for scattering an incident particle through an angle θ (the “scattering angle”) into solid angle element $d\Omega$ centered around θ is defined

$$\frac{d\sigma}{d\Omega} = \frac{\text{Number of particles scattered into } d\Omega}{\text{Total number of particles} \cdot d\Omega \cdot N_{el}} \quad (1.1)$$

where N_{el} is the number of target atoms per unit area of a given element. Figure 1.2 illustrates the generic scattering geometry.

We are concerned with the scattering of fast electrons. The definition of “fast” is

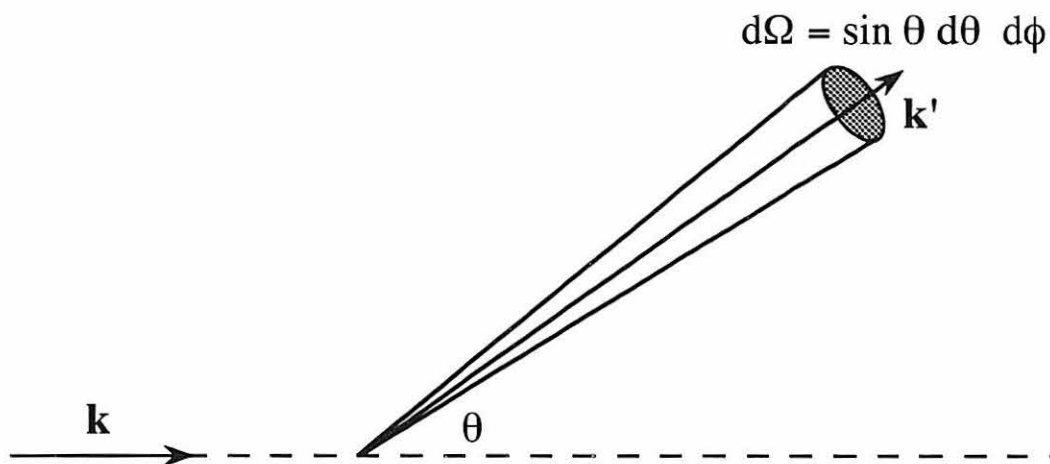


Figure 1.2: Schematic diagram illustrating the main scattering parameters.

determined by comparison of the velocity of incident electrons with the mean orbital velocity of atomic electrons in the target material, for example, the Fermi velocity in solids. In the following discussion, the fast electron has velocity v , mass M_1 , and charge $-e$. It collides with a stationary target atom of mass M_2 in an initial state Ψ_0 , and is deflected into solid angle element $d\Omega$ along the direction specified by the polar angle θ and azimuthal angle ϕ (measured in the center-of-mass frame of reference). As a result of this collision, the target atom undergoes a transition to state Ψ_n , which can be either discrete or continuum.

For the fast electron, let us denote

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \text{initial state} \quad (1.2)$$

and

$$e^{i\mathbf{k}'\cdot\mathbf{r}} = \text{final state}, \quad (1.3)$$

and for the atom, let us denote $u_0(\mathbf{r}_1, \dots, \mathbf{r}_Z)$ and $u_n(\mathbf{r}_1, \dots, \mathbf{r}_Z)$ as the initial and final atomic wave functions, respectively, in the coordinates $\mathbf{r}_1, \dots, \mathbf{r}_Z$ of the atomic electrons, whose total number is Z . The matrix element of the interaction V connecting

the final and initial states is

$$\langle e^{i\mathbf{k}'\cdot\mathbf{r}} u_n^* | V | e^{i\mathbf{k}\cdot\mathbf{r}} u_0 \rangle = \int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u_n^* V u_0 d\mathbf{r}_1 \cdots d\mathbf{r}_Z, \quad (1.4)$$

where

$\mathbf{r}$ = position of fast electron relative to center of atom,

$\mathbf{k}, \mathbf{k}'$ = initial and final momenta of fast electron,

$\mathbf{q} = \mathbf{k} - \mathbf{k}'$ = momentum transfer/ $\hbar$.

The differential cross section takes the form [1]

$$d\sigma_n = \frac{M^2}{4\pi^2\hbar^4} \frac{k'}{k} \left| \int e^{i\mathbf{q}\cdot\mathbf{r}} u_n^*(\mathbf{r}_1, \dots, \mathbf{r}_Z) V u_0(\mathbf{r}_1, \dots, \mathbf{r}_Z) d\mathbf{r}_1 \cdots d\mathbf{r}_Z d\mathbf{r} \right|^2 d\Omega \quad (1.5)$$

with M being the reduced mass $M_1 M_2 / (M_1 + M_2)$. Because the electron mass is much smaller than all atomic masses, the reduced mass is, for all practical purposes, simply replaced by the electronic mass, m .

The incident fast electron provides a Coulombic perturbation interaction potential:

$$V = \sum_{j=1}^Z \frac{e^2}{|\mathbf{r} - \mathbf{r}_j|} - \frac{Z_N e^2}{r}. \quad (1.6)$$

The first term represents the repulsive interaction of the fast electron with the atomic electrons, while the second term represents the interaction of the incident electron with the nucleus of Z protons, and is attractive. Making use of the relation

$$\int \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{|\mathbf{r} - \mathbf{r}_j|} d\mathbf{r} = \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot\mathbf{r}_j}, \quad (1.7)$$

the differential cross section becomes

$$d\sigma_n = \frac{m^2}{4\pi^2\hbar^4} \frac{k'}{k} \left| \int e^{i\mathbf{q}\cdot\mathbf{r}} u_n^* \left(\sum_{j=1}^Z \frac{e^2}{|\mathbf{r} - \mathbf{r}_j|} - \frac{Z_N e^2}{r} \right) u_0 d\mathbf{r}_1 \cdots d\mathbf{r}_Z d\mathbf{r} \right|^2 d\Omega \quad (1.8)$$

$$= \frac{m^2}{4\pi^2\hbar^4} \frac{k'}{k} (e^4) \left| \int \sum_{j=1}^Z \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{|\mathbf{r} - \mathbf{r}_j|} u_n^* u_0 d\mathbf{r}_1 \cdots d\mathbf{r}_Z \right|^2 d\Omega \quad (1.9)$$

$$= 4 \frac{(me^2)^2}{\hbar^4} \frac{k'}{k} \frac{1}{q^4} \left| \int u_n^* \sum_{j=1}^Z e^{i\mathbf{q}\cdot\mathbf{r}_j} u_0 d\mathbf{r}_1 \cdots d\mathbf{r}_Z \right|^2 d\Omega \quad (1.10)$$

$$= 4 \frac{(me^2)^2}{\hbar^4} \frac{k'}{k} \frac{1}{q^4} |V_{fi}|^2 d\Omega, \quad (1.11)$$

where

$$V_{fi} \equiv \int u_n^* \sum_{j=1}^Z e^{i\mathbf{q}\cdot\mathbf{r}_j} u_0 d\mathbf{r}_1 \cdots d\mathbf{r}_Z = \left\langle u_n \left| \sum_{j=1}^Z e^{i\mathbf{q}\cdot\mathbf{r}_j} \right| u_0 \right\rangle. \quad (1.12)$$

Equality 1.9 is due to the orthogonality of the states Ψ_n and Ψ_0 , and Equality 1.10 is obtained by use of Equation 1.7.

We will consider the case for which atomic orientations in the target material are random; thus $d\sigma_n$ is independent of ϕ . This is equivalent to averaging $d\sigma_n$ over all atomic orientations. Using $d\Omega = 2\pi \sin\theta d\theta$ and transforming to a differential in q , $d\sigma_n$ becomes

$$d\sigma_n = 4 \frac{(me^2)^2}{\hbar^4} \frac{k'}{k} \frac{1}{q^4} |V_{fi}|^2 \left(2\pi \frac{q}{k'k} dq \right) \quad (1.13)$$

$$= \frac{8\pi}{k^2} \frac{(me^2)^2}{\hbar^2} \frac{1}{q^3} |V_{fi}|^2 dq, \quad (1.14)$$

where q is now a scalar: $q = |\mathbf{k} - \mathbf{k}'|$.

1.2.2 Generalized oscillator strength and relation to photoabsorption

Instead of the differential cross section, a quantity known as the generalized oscillator strength (GOS) is more often used, because an analog can be made with the dipole oscillator strength for optical absorption. The GOS is denoted $f_n(q)$, where

$$f_n(q) = \frac{E_n}{Q} |V_{fi}|^2, \quad (1.15)$$

where $Q = (\hbar q)^2/2m$ (m is the electron mass) and E_n is the energy of the atomic electron involved in the transition. Consider the exponential in V_{fi} in the small q limit (limit of small momentum transfer):

$$\begin{aligned} e^{iqr_j} &= 1 + iqr_j + \frac{1}{2!}(iqr_j)^2 + \dots \\ &\rightarrow 1 + iqr_j \quad (\text{for } q \text{ small}) \end{aligned}$$

Thus

$$V_{fi} \simeq \int u_n^* \sum_{j=1}^Z (1 + iqr_j) u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z \quad (1.16)$$

$$= \int u_n^* \sum_{j=1}^Z u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z + \int u_n^* \sum_{j=1}^Z (iqr_j) u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z \quad (1.17)$$

$$= 0 + \int u_n^* \sum_{j=1}^Z iqr_j u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z \quad (1.18)$$

since the first term in Equation 1.17 is zero due to orthogonality of atomic eigenfunctions. With the definitions of the Bohr radius, $a_0 = \hbar^2/me^2$, and the Rydberg constant, $R = me^4/2\hbar^2$, we obtain in the small q limit:

$$\begin{aligned} f_n(q) &\rightarrow \frac{E_n}{Q} \left| \int u_n^* \sum_{j=1}^Z (iqr_j) u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z \right|^2 \\ &= \frac{E_n}{R} \frac{1}{q^2 a_0^2} \left| \int u_n^* \sum_{j=1}^Z (qr_j) u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z \right|^2 \\ &= \frac{E_n}{Ra_0^2} \left| \int u_n^* \sum_{j=1}^Z r_j u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z \right|^2. \end{aligned} \quad (1.19)$$

Comparing with the optical (dipole) oscillator strength [1]

$$f_n = \frac{E_n}{Ra_0^2} \left| \int u_n^* \sum_{j=1}^Z r_j u_0 d\mathbf{r}_1 \dots d\mathbf{r}_Z \right|^2, \quad (1.20)$$

we see that

$$f_n(q) \longrightarrow f_n \quad \text{as } q \rightarrow 0, \quad (1.21)$$

i.e., the generalized oscillator strength approaches the dipole oscillator strength in the limit of zero momentum transfers, or equivalently in the limit of forward scattering. In fact, electron energy loss spectra taken at small scattering angles and at incident kinetic energies much higher than the excitation energies involved have generally been found to agree quite well with photoabsorption spectra of the same molecule [2].

1.2.3 The case of ionization

Thus far our treatment has been for excitation to a discrete state. For excitation of an atomic electron to a continuum of states (for example, valence states), i.e., ionization, the density of accessible final states, *density* of the differential cross section, or $d\sigma/d\Omega$ per unit energy range, and the *density* of the GOS per unit energy range, are used:

$$\frac{df(q, E)}{dE} = \frac{E}{R} \frac{1}{q^2 a_0^2} \sum_{QN} |V_{fi}^{E, QN}(q)|^2; \quad (1.22)$$

$$V_{fi}^{E, QN}(q) = \left\langle \Psi_{E, QN} \left| \sum_{j=1}^Z e^{i\mathbf{q} \cdot \mathbf{r}_j} \right| \Psi_0 \right\rangle, \quad (1.23)$$

where the final continuum state is specified by E and a set QN of all the other quantum numbers (e.g., angular momentum). Then,

$$\frac{df(q, E)}{dE} = \sum_n \frac{E_n}{R} \frac{1}{q^2 a_0^2} |V_{fi}^{E, QN}(q)|^2 \delta(E_n - E). \quad (1.24)$$

The integrated cross section is obtained by integrating the differential cross section over all kinematically possible momentum transfers q and over the continuum energies E .

1.2.4 Some considerations

Although all of the above discussion has been for an incident electron scattering from an atom, in principle it is applicable to scattering from target molecules or solids (or target molecules in solids) as well. In specifying the initial and final states it is necessary to specify all the quantum numbers that describe the molecular or solid

states (electronic, vibrational, and rotational levels). Typically, rotational states have very small energy spacings (smaller than kT at room temperature) and are effectively degenerate. One can treat molecular rotation as slow compared to the collision duration, and average over all possible initial and final rotational states.

The first Born approximation involves only the leading term in the Born expansion of the scattering amplitude. It is natural to inquire about the limitations of this approximation. We will briefly consider several major concerns here: electron exchange effects, relativistic effects, and the validity of the Born approximation (also called the dipole approximation) in inelastic scattering.

First, if the incident particle is an electron, it will be indistinguishable from atomic electrons and the system will be subject to electron exchange effects. In principle, these effects will be appreciable only for the cases in which the momentum transfer involved is much greater than the binding energy of atomic electrons [1]. Since we are dealing with collisions of fast electrons, exchange effects are not important here.

Second, the derivation of the differential cross section and generalized oscillator strength has been done for nonrelativistic particles. At what incident energy does the electron velocity cease to be nonrelativistic? Let us designate $\frac{v}{c} \approx 1$ to be relativistic. An electron with an energy of 30 keV has a velocity of $\simeq c/3$, within the classical regime. The GOS data of Geiger [3] confirm the validity of the first Born approximation at 25 keV. Indeed, measurements of He excitations by Chamberlain, Mielczarek and Kuyatt [4] and Bromberg [5] suggest that an asymptotic approach within 1% of the first Born approximation occurs around an incident energy of 1 keV. Thus, relativistic effects are also not important here.

We consider the implications of the Born approximation, which assumes $\mathbf{q} \cdot \mathbf{r} \ll 1$. Simple considerations yield the minimum momentum transfer,

$$q_{min} = |\mathbf{k}_i| - |\mathbf{k}_f| \quad (1.25)$$

which corresponds to inelastic forward scattering ($\theta = 0$). Fig. 1.3 shows the q_{min} variation with energy loss for various incident beam energies. For electrons ejected

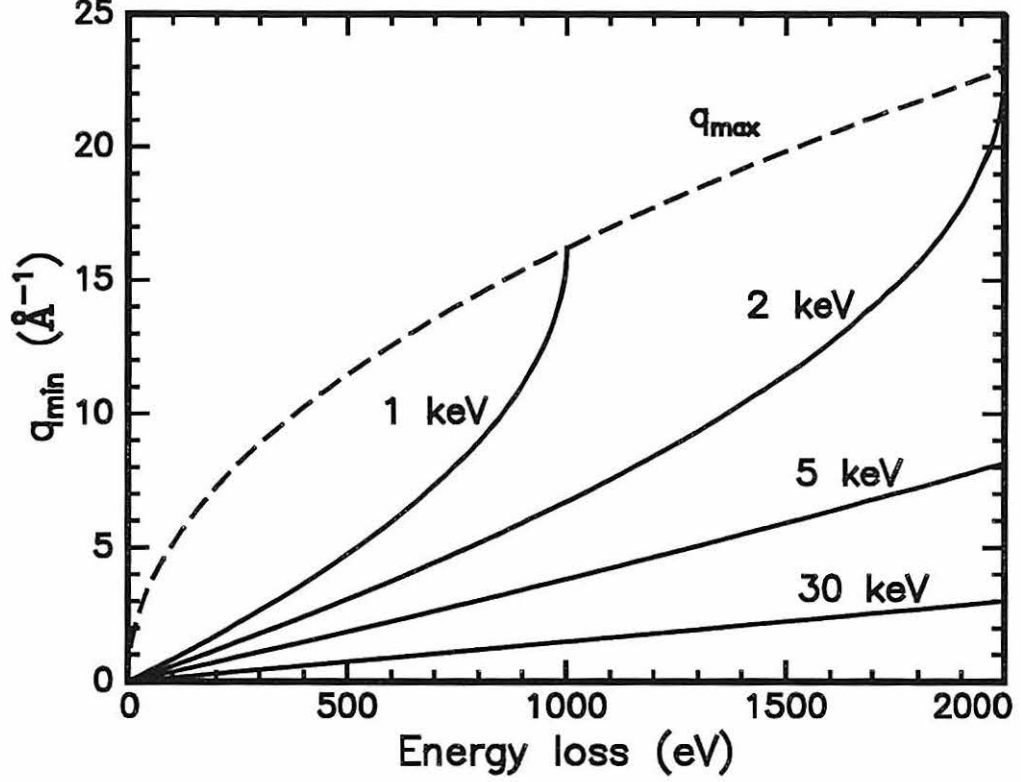


Figure 1.3: Variation of q_{min} for different primary energies E_p as a function of energy loss.

from outer shells (e.g., $3p$ orbital), qr can range from 0.1–0.7, so that the Born approximation holds reasonably well and the matrix element in the scattering amplitude has the form

$$V_{fi} \propto \langle \Psi_f | e^{i\mathbf{q} \cdot \mathbf{r}} | \Psi_i \rangle \cong \langle \Psi_f | \mathbf{q} \cdot \mathbf{r} | \Psi_i \rangle. \quad (1.26)$$

However, for deeper core losses such as the L_1 ($2s$) or K ($1s$), the momentum transfer is significantly greater, and the exponential $\exp(i\mathbf{q} \cdot \mathbf{r})$ can no longer be approximated by the dipole term $\mathbf{q} \cdot \mathbf{r}$ because the higher-order multipole transitions will be non-negligible. In practice, it is found that the main contribution to inelastic scattering comes from the dipole term, and higher-order transitions are in general detectable only when the dipole transition is forbidden or when the density of states is high for a multipole transition, as is true for the $s \rightarrow d$ transitions of the L_1 edge [6].

These observations can be understood by considering the generalized oscillator

strength,

$$GOS = \frac{2m\Delta E}{\hbar^2 q^2} \sum_{\ell'} \left| \langle \epsilon, \ell' | e^{i\mathbf{q}\cdot\mathbf{r}} | n, \ell \rangle \right|^2, \quad (1.27)$$

where ϵ is the energy of the ejected electron above the edge and ℓ' is the angular momentum of the continuum final states. Natoli and Benfatto [7] have computed the GOS for the Si K edge as a function of q , and found that the main contribution ($> 90\%$) to the GOS comes from the dipole term. Surprisingly, this is true even if the incident beam energy is comparable to the energy loss. In general, however, the dipole approximation is better justified with increasing incident energies.

1.3 Molecular beam epitaxy and *in situ* characterization with RHEED

1.3.1 Fundamentals of MBE

Molecular beam epitaxy (MBE) is a versatile deposition technique used for growing thin epitaxial films of semiconducting, metallic, or insulating materials. The word “epitaxy” is derived from the Greek *epi*, “on,” and *taxis*, “order, arrangement.” Epitaxial films are highly ordered, or arranged, on a substrate material and assume the crystallographic structure that comprises its minimum-energy configuration. The pioneer of MBE is Alfred Y. Cho, who developed the technique and transformed it from a seemingly esoteric process into one of tremendous scientific and technological significance. MBE is, in its simplest definition, a refined form of evaporation in vacuum. Growth rates range from a few monolayers (ML) per second to a few tens of ML per hour; thus deposition can be slow enough to permit precise control of the growth process. This precise control is the basis of films for devices with exceptional electrical, optical, and other properties which are very sensitive to interface roughness, impurity dopant concentrations, and alloy composition. For example, the novel electrical properties of buried, ordered monolayers of boron in Si(100) and Si(111) [8] are a result of successful delta-doping by MBE.

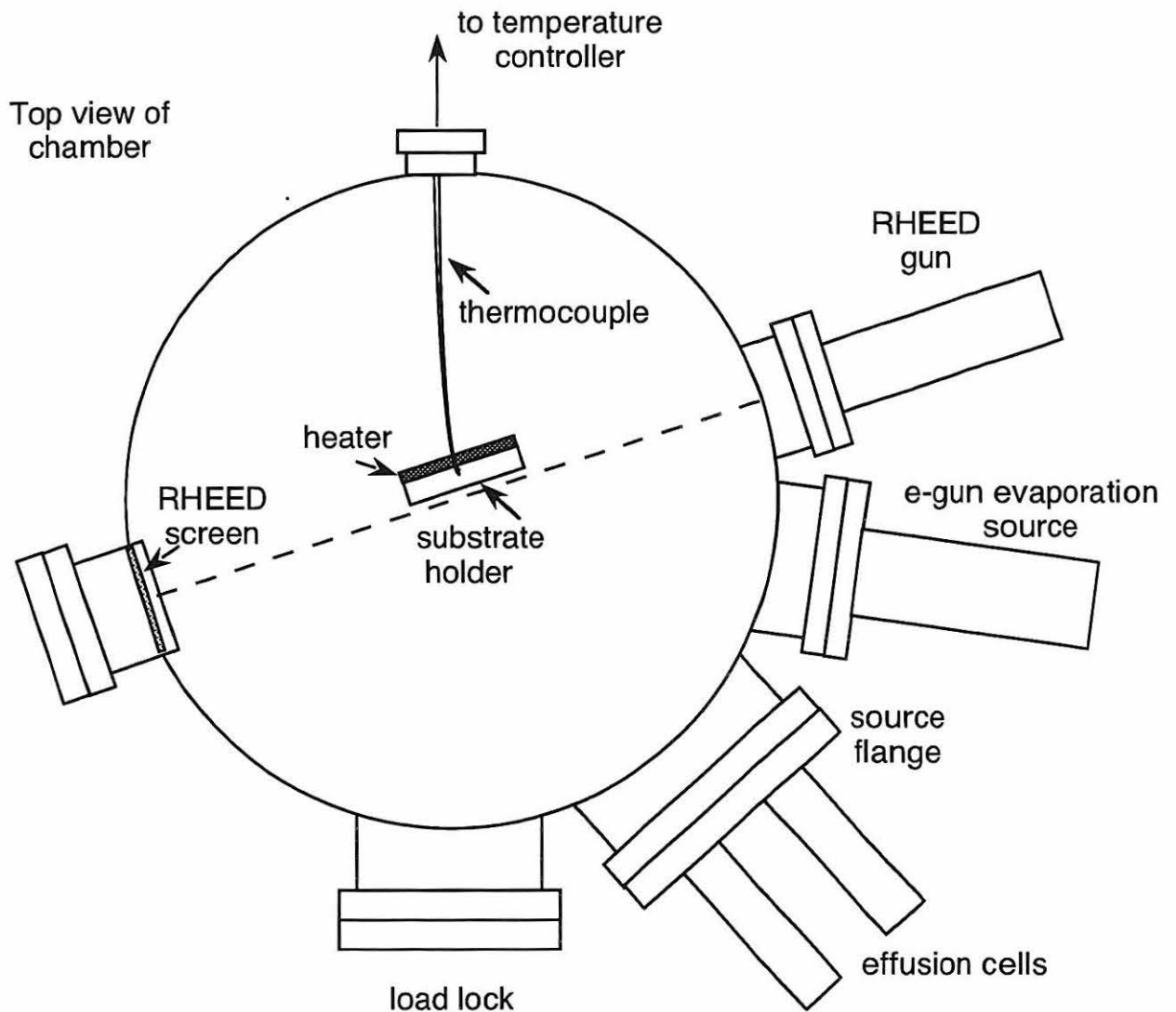


Figure 1.4: The typical MBE apparatus includes: several source evaporators, including (but not limited to) effusion cells and electron-beam evaporators; individual mechanical shutters for each source (not shown); radiative substrate heating; sample holder with rotation capability; and a thermocouple for substrate temperature monitoring.

Figure 1.4 illustrates schematically a typical MBE apparatus. The molecular beams are produced by evaporation or sublimation from heated liquid or solid sources, and the beam fluxes (and thus growth rates) are determined by the vapor pressure of the source material at elevated temperatures. Evaporation is done in an ultra-high vacuum (UHV) environment to ensure near-collisionless molecular beam propagation from the source material to the substrate and to reduce impurity concentrations of ambient gases in the growing films. The substrate is also held at an elevated temperature to provide extra energy for surface migration and other kinetic processes in order that adsorbed species attain minimum-energy positions.

Sources are commonly evaporated by effusion from a radiatively heated cell with a small opening. This is known as the Knudsen technique [10] and is used to heat materials up to a maximum temperature of about 1200 °C. For materials which do not have an appreciable vapor pressure at this temperature, electron-beam bombardment is used, in which ~ 5 keV electrons are focused onto the surface of the source material, producing local temperatures up to 3000 °C [10]. This method has the advantage that the bulk of the source material and the cell walls are held at significantly lower temperature, thereby reducing any chemical reactions between them. Appendix B illustrates a typical Knudsen effusion cell and electron beam evaporator.

MBE is capable of producing epitaxial films of precise chemical composition and thickness, free of impurities and structural defects and so forth; however, numerous factors must be considered and meticulously controlled. System components must be made of materials that outgas minimally and do not react with substrate, sources, residual gases, or each other at the pressures and temperatures of operation. All components must be rigorously cleaned, mechanically and/or chemically, before installation. Heater filaments must be of high purity ($\geq 99.99\%$) and have low oxygen content [10]. Liquid cooling, with water or nitrogen, of effusion cells and other evaporators which generate hot spots is necessary to prevent irregular outgassing and therefore contamination of films grown. The base pressure must be low enough such that the source beams do not become degraded by collisions with residual gas molecules, and also such that the deposition of source material onto the substrate occurs much more

rapidly than the adsorption of residual species. The sticking probability of a source species (i.e., probability of adsorption onto the substrate) must be taken into account and beam fluxes adjusted accordingly in order to achieve a desired composition for alloy films. Also of extreme importance is that the substrate surface be clean and free of contaminants on the *atomic* level prior to film growth. Although conceptually simple, substrate preparation and surface analysis for cleanliness on the atomic level continues to be of great interest to crystal growers, and is in fact the subject of Chapter 3 of this thesis.

1.3.2 Reflection high energy electron diffraction (RHEED)

In order to achieve the precise compositional and configurational control of films grown by molecular beam epitaxy, *in situ* film surface characterization capability must be realized. The most widely used *in situ* surface analysis tool in the MBE environment is reflection high energy electron diffraction (RHEED), in which the electrons being diffracted have energies of 10-30 keV. The electron beam is directed at grazing incidence (0.5° to several degrees) to the sample of interest. With this incident geometry, RHEED is very surface-sensitive and provides information on long-range surface crystallographic structure and surface morphology. At RHEED energies, the incident beam is strongly scattered in the forward direction (i.e., momentum transfers are small) so that both the source electron gun and detection apparatus are placed in a line perpendicular to the line of film growth, with molecular source beams typically impinging the substrate normally. Thus, RHEED has the important feature of being compatible with the growth configuration, permitting real-time structure monitoring of the growing film. In addition, with the discovery of RHEED intensity oscillations [9], it is possible to extract information on MBE growth dynamics. This and other experimental triumphs obtained with RHEED will be discussed in greater detail in Section 1.3.2 and subsequent chapters.

Electron diffraction

Due to the wave-particle duality of matter, electrons may exhibit wave-like behavior in certain regimes. The criterion for establishing regime boundaries is the de Broglie wavelength; if this wavelength of a probing beam is comparable to or smaller than the characteristic dimension of the system being investigated, then the probe will be able to yield useful structural information about the system. Crystalline materials have lattice constants of the order of 2–10 Å. Visible light shone onto such materials obeys the rules of geometrical optics and yields no structural information. On the other hand, x rays have typical wavelengths less than 1 Å; when a beam of x rays is directed at a crystalline sample, Bragg diffraction occurs. A beam of 30 keV electrons has a characteristic wavelength of ~ 0.07 Å, and is subject to diffraction.

The reflection high energy electron diffraction pattern (i.e., RHEED pattern) of a surface is an image of the Fourier transform of the surface [12]. While the real surface exists in coordinate space, the Fourier transform, or RHEED pattern, resides in reciprocal space, also known as k -space. For a structure with lattice vectors $\mathbf{a}_1, \mathbf{a}_2$, and $\mathbf{a}_3$ in real space, the reciprocal lattice vectors are given by [11]

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \quad (1.28)$$

An arbitrary point in k -space is described by the general reciprocal lattice vector $\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3$. For a surface, which we may model as a monolayer of atoms adsorbed onto a substrate, $\mathbf{a}_3 \rightarrow \infty$, with the vertical direction normal to the plane of the film. The corresponding reciprocal lattice vector has infinitesimal length, i.e., adjacent points in this direction in k -space are infinitesimally close to each other. The Fourier transform of a surface becomes an array of k points which are densely spaced along the perpendicular direction, yielding a structure of effectively continuous Bragg rods resembling a bed of nails, with the nails perpendicular to the surface (Figure 1.5).

The indexing system for crystal planes is the set of Miller indices, determined by the following rules:

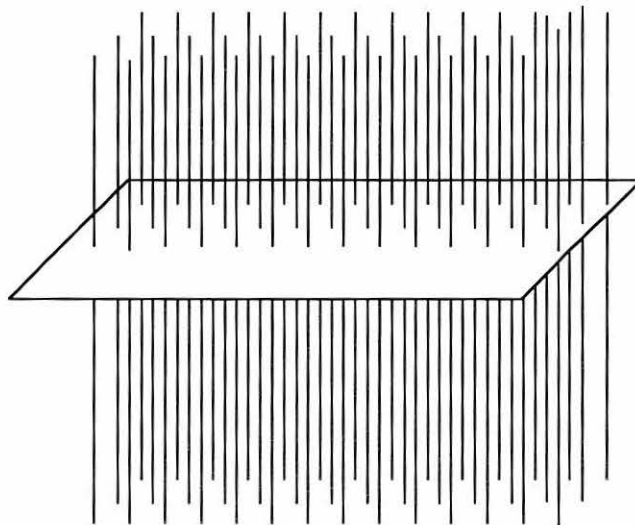


Figure 1.5: The reciprocal space for a 2-dimensional surface net is a structure of rods resembling a bed of nails which are perpendicular to the net.

1. Find the intercepts on the real space axes in terms of $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$.
2. Take the reciprocals of these numbers and convert to three integers having the same ratio.

The resulting three numbers, denoted by hkl and enclosed in parentheses, give the index of the crystal plane; for example, Si(100) gives the (100) plane of Si. Crystallographic directions are denoted by $\langle hkl \rangle$.

Diffraction will occur if the diffraction requirement is satisfied; in the Von Laue formulation this condition is that $\mathbf{k} - \mathbf{k}' = \mathbf{G}$, that is, the momentum transfer between the initial and final states of the incident particle must equal a reciprocal lattice vector.

The Ewald sphere

An abstract construction known as the Ewald sphere is helpful in visualizing diffraction patterns. The Ewald sphere is embedded in the reciprocal space of the system of interest. It has a radius equal to the magnitude of $\mathbf{k}$, the incident momentum vector, which is drawn in the direction of the incident beam such that the head of $\mathbf{k}$ coincides with any reciprocal lattice point [11]. The diffraction pattern consists of

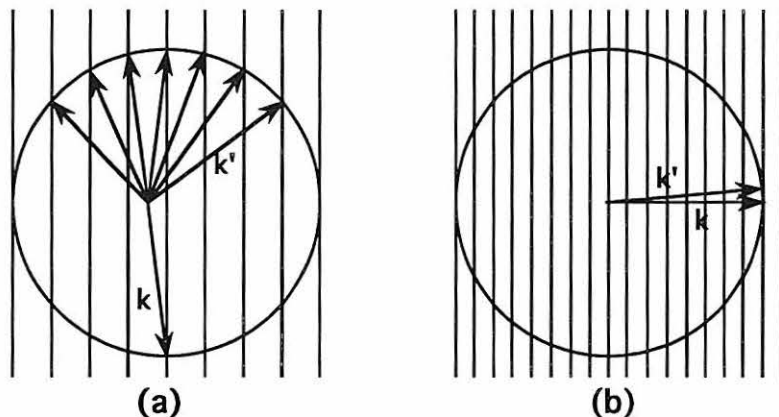


Figure 1.6: Intersection of the Bragg rods with the Ewald sphere in the case of (a) LEED and (b) RHEED.

the intersection of the Ewald sphere with all reciprocal lattice vectors $\mathbf{k} - \mathbf{k}' = \mathbf{G}$. In low energy electron diffraction (LEED), detected electrons have been backscattered almost 180° , resulting in momentum transfers $\mathbf{k} - \mathbf{k}'$ that intersect the Ewald sphere surface at almost normal incidence, as shown in Figure 1.6(a). Thus, a LEED pattern of a surface consists of spots. In the case of RHEED, $\mathbf{k}$ and $\mathbf{k}'$ point in almost the same direction so that $\mathbf{G} (= \Delta\mathbf{k})$ is almost parallel to the Bragg rods. At RHEED energies, $\mathbf{k}$ is large and the Ewald sphere is almost planar; thus its intersection with $\mathbf{G}$ is also rod-like but has finite length because of the small Ewald sphere curvature, as shown in Figure 1.6(b). If the crystal structure is perfect, the rods will have zero width. For a surface with structural disorder, the rods have a finite width and the diffraction pattern is composed of features that are oblate (prolate) spheroids of extreme aspect ratio and thus resemble cigars [12]. The Ewald sphere has in principle a finite contribution to its thickness due to electron energy spread, but in practice this usually contributes little to the width of the Bragg diffraction features as compared with surface disorder.

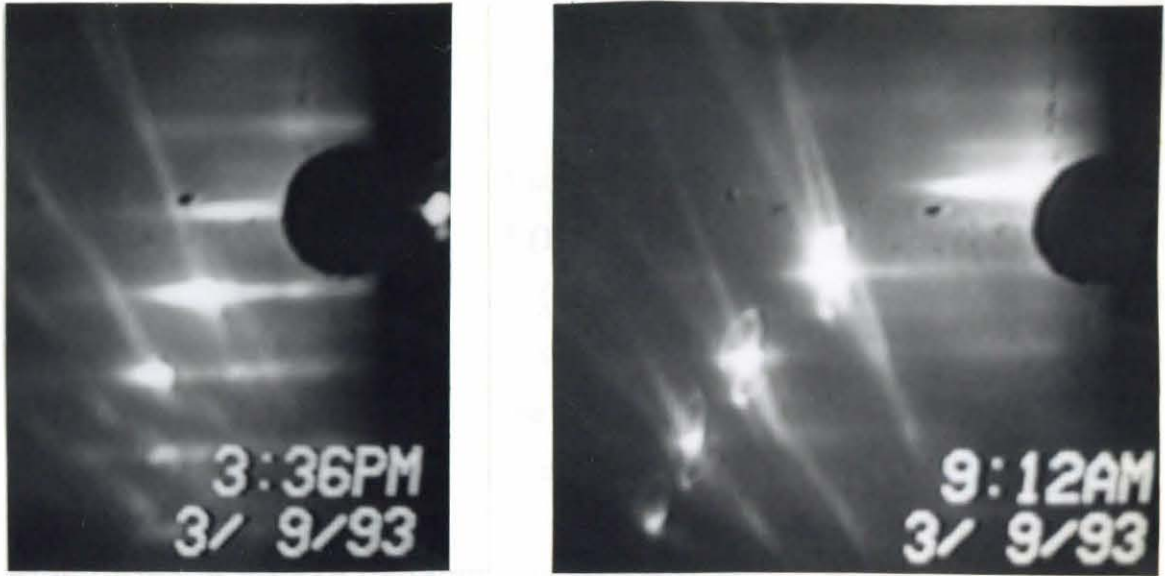


Figure 1.7: RHEED patterns of the unreconstructed (1×1) Si(100) surface (left), and of the reconstructed (2×1) Si(100) surface (right).

Interpretation of RHEED patterns

In general, a RHEED pattern will consist of several distinct regions, known as Laue zones, of Bragg rod-like features. The first-order Laue zone corresponds to those rods formed by intersection of the Ewald sphere with the shortest vectors $\mathbf{G} = \Delta\mathbf{k}$. Second-order Laue zone diffractions are fainter in intensity, having resulted from the beam scattering through a larger angle. Higher-order Laue zones are possible and in principle can be viewed if the detecting screen and incident electron energy are sufficiently large.

The distance between two adjacent rods in the same Laue zone provides direct information on the in-plane lattice constant of the surface crystallographic structure. If the surface is characterized by an in-plane lattice constant $a_{\parallel}$, then the distance between adjacent rods in k -space is $2\pi/a_{\parallel}$.

A good example of RHEED pattern features is the pattern produced by a surface which has a different structure from the underlying bulk structure, but whose periodicity is correlated with that of the bulk. A perfectly clean Si(100) surface, in order to saturate the two dangling bonds of each Si atom on the surface, will undergo a (2×1) reconstruction and form dimer rows, which have a periodicity twice that of

the bulk structure. The lattice vector of the surface in real space is twice as long as the bulk vector, and thus the corresponding reciprocal lattice vector is half as long as the original k -space vector. Hence the RHEED pattern will contain additional, “half-order” rods midway between adjacent integral-order rods. Figure 1.7 shows the RHEED patterns of unreconstructed (1×1) and reconstructed (2×1) Si(100), respectively. As another example, for a (5×1) surface reconstruction, one real space lattice vector is five times the length of the same vector in the bulk, and the other real space lattice vector is unchanged. The RHEED pattern will consist of “fifth-order” rods equally spaced between adjacent integral-order rods.

Monitoring of growth dynamics by RHEED

One of the most important achievements in attaining atomic-order control during molecular beam epitaxy is the discovery of oscillations in the RHEED specular beam intensity [9]. RHEED oscillations are based on the simple concept that the specular beam is more intense from a smooth surface than from a surface with asperities. Sakamoto *et al.* [13] measured the RHEED intensity of the specular beam during Si homoepitaxy onto Si(100). The resulting intensity oscillations were deduced to correspond to layer-by-layer growth, and a period of oscillation corresponded to the growth of one monolayer. Prior to growth, the surface is clean and smooth and the specular beam intensity is large. In the initial stages of growth, isolated domains nucleate on the surface, making it rough and reducing the RHEED intensity. As the growth of one monolayer approaches completion, the surface smoothens and the RHEED intensity once again becomes strong. Thus, by counting the number of oscillations during growth, it is possible to deposit films with a thickness resolution of one monolayer.

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Chapter 2 Reflection Electron Energy Loss Spectrometry (REELS)

2.1 Overview of technique

The surface analysis technique of reflection electron energy loss spectrometry (REELS) is not new; it has been performed in a transmission electron microscope (TEM) operating in reflection mode, but has had limited application because it may only be used as an *ex situ*, post-growth characterization tool. Ahn and Atwater [1][2][3] have pioneered a technique which enables REELS to be performed in the MBE environment, via the spectroscopic analysis of RHEED electrons. In the remainder of this thesis, all discussions of REELS will refer to REELS in the MBE chamber.

Figure 2.1 is a photograph of the REELS system used in most of this thesis, and Figure 2.2 schematically illustrates the REELS geometry. After impinging on a sample surface at grazing incidence ($\sim 0.5^\circ$), the scattered RHEED electrons strike a phosphorescent screen and form a diffraction pattern that yields long-range structural information about the surface. The energies and spatial distribution of these reflected, diffracted, and inelastically scattered electrons yield a wealth of additional information that is literally thrown away on the RHEED screen. Ahn and Atwater have addressed this dilemma by drilling a small circular aperture in the center of the RHEED screen to allow a small component of the scattered beam to pass through the screen (see Figure 2.4). A magnetic prism spectrometer, energy-selecting slits, and photomultiplier tube (PMT) are installed behind the screen to provide the advertised spectroscopic analysis. Data acquisition is serial and is made possible by interfacing the PMT to a multichannel scaler and personal computer. The reflection geometry of RHEED/REELS gives it the advantage of use *during* film growth, making possible real-time determinations of surface structure (by RHEED) and composition on the

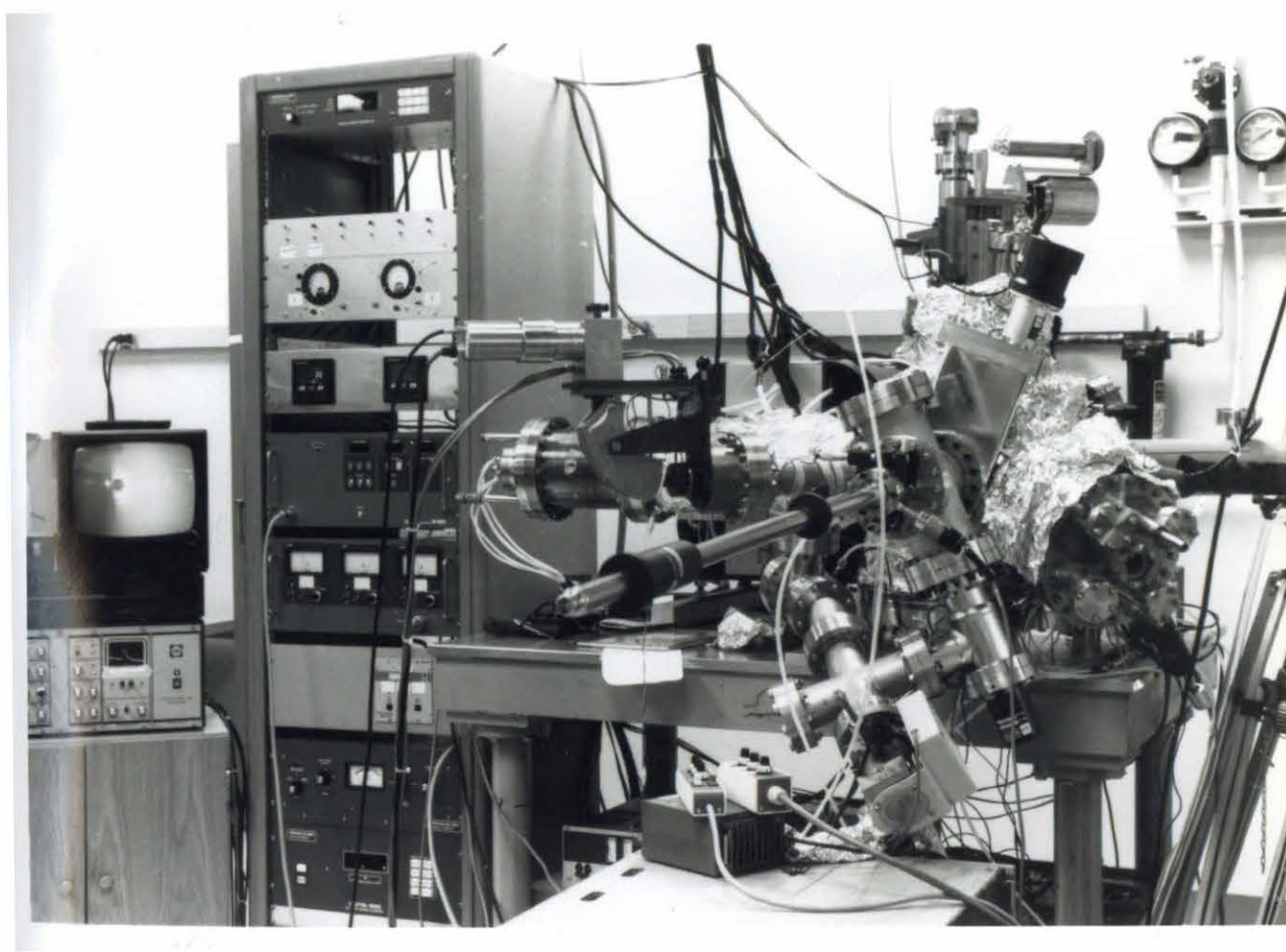


Figure 2.1: Photograph of the REELS system used for the experiments of this thesis.

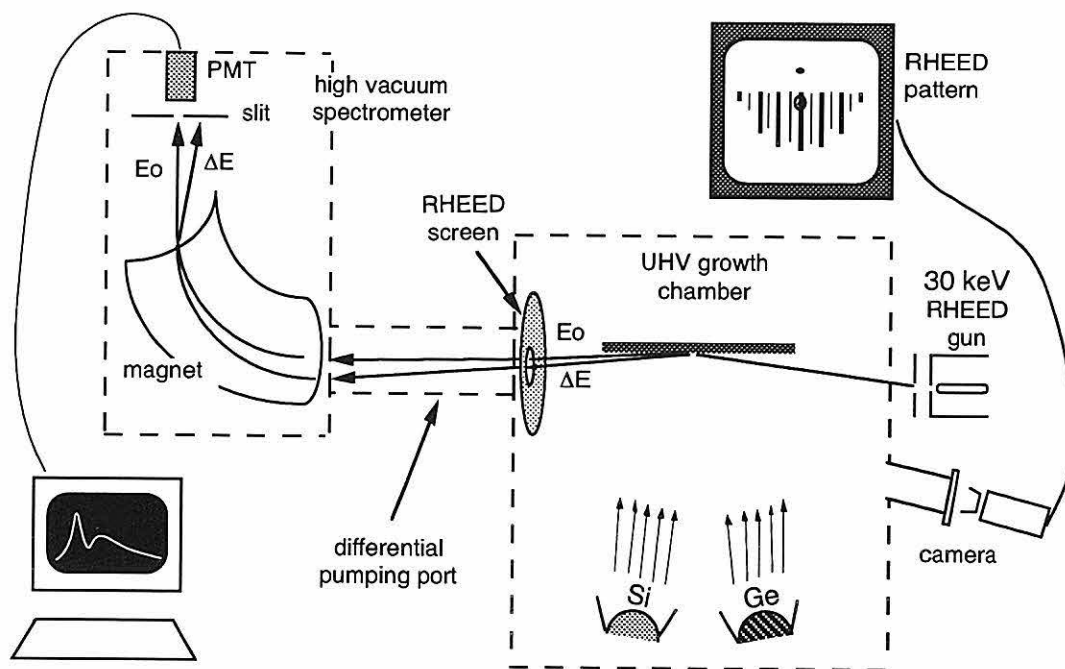


Figure 2.2: Schematic of REELS system.

atomic level (by REELS).

2.2 REELS instrumentation

The RHEED gun used in the experiments of this thesis is a Vietch 30 keV electron gun. Electrons are produced by thermionic emission from a tungsten hairpin-type filament, and emerge from the gun through a small aperture, highly collimated and with a spot size of about 0.2 mm and an energy spread of ~ 5 eV. Samples are mounted on a sample manipulator (ISA Riber type) with x , y and z translation, and sample rotation capability. Mounted on a custom-made, water-cooled source flange was a standard EPI effusion cell with 10cc crucible capacity, used for evaporation of Ge and Sn. A 4 kV Thermionics rod-fed electron-beam evaporator was used for deposition of silicon.

The RHEED screen hole has a diameter of 6.3 mm. The magnetic prism spectrometer is a Gatan 607 second-order aberration-corrected sector, designed for use in a TEM at 100 to 200 keV. Modifications made to adopt the spectrometer to the MBE

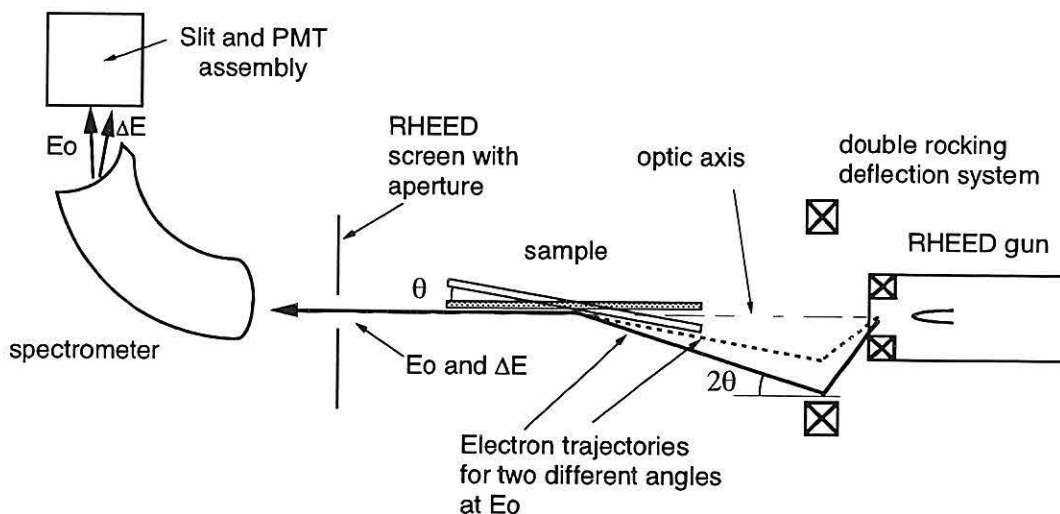


Figure 2.3: A set of dipole magnets is used in conjunction with the magnets built into the RHEED gun assembly to doubly deflect the incident electron beam.

environment included using the sample surface as the object point of the optical system [1], and installing a differential pumping aperture (~ 6 mm diameter, 0.68" long) between the spectrometer and the main chamber. This was necessary due to the fact that the spectrometer is not compatible with the ultrahigh vacuum (UHV) environment of the growth chamber, which maintained a typical base pressure of 5×10^{-10} Torr using a sublimation pump, differential ion pump (Perkin-Elmer, 400 liters/sec), and load lock with a turbomolecular pump (Balzers, 50 liters/sec).

The sample surface is approximately 43 cm (17") from the spectrometer entrance, giving a collection semi-angle of ~ 1 mrad, depending upon the spectrometer entrance aperture chosen (sizes of 1, 2, 3, and 5 mm available). A larger entrance aperture increases the amount of intensity allowed into the spectrometer and improves the signal to noise ratio, but degrades the energy resolution. The main degradation of energy resolution comes from the tungsten filament and power supply of the RHEED gun (5 eV). At grazing incidence, the electron beam probes a considerable length of sample surface (up to ~ 2 cm), further imposing a limit to energy resolution. The final resolution of the REELS configuration is about 7 eV.

In an attempt to preserve energy resolution as well as possible, a pair of dipole magnets (one for each transverse direction of the beam) was placed in the path of

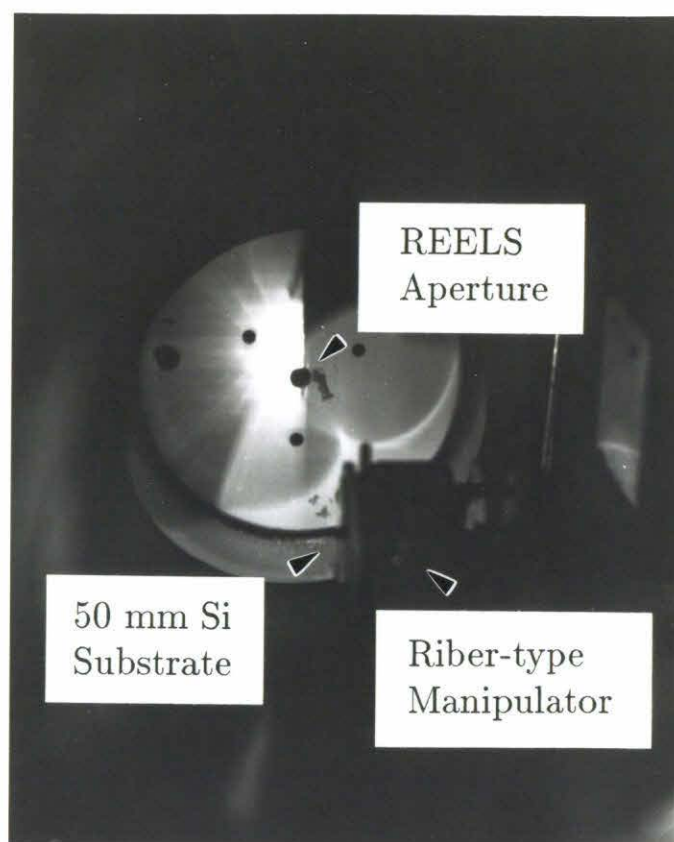


Figure 2.4: Photograph of RHEED beam scattering from a sample at grazing incidence and forming a RHEED pattern on the phosphor screen. The circular aperture through which a component of the scattered beam travels for spectroscopic analysis is indicated.

the RHEED beam, as shown in Figure 2.3. These external magnetic lenses, together with the set of deflection coils built into the RHEED gun assembly, provide a “double rocking” of the electron beam. A unique combination of beam deflections and sample tilt angle ensures that the scattered beam travels along the optic axis as it enters the spectrometer in all cases.

Appendix A provides a much more detailed discussion of the REELS instrumentation.

2.3 Obtaining and interpreting a REELS spectrum

2.3.1 Partial cross sections

For purposes of quantifying an electron energy loss spectrum, it is useful to introduce the partial ionization cross section, $\sigma(\Omega, \Delta E)$, where σ is the integrated cross section for ejection of an electron from a specific electronic level in an atomic species within a collection semi-angle Ω and energy loss range ΔE . This partial cross section gives the probability of ionization where the incident (fast) electron suffers an energy loss in the range $(E_0, E_0 + \Delta E)$ with E_0 being the ionization threshold energy, and with scattering angles less than Ω .

In order to relate the energy loss spectrum to the composition of a sample, we note that the number of atoms per unit area of an elemental species, N_{el} , is found by

$$N_{el} = \frac{I_c(\Delta E, \Omega)}{I_0(\Delta E) \sigma(\Delta E, \Omega)} \quad (2.1)$$

where $I_c(\Delta E, \Omega)$ is the characteristic core-loss signal intensity resulting from ejection of electrons from a specific level, e.g., $1s(K)$. The quantity $I_0(\Delta E)$ is the integrated low-loss intensity with a range ΔE ; it includes mainly unscattered and slightly inelastically scattered electrons and provides a direct measure of the incident electron flux [4].

2.3.2 Empirical cross sections

Due to multiple inelastic scattering and small variations in the collection geometry, empirical electron energy loss data vary systematically from that expected from calculated ionization cross sections. It is common practice to use empirical cross sections deduced from energy loss spectra of materials of known stoichiometry and thickness. Furthermore, in many cases of microanalysis it is not necessary to determine the absolute number of atoms of a particular species; only the ratio of numbers of two

species is of interest. Then, it is the empirical cross section ratio that is relevant, and the ratio of numbers of two species is given by

$$\frac{N_a}{N_b} = \frac{I_a}{I_b} \left(\frac{\sigma_b}{\sigma_a} \right). \quad (2.2)$$

This eliminates the need for knowledge of absolute cross sections, which are difficult to obtain accurately.

2.3.3 Hydrogenic vs. Hartree-Slater cross sections

There remains the question of how to calculate the atomic wave functions, the knowledge of which is needed to determine the ionization cross sections. A hydrogen-like atomic model is a very good description of *K*-shell wave functions for light elements [5] and may be a satisfactory description of *L*-shell wave functions as well, but for more outer-shell wave functions and for heavy atoms, the potential field seen by the electrons will be substantially non-Coulombic. The self-consistent field equations of Hartree, Fock and Slater [6], based on the free-electron exchange approximation, have been solved by iterative techniques to yield approximate electron wave functions. However, for *K*-shell and *L*-shell wave functions for light elements the difference between hydrogenic and Hartree-Slater partial cross sections has been found to be quite small ($\sim 1-2\%$) [7]; thus this justifies the use of the hydrogenic atom model for *K*- and *L*-shell transitions, which considerably simplifies cross section calculations. Figure 2.5 exemplifies hydrogenic model calculations for these shells. For *M*-shell and more outer-shell transitions, there are no calculations based on the hydrogenic model and full treatment of the transitions using Hartree-Slater self-consistent field equations must be used.

2.3.4 The REELS spectrum

Figure 2.6 shows a typical REELS spectrum which illustrates the important features. This energy loss measurement was obtained from a clean Si(100) surface with a 30

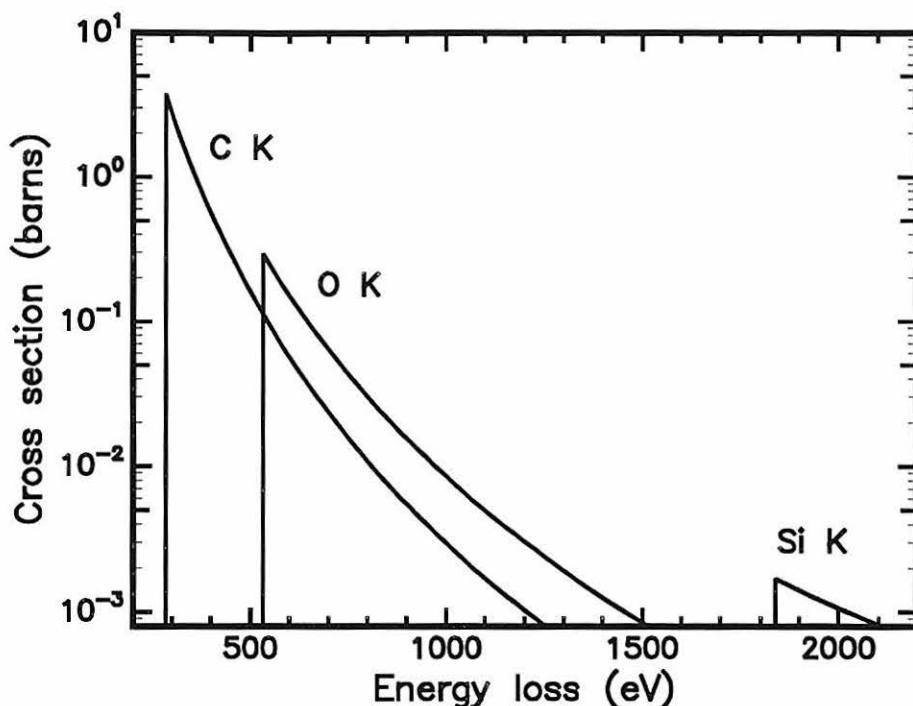


Figure 2.5: Hydrogenic cross sections for Si K , C K and O K . Calculations were made using an incident beam energy of 30 keV and a collection angle of 1 mrad.

keV incident beam making an angle of approximately 1° with the sample surface. The leftmost peak corresponds to the zero-loss, or elastic scattering, intensity. The two peaks to the immediate right of the elastic scattering peak correspond to the “low-loss” intensity due to excitation of surface and bulk plasmons, which in silicon occur every 12 and 17 eV of energy loss, respectively. The ratio of zero-loss to low-loss intensity provides a measure of surface sensitivity of the probing electron beam: when the incidence angle is small ($\leq 1.0^\circ$), the beam is very surface-sensitive and excites a large number of surface plasmons, giving a large low-loss intensity relative to elastic intensity; when the incidence angle is large ($\geq 1.5^\circ$), the inelastically-scattered component of the beam becomes extinguished in the sample bulk, resulting in decreased low-loss intensity compared with that for elastic scattering. Figure 2.7 illustrates these two cases. With still increasing incidence angle, the ratio of zero-loss to low-loss intensity continues to increase, and the energy loss spectrum resembles more and more a transmission EELS spectrum obtained in the TEM, an example of

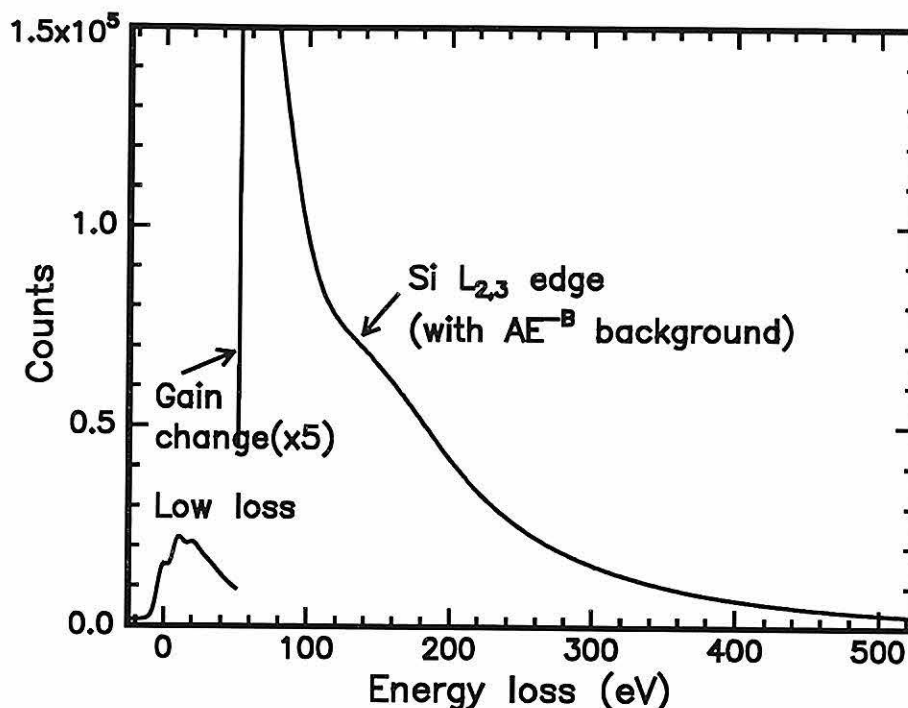


Figure 2.6: A typical REELS spectrum, obtained from a Si(100) surface. The low loss region consists of a zero loss component and a surface and bulk plasmon component. A gain change of ~ 5 is employed in order to observe the core loss of interest, in this case, a Si $L_{2,3}$ edge (with threshold at 99 eV). The edge is superimposed upon a large background that is usually modeled as an inverse power law.

which is shown in Figure 2.8.

The core losses of interest in microanalysis are typically much smaller in intensity than the elastic and low-loss features. The sudden rise in intensity in Fig. 2.6 reflects a gain increase of 5 in the detection electronics, as the mode of data collection is switched from current measurement to pulse counting of electrons that strike a scintillator. The $L_{2,3}(2p)$ core electron loss of silicon begins at the ionization threshold of 99 eV and exhibits a long, slowly decreasing tail typical of inner-shell losses. The core-loss intensity is superimposed upon a smoothly decaying plasmon background which is found experimentally to obey an inverse power law AE^{-B} (A and B are constants, with B varying between 2.8 and 4.5) over a wide range of energy losses [8]. If the spectrum is obtained from a sample of condensed matter with at least local order of atoms of a given species, the spectrum will exhibit near-edge and extended-

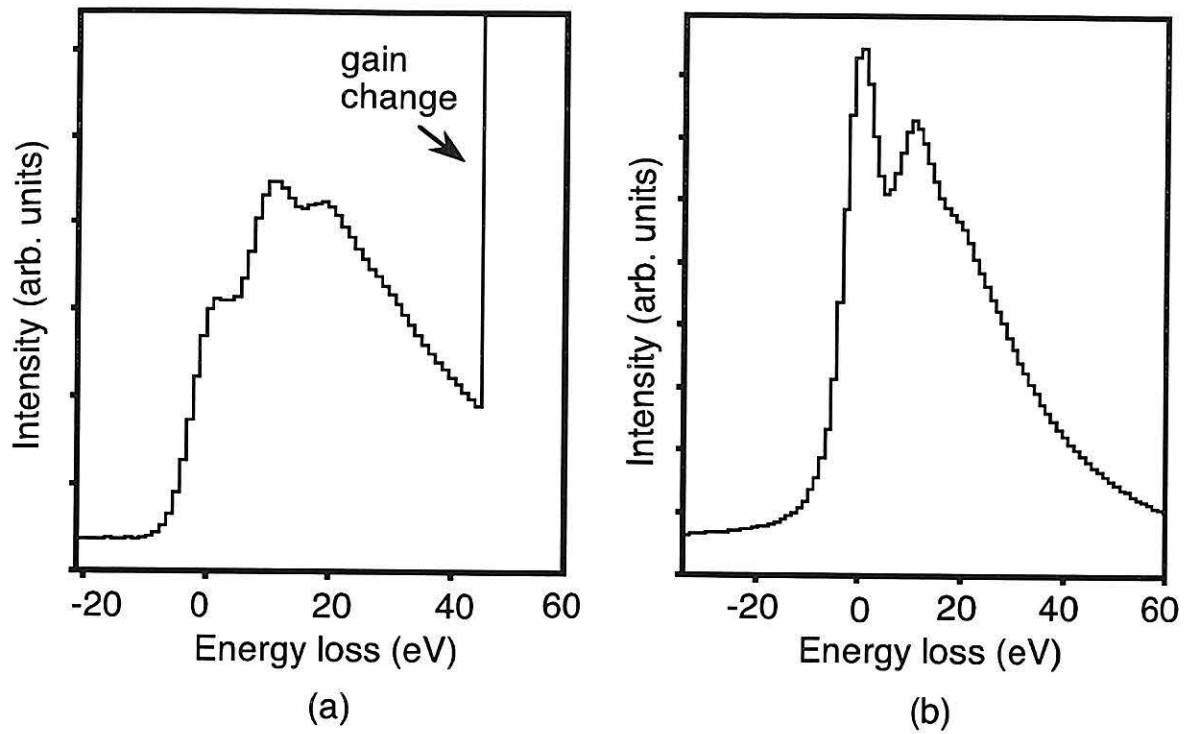


Figure 2.7: Illustration of the low loss region of the REELS spectrum for (a) shallow RHEED beam incidence ($\leq 1.0^\circ$) and (b) steeper RHEED beam incidence ($\geq 1.0-1.5^\circ$).

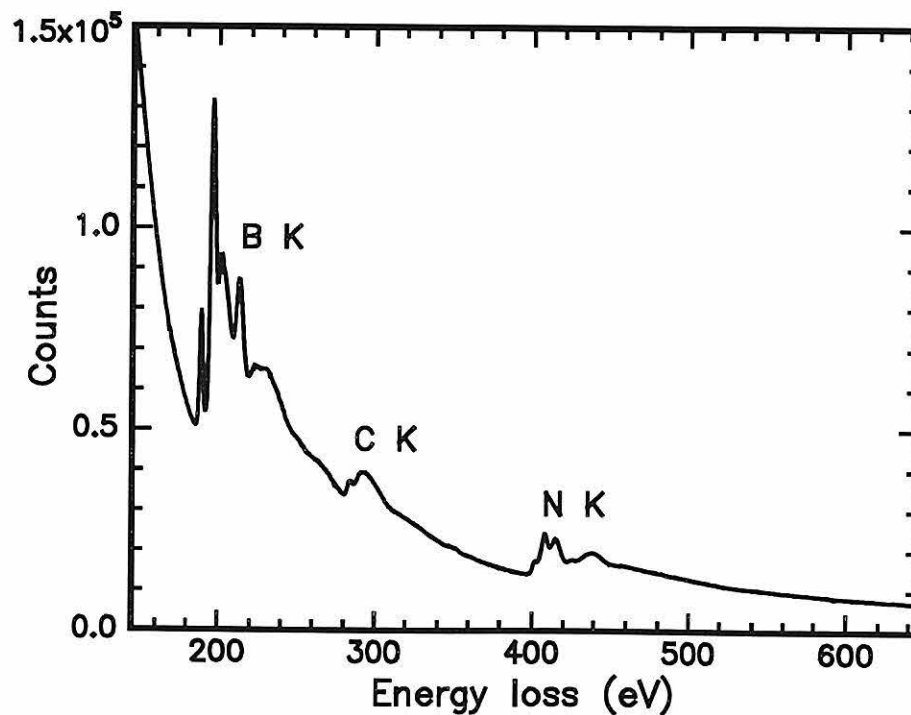


Figure 2.8: Typical transmission EELS spectrum, taken from a sample of boron nitride on holey carbon. [Data courtesy of Gatan, Inc., Pleasanton, CA.]

edge energy loss fine structure (NEELFS and EXELFS) oscillations, superimposed on the core-loss intensities of interest. Although the REELS spectrometer energy resolution, together with multiple inelastic scattering make NEELFS measurements impossible, EXELFS is possible, and the study of EXELFS features to gain local order information in microanalysis is the subject of Chapter 4.

2.4 Other analysis techniques used

Because REELS performed in a MBE chamber is a relatively new technique, results of initial core level ionization cross section experiments were compared with results obtained from measurements performed on the same samples using other analysis techniques. This section will briefly describe x-ray photoelectron spectroscopy and Rutherford backscattering spectrometry, two chemical analysis tools which were used for measurements described in this thesis.

2.4.1 X-ray photoelectron spectroscopy (XPS)

Surface analysis by x-ray photoelectron spectroscopy (XPS), more commonly called electron spectroscopy for chemical analysis (ESCA), is concerned with the measurement of core-electron binding energies. A sample is bombarded with a source of high-energy x rays (usually Mg K_α (1254 eV) or Al K_α (1487 eV) for laboratory-based analyzers) which cause emission of inner-shell electrons from sample atoms. Figure 2.9 illustrates this physical mechanism. The emitted electrons have kinetic energies given by

$$E_{kin} = h\nu - E_b - \phi_s, \quad (2.3)$$

where $h\nu$ is the photon energy, E_b is the core-electron binding energy relative to the Fermi level, and ϕ_s is the work function of the spectrometer (a constant for a given analyzer). The kinetic energy of the ejected electron is thus characteristic of the atom and the chemical environment from which it originated. Although the x rays penetrate deeply into the sample material, only those photoelectrons ejected from the

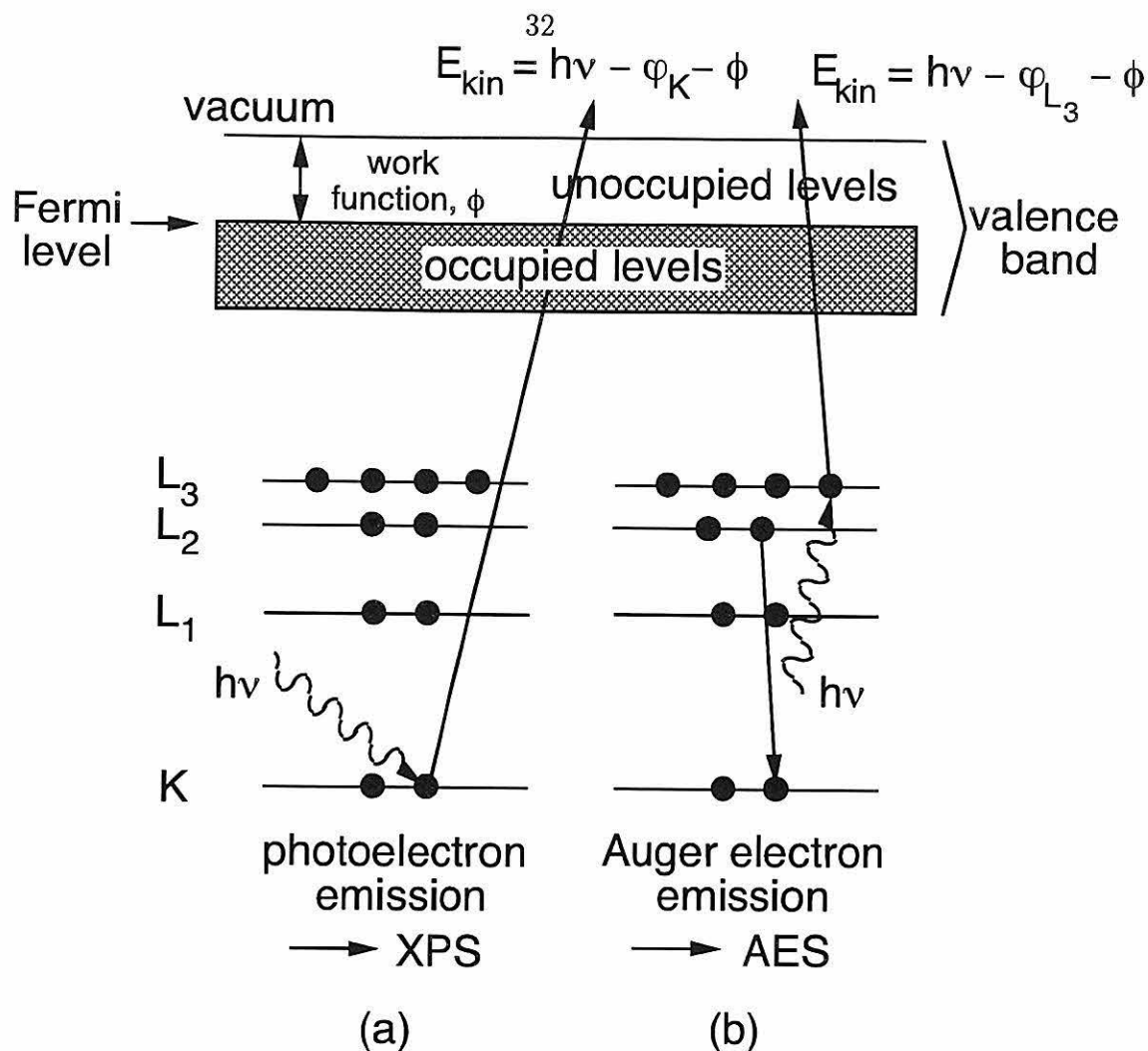


Figure 2.9: Schematic diagrams illustrating the physical mechanisms underlying the analytical techniques of (a) x-ray photoelectron spectroscopy (XPS) and (b) Auger electron spectroscopy (AES).

top $\sim 20 \text{ \AA}$ of the sample have any chance to escape and be analyzed by the detector. Thus, XPS is a surface-sensitive technique.

An advantage of XPS is its ability to detect “chemical shifts” in electron binding energies. The binding energies of core electrons are affected by the valence electrons and therefore by the chemical environment of the atom. The shifts are typically of the order of $\sim 1\text{--}2 \text{ eV}$ and provide chemical structure information. For example, a silicon atom in single-crystal Si has a binding energy of 99 eV, whereas a silicon atom in SiO_2 has a binding energy of 103.4 eV (which is a relatively large chemical shift). XPS can differentiate between Si atoms of these two chemical environments; REELS

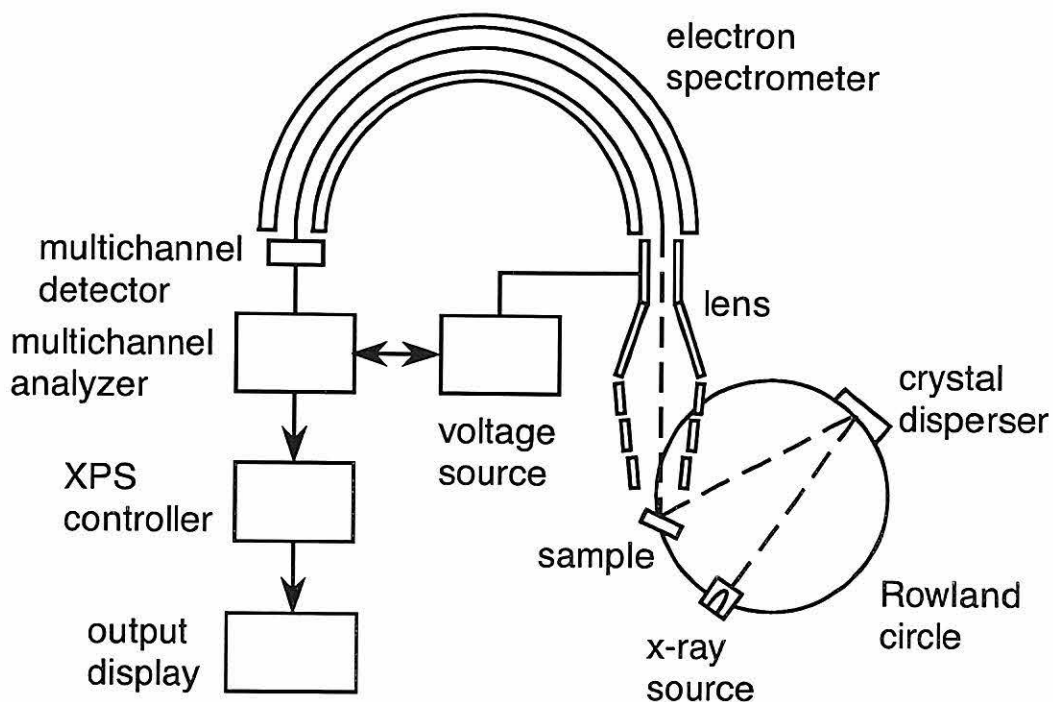


Figure 2.10: Schematic diagram of typical instrumentation used for XPS, showing the large hemisphere-shaped analyzer which must be placed in close proximity to the sample surface.

with an energy resolution of 7 eV achieved by the current instrumentation, cannot. However, this is not an inherent REELS limitation; in principle, it can be improved with an electron gun with smaller thermal energy spread and power supply of higher stability, for example. This would bring the detection of large chemical shifts within the realm of possibility for the REELS technique.

The XPS spectrometer which analyzes photoelectrons according to their kinetic energy is typically a hemisphere-shaped analyzer. The travel directions of ejected electrons from the sample are random; thus the hemispherical analyzer must be placed very close to the sample in order to encompass as large a solid angle as possible (see Figure 2.10). Because of this, XPS cannot be performed in the MBE environment because the close proximity of the photoelectron analyzer interferes with requirements of the film growth geometry.

Nevertheless, XPS as an *ex situ* analysis provides valuable information that sup-

plements and/or corroborates information obtained with REELS. The XPS measurements discussed in this thesis were performed in a VGHB50A surface probe.

2.4.2 Rutherford backscattering spectrometry (RBS)

As its name implies, this technique is based on the backscattering of particles from a target sample. The scattering cross sections can deviate significantly from that given by the classical Rutherford scattering formula; a more appropriate name for this technique might be simply backscattering spectrometry [9]. The probe beam is composed of alpha particles (^4He nuclei) and impinges normally upon the sample. Alpha particles which are backscattered are energy analyzed by a detector placed at a scattering angle of $170 - 180^\circ$. The mass of the target atom can then be calculated, since the projectile mass and scattering angle are known. This technique is, in a sense, a form of mass spectrometry.

Because of the scattering geometry, RBS is a bulk characterization technique and is well suited for sample thickness measurements and alloy composition determinations. RBS measurements discussed in this thesis were performed using 1 MeV He^+ ions produced with a Pelletron tandem accelerator at Caltech.

2.5 Still other analytical techniques

The following analysis tools were not utilized in the work of this thesis, but will be described briefly because they are conventional techniques used for surface and bulk analysis, and are in widespread use.

2.5.1 Auger electron spectroscopy (AES)

This technique involves bombardment of a sample with electrons and the measurement of electrons emitted from the surface. The process consists of several steps and is illustrated in Figure 2.9. The first step is the ionization of an inner-shell electron by an incident electron. Relaxation of this excited state can occur by emitting either

a photon (x-ray fluorescence) or an electron. The latter involves filling the inner-shell vacancy with an atomic electron from a higher-energy orbital; the energy subsequently released is used to eject another atomic electron, called the Auger electron, into the continuum. The energy of the Auger electron depends only upon the energy levels involved in the Auger transition, and thus provides a signature of the atom from which it came. The nomenclature that describes Auger transitions consists of three letters. For example, a *LMM* transition indicates that an electron from an *L*(2*p*) orbital suffered the initial ionization; an electron from an *M*-shell filled the vacancy in the *L* orbital, and another *M* orbital electron was ejected as the Auger electron.

Intensities of Auger transitions are typically small and a standard practice is to differentiate the signal. Thus peak positions can be determined with an accuracy of ~ 1 eV. As in XPS, Auger electrons are low in energy and must have been ejected from the first few atomic layers in order to escape the surface of the sample and be detected. Most commonly used for elemental identification, AES has a depth sensitivity of ~ 20 Å, similar to that of XPS.

The cylindrical mirror analyzer used as the electron spectrometer in AES is rather large and must be placed in close proximity to the sample surface. As is true for XPS, Auger electron spectrometry is incompatible with the MBE environment and can be used only as a post-growth characterization tool.

2.5.2 Secondary ion mass spectrometry (SIMS)

In SIMS, an energetic primary ion beam, typically Ar^+ , strikes a sample surface and releases secondary ions. Both atomic and molecular ions can be detected; molecular ions can dissociate to give positive and negative ion mass spectra. SIMS provides qualitative identification of all surface elements, including hydrogen. If a state-of-the-art quadrupole mass spectrometer is used, SIMS permits isotope identification. This technique is very surface-sensitive, with the primary beam probing the first two or three atomic layers, and the detection sensitivity is very high (parts per million levels).

A serious disadvantage of SIMS is that it does not afford much quantitative analysis. The interactions of the sample with the primary ion beam are complex and measured elemental percentages can vary by as much as several orders of magnitude[10]. Also a disadvantage of SIMS in the context of molecular beam epitaxy is that the primary ion beam is directed normally onto the sample surface, necessitating the placement of the ion source and primary beam optics in the position occupied by MBE growth sources. Lastly, and possibly the most serious disadvantage of SIMS is that it is a destructive analytical technique.

2.5.3 Ellipsometry

This materials characterization tool is surface-sensitive and is, in fact, compatible with the MBE geometry (shown in Figure 2.11), and is thus a viable in-growth diagnostic technique used by MBE practitioners. In its most basic description, the incident beam is polarized light, typically from a laser or an arc lamp. The ellipsometer collects light reflected from the sample and measures the change(s) in its polarization state. Ellipsometry has been successfully used in studying the roughness and reconstruction of the Si(111) surface, and in determining the composition and initial MBE growth rate of gallium arsenide (GaAs) thin films [11][12]. However, a disadvantage of ellipsometry is that the optical constants of the material being analyzed must already be known; thus, while the technique is useful for probing epitaxial growth, the ability to obtain quantitative information has only been demonstrated for a limited number of systems.

2.6 REELS analysis of $\text{Ge}_x\text{Si}_{1-x}$ alloys

The alloy system $\text{Ge}_x\text{Si}_{1-x}$ is of great interest for semiconductor devices. In particular, fabrication of $\text{Ge}_x\text{Si}_{1-x}$ strained-layer superlattices for modulation-doped field-effect transistors requires detailed knowledge of the effects of alloy concentration, layer thickness and dopant concentrations on the electronic transport properties of the $\text{Ge}_x\text{Si}_{1-x}$ system. Conversely, it is desirable to know how the properties of $\text{Ge}_x\text{Si}_{1-x}$

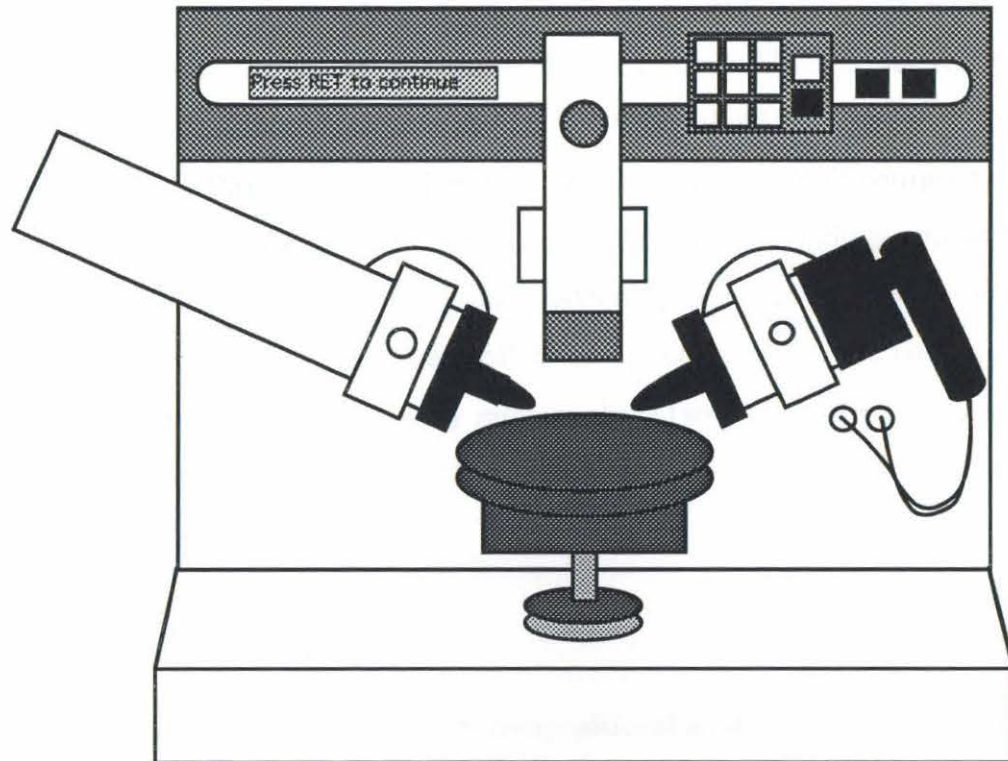


Figure 2.11: Illustration of a typical ellipsometer, which is compatible with the MBE environment. The probe apparatus (tilted module on left side) includes a light source, polarizer and quarter wave plate. The analyzing apparatus (tilted module on right side) includes a rotating analyzer and photomultiplier tube.

limit or enhance these device parameters.

2.6.1 Background investigations

Compositional analysis of $\text{Ge}_x\text{Si}_{1-x}$ alloys by REELS in the molecular beam epitaxy chamber has recently been demonstrated [13][1]. Epitaxial $\text{Ge}_x\text{Si}_{1-x}$ films were deposited on Si(100) substrates at a growth temperature of $\sim 410^\circ\text{C}$ in a custom-designed MBE system, with intended compositions of $x = 0$ to $x = 0.5$, measured by quartz crystal oscillators placed near the Si and Ge sources. REELS analysis was performed on the Ge $L_{2,3}$ core loss intensity (1217 eV threshold) and the Si K core loss intensity (1839 eV threshold) (see Figure 2.12). Determination of compositions was based on empirical cross sections obtained from an alloy of $\text{Ge}_{0.02}\text{Si}_{0.98}$, whose composition was independently measured by backscattering spectrometry and confirmed by TEM and x-ray microanalysis. The REELS composition data were consistent with the data obtained with RBS and x-ray microanalysis (within experimental uncertainties), indicating great potential for REELS as a valuable quantitative tool for *in situ* real-time surface chemical analysis.

2.6.2 A new twist

As a continuation of this work, REELS compositional analysis of $\text{Ge}_x\text{Si}_{1-x}$ alloys was also performed using the Ge $L_{2,3}$ intensity and the Si $L_{2,3}$ intensity (instead of Si K). In the previous work, the use of Ge $L_{2,3}$ and Si K was found to be favorable for analyzing small concentrations of Ge [13] because the Ge $L_{2,3}$ ionization cross section is much larger than that of Si K . Analysis using Si $L_{2,3}$ is, in a sense, also sensitive to small Ge concentrations, because although the Si $L_{2,3}$ cross section is considerably larger than that of Ge $L_{2,3}$ (see Figure 2.13), the Si $L_{2,3}$ ionization threshold of 99 eV is well isolated from the 1217 eV threshold for Ge $L_{2,3}$. Thus, the tail of the Si $L_{2,3}$ core loss intensity has decayed to nearly background level at the energy loss corresponding to Ge, avoiding complications due to superposition of the two core losses of interest.

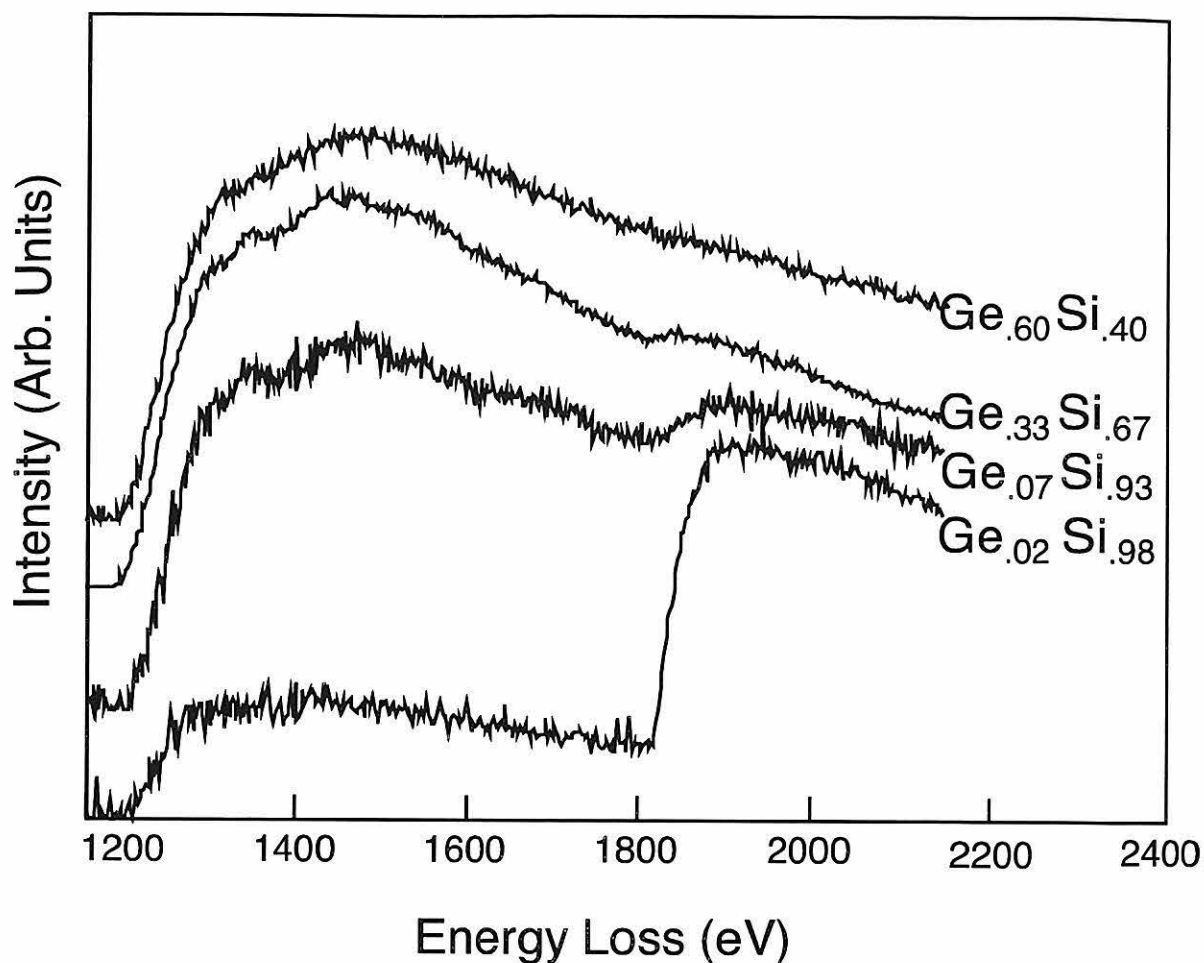


Figure 2.12: REELS core loss intensity of Ge $L_{2,3}$ (1217 eV) with Si K (1839 eV) core loss superimposed, for several $\text{Ge}_x\text{Si}_{1-x}$ alloy concentrations. [From S. Nikzad, C. C. Ahn and H. A. Atwater, *J. Vac. Sci. Tech. B* 10(2), 762 (1992).]

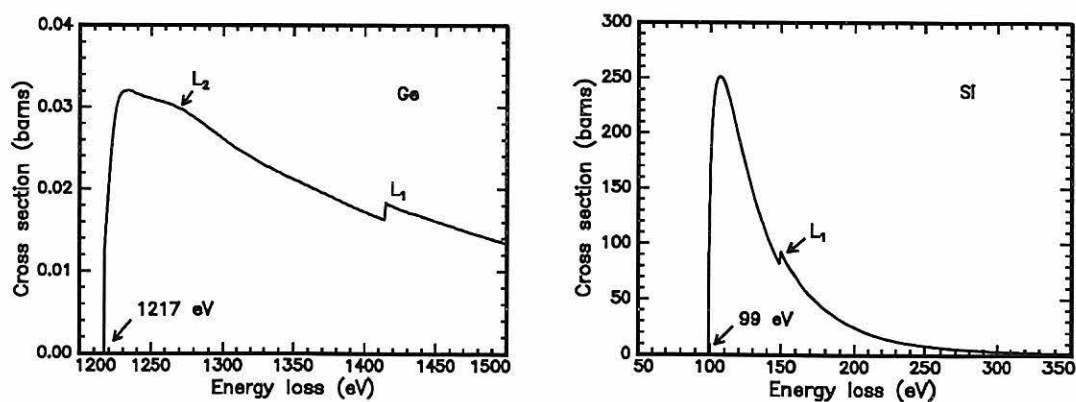


Figure 2.13: Hartree-Slater ionization cross section for Ge $L_{2,3}$ and hydrogenic ionization cross section for Si $L_{2,3}$. In both calculations, the L_1 edge is clearly visible.

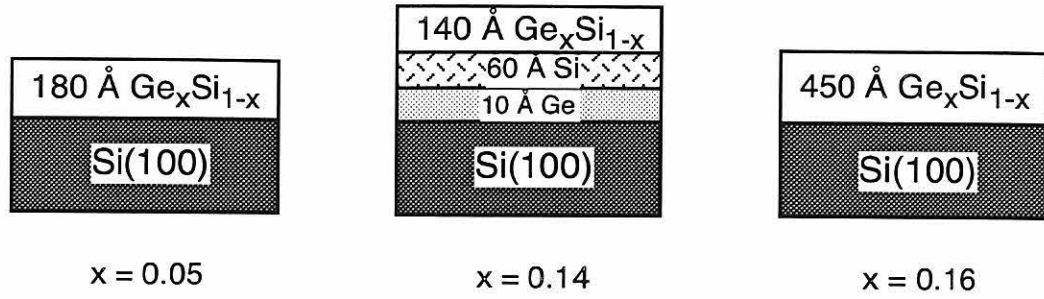


Figure 2.14: Schematic illustration of a few representative $\text{Ge}_x\text{Si}_{1-x}$ alloys studied. Films were grown on bare Si(100) substrate and on thin Ge or Si buffer layers.

Molecular beam epitaxial growth of the $\text{Ge}_x\text{Si}_{1-x}$ alloys was achieved using an effusion cell at temperatures ranging from 925 to 1200 °C for Ge, and a rod-fed electron beam evaporator (operating at 4 kV and 50-250 mA emission current) for Si. Substrates of Si(100) were chemically cleaned in a hydrogen peroxide-based solution (1:1:5 ratio of NH_4OH , H_2O_2 and 19 MΩ ultrapure water) and dipped in a HF solution (48% HF diluted to ~10% with 18 MΩ H_2O) before insertion into the growth chamber, and prebaked for approximately 90 minutes at 200-225 °C prior to film deposition to desorb residual physisorbed contaminants from the sample surface which are typically adsorbed from the cleaning solutions, laboratory atmosphere and handling. After the prebake, the substrate temperature was ramped to 650 °C at a rate of 12 °C/minute. Atomic-level surface cleanliness was indicated by the (2×1) reconstruction characteristic of the clean Si(100) surface (sharp Bragg rods with fainter half-order lines) which was constantly monitored. If the (2×1) RHEED pattern was not observed on a particular substrate, $\text{Ge}_x\text{Si}_{1-x}$ growth was not attempted.

Nominal base pressure of the vacuum chamber was $\sim 5 \times 10^{-9}$ Torr. Growth rates were typically low and ranged from 2-4 Å/min because of the relatively large source-to-substrate distances (~ 51 cm (20") from e-beam evaporator to substrate). In some of the depositions, a Ge or Si buffer layer (10-60 Å) was deposited before deposition of the $\text{Ge}_x\text{Si}_{1-x}$ alloy film. The Si buffer layer serves to smoothen the substrate surface, which is rough on the atomic scale.

Figure 2.14 illustrates schematically the layer structure of a few representative alloys grown. Multiple REELS spectra were obtained during alloy deposition, and

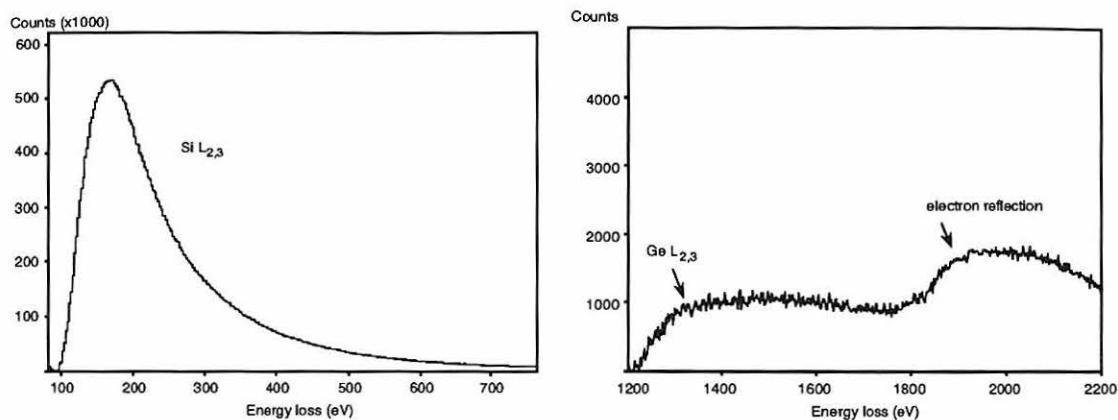


Figure 2.15: Typical background-subtracted Si $L_{2,3}$ and Ge $L_{2,3}$ core loss intensities, measured from the alloys discussed in this section.

comparison of the Ge $L_{2,3}$ and Si $L_{2,3}$ core loss intensities indicated a constant composition of the alloy during growth. Figure 2.15 shows typical background-subtracted Si $L_{2,3}$ and Ge $L_{2,3}$ core loss intensities. Measurements were made on a diffracted beam component (i.e., a Bragg feature) with a 30 keV incident beam at an angle of $\sim 0.5^\circ$ with the sample surface. Compositional analysis was performed using an empirical cross section ratio $\sigma(\text{Ge } L_{2,3})/\sigma(\text{Si } L_{2,3})$ obtained with an alloy of $\text{Ge}_{0.16}\text{Si}_{0.84}$ whose composition was independently measured by RBS. Table 2.1 shows a comparison of REELS composition analysis results (using Ge $L_{2,3}$, Si K , and Si $L_{2,3}$ core losses) with analyses obtained by Rutherford backscattering spectrometry. All REELS data agree well within experimental uncertainties with the data measured by RBS, the more conventional analysis technique. It is relevant to note that some of the deviation of REELS results with RBS results can partially be explained by the fact that REELS is inherently a surface-sensitive technique, while RBS is a bulk-sensitive technique; thus, any differences in surface composition compared to the bulk composition would be reflected in the differences in the REELS and RBS measurements.

2.6.3 Discussion

It has been demonstrated that REELS is a viable analysis technique capable of accurately determining alloy compositions, with the added advantage of doing so *during* film growth. Measurements on $\text{Ge}_x\text{Si}_{1-x}$ alloys using the Si $L_{2,3}$ as well as the Si K , in

REELS		RBS (± 0.05)
0.02	†	0.02
$0.05 \pm .02$	*	0.04
0.07	†	0.06
$0.14 \pm .02$	*	0.16
$0.16 \pm .03$	*	0.20
0.21	†	0.13
0.33	†	0.30
0.60	†	0.65

* denotes analysis of Ge $L_{2,3}$ and Si $L_{2,3}$ core losses

† denotes analysis of Ge $L_{2,3}$ and Si K core losses

Table 2.1: Comparison of REELS composition analysis results with results obtained by Rutherford backscattering spectrometry.

conjunction with Ge $L_{2,3}$ intensity, have been found to be suitable for measuring very small Ge concentrations. From these measurements, we establish a REELS detection limit of $\sim 2\%$ for Ge in $\text{Ge}_x\text{Si}_{1-x}$ alloys. With an incident beam angle of $\sim 0.5^\circ$, REELS was found to be very surface-sensitive; in fact, measurements made on very thin (~ 1 ML) Ge films have yielded easily detectable Ge $L_{2,3}$ core loss intensities [2][14], suggesting that the surface sensitivity is perhaps a fraction of a monolayer and that the Ge detection limit is also a fraction of a monolayer in thin Ge films.

2.7 Summary

Table 2.2 summarizes and compares the basic features of REELS and several of the more conventional materials analysis techniques described in this chapter.

	REELS	XPS	AES	SIMS
Detection limit	~5% ML; ~1 at. % in GeSi alloys	0.1 at. %	0.1 at. %	few ppm
Surface sensitivity/ depth resolution	Fraction of a ML to 20 Å (variable)	< 20 Å (variable)	< 20 Å (variable)	first 2--3 atomic layers
Spatial resolution	Beam spot size ~100 µm x 1 mm	~2 mm x 2 mm	~0.05--3.0 mm	50-300 µm
Materials able to be studied	Metals, insulators, semiconductors	Metals, insulators, semiconductors, polymers	Metals, insulators, semiconductors; not polymers	Metals, insulators, semiconductors; not polymers
Chemical information	Alloy composition; possibly can detect large chemical shifts; local order (EXELFS)	Elemental identification; chemical shifts easily detectable	Elemental identification; not well understood regarding chemical bonding	Isotope identification
MBE compatible?	Yes	No	No	No
Advantages	Real-time monitoring capability during film growth; local surface order information possible	Chemical bonding information; nondestructive of polymeric targets	Low cost; small beam spot size allows microanalysis	Most surface sensitive of all techniques; microanalysis possible, but difficult
Disadvantages	Currently cannot detect most chemical shifts	Difficult to focus beam; long analysis time	Mainly useful for analyzing light elements	Destructive

Table 2.2: Comparison of REELS with more widely used materials analysis techniques

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Chapter 3 Surface Contaminant Detection and Time-Dependent Measurements of Hydrocarbon Desorption

3.1 Introduction

The ability to achieve epitaxial thin film growth at low temperatures ($\leq 550^\circ\text{C}$) is essential to fabricating metastable alloys, for preserving sharp doping profiles and heterojunction interfaces [1], and for growth on preprocessed very large-scale integrated (VLSI) circuits [2][3]. Successful epitaxy requires an atomically clean starting substrate surface, and mandates that this atomic-level cleanliness be maintained throughout the growth. In conventional silicon molecular beam epitaxy, the native thermal oxide (SiO_2) on Si substrates is removed by desorption at $\sim 800^\circ\text{C}$. In addition to the high-temperature growth and annealing being unfavorable in terms of dopant diffusion, degradation of sharp interfaces, etc. as mentioned above, the clean surface at 800°C is very reactive and therefore susceptible to impurity adsorption.

In light of these considerations, a reliable *in situ* low-temperature substrate surface cleaning prior to film deposition is highly desirable. Moreover, *in situ* measurement of the concentrations of typical surface contaminants would be especially useful in characterizing the surface and determining whether the cleaning procedure [2] used has rendered the surface suitable for growth. There have been many efforts to develop an appropriate cleaning procedure for use with epitaxial growth and to quantify the coverage of critical contaminants using *ex situ* analytical techniques such as x-ray photoelectron spectroscopy (XPS) [4], ultraviolet photoelectron spectroscopy (UPS) [4], Fourier transform infrared (FTIR) spectroscopy [4][5][6], and Auger electron spectroscopy (AES) [5][7]. Although the best indication of a clean substrate surface is the successful growth of epitaxial films, it would be more desirable to determine

accurately the surface quality before growth is attempted. Hence, *in situ* analysis of surface contaminants will ultimately be the most useful guide to conditions for epitaxial growth.

Substrate surface quality, i.e., roughness, reconstruction, etc., is commonly assessed during MBE using RHEED because of its compatibility with the MBE environment, as discussed in Chapter 1. However, RHEED probes long-range structure and is relatively insensitive to the presence of crystallographic defects (e.g., dislocations and stacking faults), and it has been demonstrated that transmission electron microscopy of epitaxial films exhibiting acceptable RHEED patterns can indicate the presence of defects of unacceptably high density [8].

Eliminating the need for thermal oxide desorption of the Si substrate surface at 800 °C is the first step towards low-temperature cleaning. The reactive silicon atoms of the clean surface are passivated with a hydrogen termination; i.e., each of the dangling orbitals is saturated with a hydrogen atom. Methods of hydrogen termination have included dipping or spin-etching the substrate in liquid hydrofluoric (HF) acid, and immersion of the substrate in a gaseous HF environment. Although the H-termination achieved by any of these methods is successful in preventing oxide and carbide formation on the surface, residual physisorbed hydrocarbons exist on the surface and must be removed before epitaxy is attempted. Ideally, hydrocarbon desorption would be verified by analysis performed inside the deposition chamber prior to growth. This chapter will discuss the detection and quantification of concentration of typical surface contaminants on H-terminated Si(100) substrates by REELS, and describe the first quantitative measurements of hydrocarbon desorption from these surfaces in a conventional MBE chamber equipped with RHEED.

3.2 Background

3.2.1 Silicon bonds with common elements

We have mentioned that Si—O bonds on the substrate surface are undesirable because their removal would require bringing the substrate to ~ 800 °C. What about other typical bonds which might be formed? Atmospheric nitrogen (N_2) is very stable against Si—N bond formation, and in fact, substrate cleaning procedures carried out in a nitrogen ambient have been successful in reducing oxygen surface contamination which is found on substrates cleaned using the same procedure but in an air environment [10]. Carbon is an element commonly found in the ambient in the form of hydrocarbons. The Si—C bond is an especially strong one, and thermal desorption of the carbide would require heating at ~ 1100 °C [9]. Hence, great lengths are usually taken to prevent formation of surface silicon carbide.

3.2.2 Hydrogen termination of the Si surface

The clean Si(100) surface, constructed by cleaving bulk silicon along this plane in vacuum, will consist of Si atoms having the same structure as the bulk. Because each surface Si atom will have two unsaturated orbitals (“dangling bonds”), this structure is thermodynamically unstable and will spontaneously assume the (2×1) dimer-row structure, in which rows of two bond together via the bonding of adjacent Si atoms with each other. In this configuration, each surface Si atom has one remaining dangling bond. The resulting surface structure is known as the Si(100) (2×1) reconstruction; i.e., the surface has a periodicity twice that of the bulk in one direction, and is unchanged in the other direction (discussed in Chapter 1).

Hydrogen bonding to the Si(100) surface may take several forms, depending upon the temperature and the defect density of the surface. At temperatures lower than ~ 370 °C, bonding predominantly has the stoichiometry Si—H₂, with one H atom saturating each dangling Si bond. This H termination yields a surface with the bulk Si structure (1×1) . Due to microscopic roughness and the existence of steps

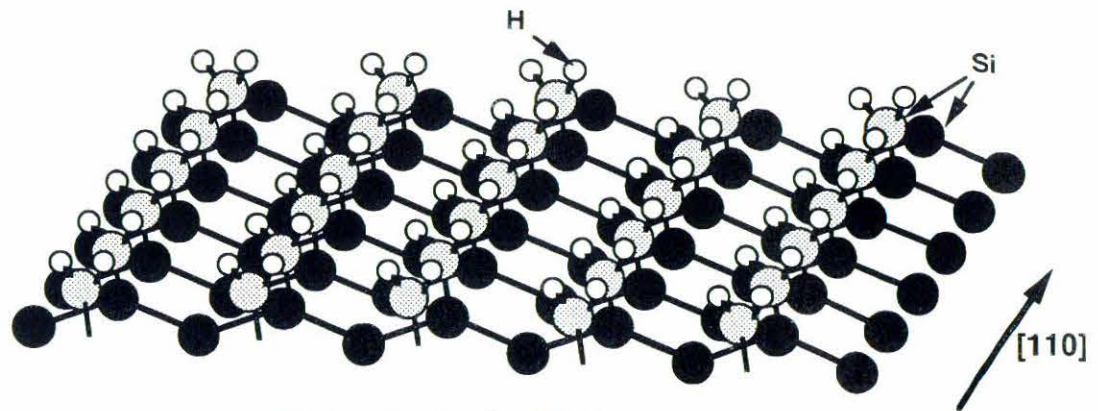
in the surface, monohydrided and trihydrided silicon atoms can also be found [6]. The dihydride termination is unstable upon heating to temperatures above 370 °C. Temperature-programmed desorption indicates that in the range 370 °C < T < 450 °C, partial hydrogen desorption from the surface occurs, leaving monohydrided silicon on a (2×1) reconstructed surface [11]. Fig. 3.1 shows the hydrogen termination expected for the two temperature regimes.

3.3 Experimental

3.3.1 Surface preparation methods

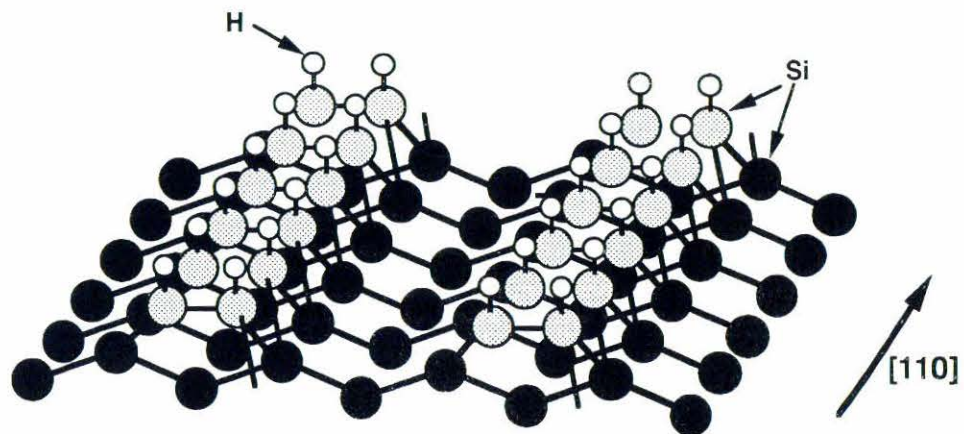
Various methods of surface preparation involving hydrogen termination have been successful in yielding clean substrates for epitaxial growth. For example, substrates spin-etched in HF/ethanol in a nitrogen ambient and subsequently analyzed were found to have 7% of a monolayer (ML) of oxygen and 17% ML of fluorine on the surface after ~ 2 minutes of exposure. By contrast, substrates spin-etched with HF/ethanol in air were found to have 14% ML of oxygen and 12% ML of fluorine on the surface [10]. It has also been demonstrated that epitaxy is possible on a Si(100) surface hydrogen-terminated via a buffered HF dip and prebaked at 200 °C [12]. The prebake is necessary to desorb residual hydrocarbons which have physisorbed on the surface between hydrogen termination and sample loading into the chamber. It has been shown [12] that if hydrocarbons are not eliminated from the surface, growth at low temperatures (< 370 °C) will be amorphous and at high temperatures (> 600 °C) will be epitaxial but will not wet the substrate surface, due to the presence of a thin $\text{Si}_{1-x}\text{C}_x$ or SiC layer.

We have exploited the surface sensitivity of REELS to study hydrocarbon concentrations on Si(100) substrate surfaces prepared with several methods. Wafers were Czochralski grown, test grade, n/p-doped, 2-inch diameter with resistivity 10–50 Ω cm and thickness 229–356 μm . In one method, samples were chemically cleaned in a hydrogen peroxide-based solution at 80 °C (1:1:5 ratio of NH_4OH , H_2O_2 , and 18



Dihydride Si(100), 1x1

$T \leq 370^\circ\text{C}$



Monohydride Si(100), 2x1

$370^\circ\text{C} \leq T \leq 450^\circ\text{C}$

Figure 3.1: (a) Below 370°C and with sufficient hydrogen exposure, two H atoms saturate the dangling bonds of each surface Si atom of the Si(100)(1×1) surface. (b) Between 370°C and 450°C , some of the hydrogen desorbs, leaving monohydrided silicon atoms on a Si(100)(2×1) reconstructed surface.

**(1) Chemically
untreated**

(2) HF/H₂O dipped

**(3) HF dip, methanol dip
(4) HF/methanol mixture**

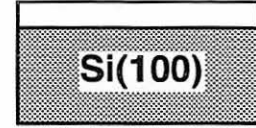
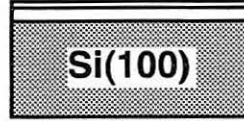
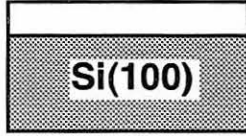


Figure 3.2: REELS measurements were performed on samples (a) subjected to no chemical cleaning treatment, (b) dipped in HF/H₂O, and (c) dipped in HF/methanol.

M Ω ultrapure water) and then etched by dipping in dilute HF (48% HF diluted to $\sim 10\%$ with 18 M Ω water). Alternate oxidation and stripping of the oxide was performed several times to remove inorganic and organic species bonded to the surface. After the final HF dip, samples were blown dry with nitrogen and immediately inserted into the chamber load-lock region. For purposes of systematically varying the carbon contamination levels on our substrates, we have also performed REELS measurements on samples dipped in HF and then in methanol, and on samples dipped in a HF/methanol mixture. Lastly, for comparison, we have also examined the surface of a sample as-is from the manufacturer's packaging, subjected to no cleaning treatments except for blowing with nitrogen to remove gross contaminants (e.g., dust particles) which may have settled on the sample during handling. The various surface preparation methods employed in our REELS measurements are illustrated in Fig. 3.2.

3.3.2 Empirical cross sections

The core loss ionization cross sections of the major surface contaminants were calculated using a simple hydrogenic atom model. Fig. 3.3 shows the Si $L_{2,3}$, C K and O K cross sections. The ratios of the Si $L_{2,3}$ cross section to those of C and O are about 100 and 1000, respectively, at the ionization thresholds.

Due to multiple inelastic scattering and variations in data collection geometry which would produce artifacts in REELS data (discussed in Chapter 2), we opted to use empirical ionization cross sections from energy loss spectra from materials of

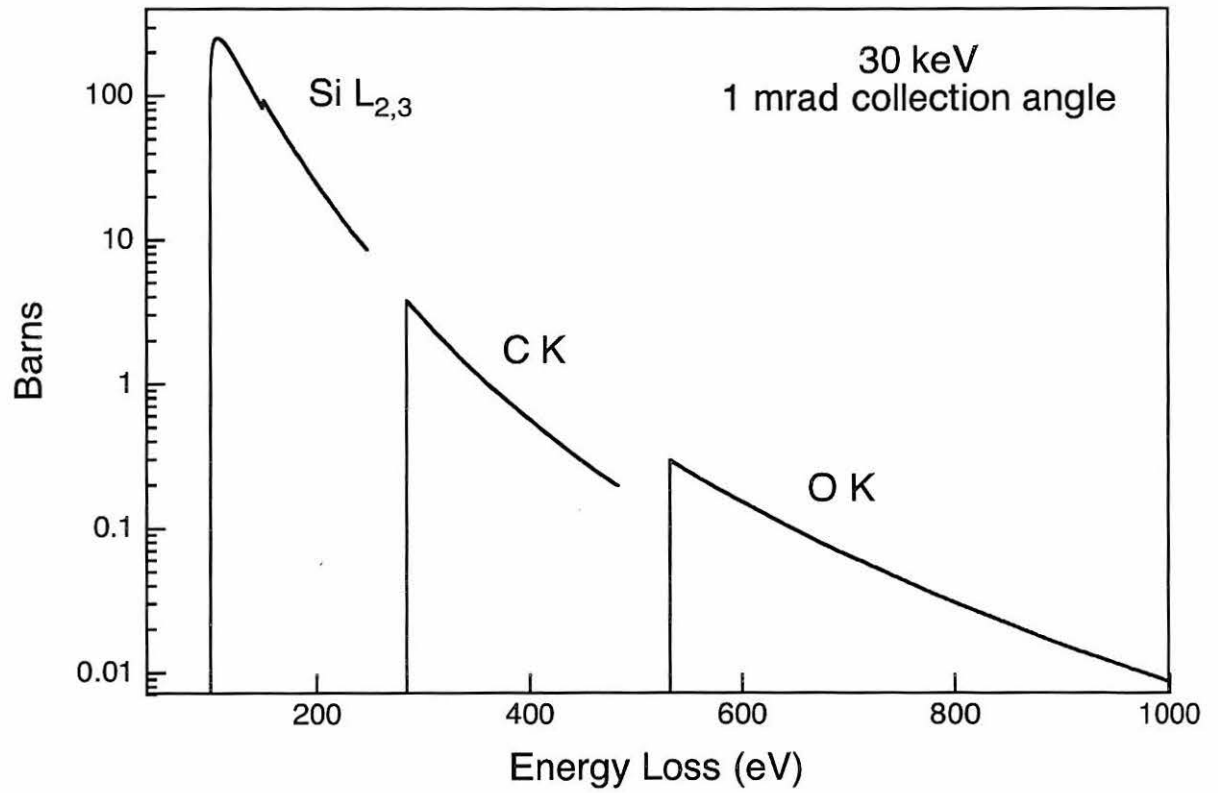


Figure 3.3: Ionization cross sections for the Si $L_{2,3}$, C K and O K core losses, based on a hydrogenic atom model.

known stoichiometry. We chose to investigate oxygen surface concentration as well as that of carbon. For our carbon reference we used a 1000 nm (10,000 Å) layer of SiC grown by chemical vapor deposition on a Si(100) substrate. By comparing the C K and Si $L_{2,3}$ intensities for this stoichiometric sample of SiC, an empirical cross section ratio was obtained. Similarly, for an oxygen reference, a 100 nm (1000 Å) layer of SiO₂ on Si(100) was used, and an empirical ratio of cross sections was obtained in the same way. As a check for stoichiometry, XPS measurements were also performed on the SiC and SiO₂ references (see Fig. 3.4). The empirical cross sections obtained were found to be consistent with the theoretical cross sections (integrated over an energy window of 200 eV) to within 10%.

3.3.3 Results

XPS and REELS measurements were made on Si(100) substrates prepared with the methods described above, and XPS was thus employed as an independent measure of the carbon surface contamination. For the REELS experiments, typical parameters for the RHEED gun were 30 keV energy with $\sim 50 \mu\text{A}$ emission current and about 0.5–2 μA of sample current. The electron beam spot size on the sample was approximately $0.02 \text{ cm} \times 2 \text{ cm}$, yielding a sample current density of approximately $25 \mu\text{A}/\text{cm}^2$. Typical measurement times were 600–1000 seconds (~ 10 –20 minutes). Measurements were performed with an incident beam angle as shallow as possible, and in most cases the angle was about 0.5° .

Oxygen was not detected on any of the substrates except the untreated one, as deduced from REELS measurements of the O K core loss intensity. These surfaces were found to have an oxygen coverage of 2 ± 1 monolayers. XPS analysis on the HF/H₂O-dipped surface found 0.08% ML of oxygen. From these and previous REELS measurements performed within our research group on native oxide layers, the REELS sensitivity to oxygen is estimated to be between the XPS-detected quantity of 0.08% and 0.5 ML.

REELS measurements of surface carbon concentration on the substrates prepared

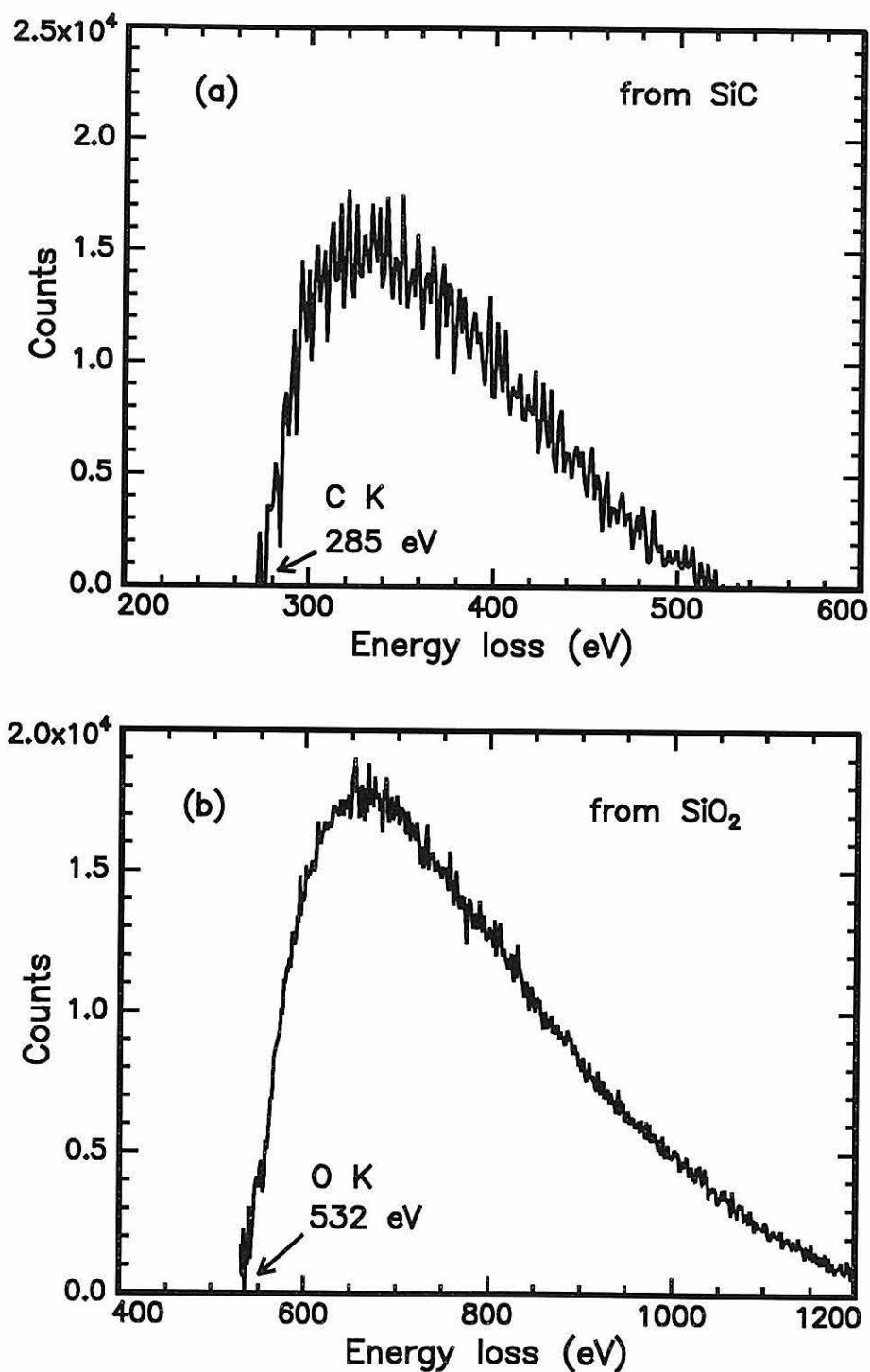


Figure 3.4: Empirical cross sections for C K and O K were obtained from REELS spectra from SiC (a) and SiO₂ (b), respectively. Measurements were made with a 0.5° incident RHEED beam.

Preparation method	Carbon coverage (% ML)
Untreated	14 ± 4
HF/H ₂ O dip	5 ± 2
HF dip, MeOH dip	16 ± 5
HF/MeOH dip	8 ± 2

Table 3.1: Surface carbon concentrations found by REELS on the substrates prepared with various cleaning methods.

with the various methods are listed in Table 3.1. Not surprisingly, substrates which were hydrogen-terminated with a HF/H₂O dip exhibited the smallest carbon surface concentration. Because these cleanest samples are the most relevant for crystal growers, we chose to focus our study on the HF/H₂O-dipped surface.

Fig. 3.5 shows representative REELS data obtained from the HF/H₂O surfaces. Without a background subtraction to remove energy loss contributions due to plasmons, plural scattering and the tails of other core losses with smaller ionization thresholds, the carbon *K* edge intensity is not discernible even as a very slight change in slope in the raw data. The edge was extracted after employing a standard exponential decay background subtraction [13]. The signal-to-noise ratio for the background-subtracted C *K* edge was quite small, indicating a very small C *K* intensity.

In order to better quantify our measurements, we used a standard second difference filtering technique [14], which is useful in analyzing data with low signal-to-background ratios. The operation yields a spectrum which is similar to a negative second derivative, and may be somewhat easier to interpret than a first-derivative spectrum because a peak in the second difference spectrum corresponds to a peak in the raw data spectrum; i.e., the second difference is proportional to the raw signal. Thus, the ratio of carbon atoms to silicon atoms on the surface as measured by

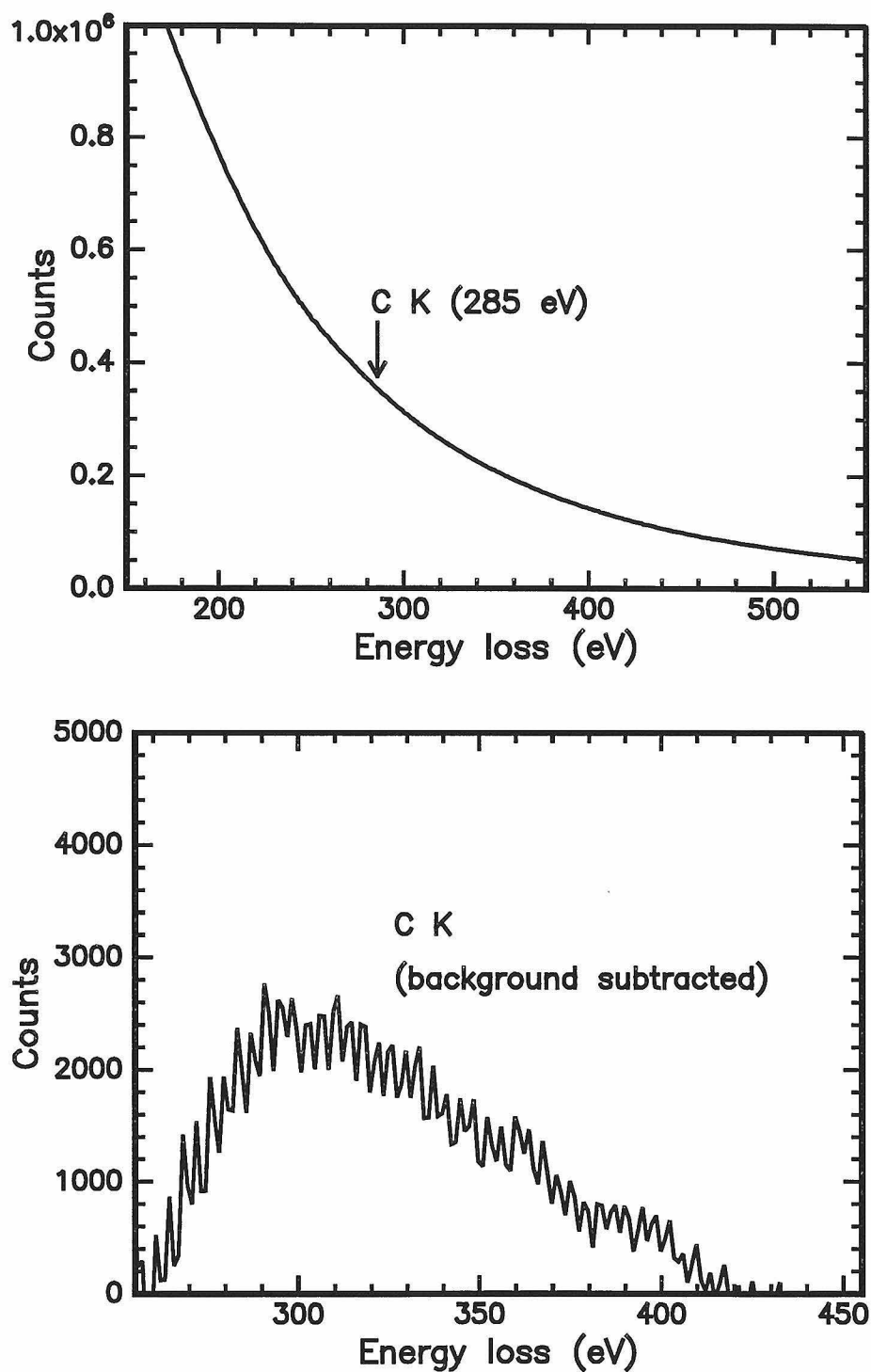


Figure 3.5: REELS data from HF/H₂O-dipped surface. (a) The carbon *K* edge is not apparent from the raw data (C *K* edge threshold is 285 eV). (b) Background-subtracted C *K* edge, with low signal-to-noise ratio, indicating very small C *K* intensity.

REELS was obtained using the relation

$$\frac{N_C}{N_{Si}} = \left[\frac{S_C''(Si)}{S_C''(SiC)} \right] \left[\frac{S_C^{(SiC)}}{S_{Si}^{(SiC)}} \right] \left[\frac{S_{Si}^{(SiC)}}{S_{Si}^{(Si)}} \right] \quad (3.1)$$

where double primes indicate second differences. The notation S_α^β denotes signal intensity S of core loss α from sample β . The first bracketed quantity is determined with the second-difference spectrum; the second quantity is the empirical cross section ratio σ_{Si}/σ_C , obtained from the SiC reference spectra; and the last quantity is a ratio of normal core loss intensities.

Fig. 3.6 illustrates the second difference of the spectra obtained from a HF/H₂O substrate after isochronal anneals at various temperatures between room temperature and 200 °C. The incidence angle of the RHEED beam was $0.5^\circ \pm 0.1^\circ$. Temperature was increased between measurements at a constant rate of 6 °C/minute. The substrate was annealed for ~25 minutes at each temperature. Quantitative REELS analysis of the C K intensity at room temperature immediately after sample insertion, normalized to the Si $L_{2,3}$ intensity, yielded a surface C concentration of $(5 \pm 2)\%$ ML. For comparison, our XPS measurements found $(5 \pm 2)\%$ ML of carbon on a substrate prepared in the same manner. The SiC spectrum indicates a possible chemical shift in the C K threshold, which is consistent with our XPS data which found a shift of approximately 2 eV. As seen in Fig. 3.6, carbon is present at all temperatures between room temperature and 200 °C. However, at 200 °C the C K signal begins to be comparable to the noise level. The C K core loss intensity increases between 100 and 200 °C, which is most likely due to transient outgassing of the sample holder during heating, which could influence the rate of hydrocarbon adsorption to the surface. The RHEED pattern was monitored simultaneously during the entire set of measurements, and the onset of the (2×1) reconstruction occurred at ~405 °C. A subsequent second difference of a spectrum obtained from a sample at 435 °C yielded no detectable C K signal.

It is also interesting to investigate the nature of the hydrocarbon desorption from the Si(100) surfaces. We set forth to obtain REELS spectra from the surface as a

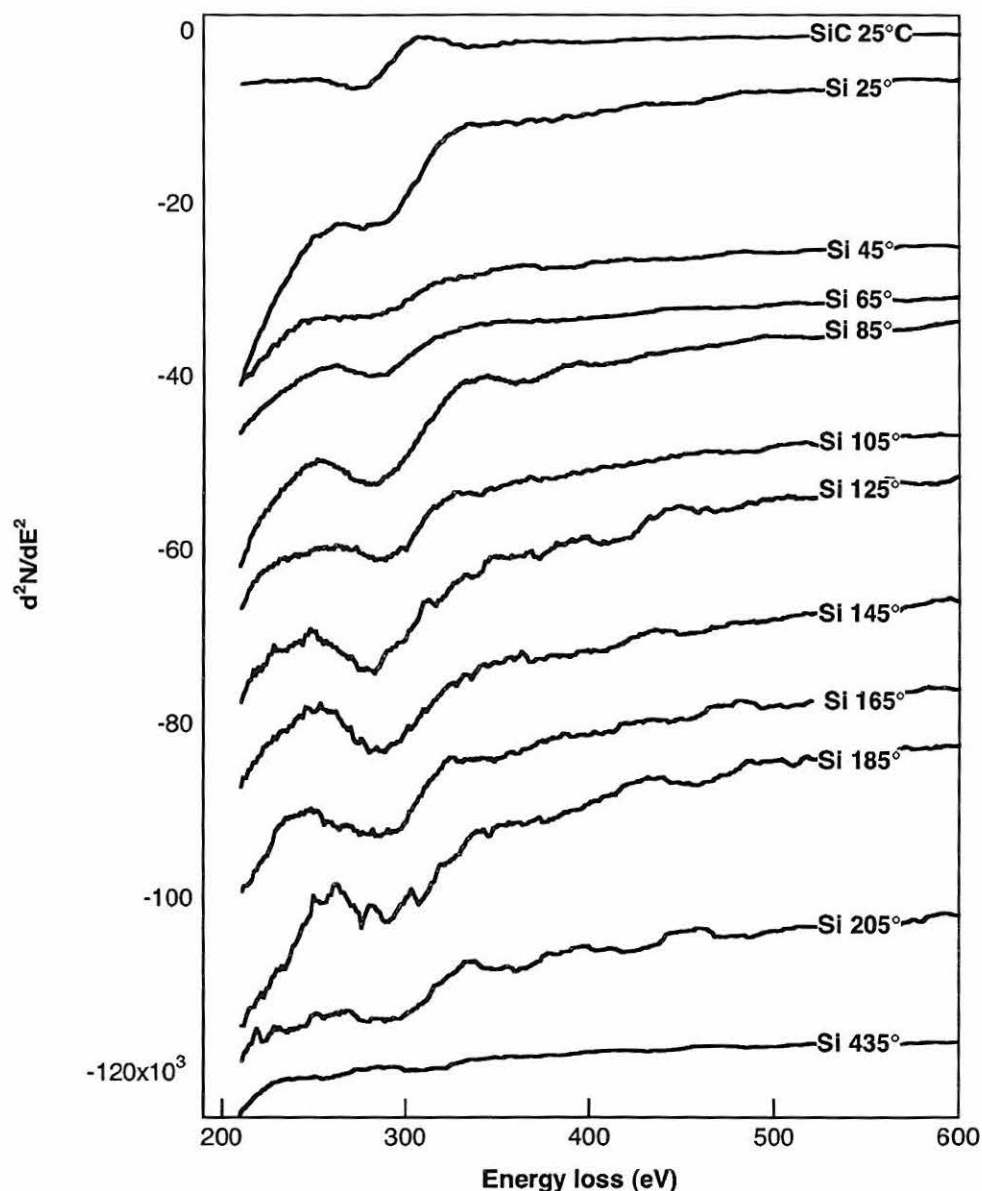


Figure 3.6: Second difference spectra of C K intensities from HF/H₂O-dipped Si(100) at various temperatures between 25 and 200 °C. The arrow indicates a local minimum in the second difference, corresponding to the onset of the C K ionization edge at 284 eV. The SiC reference spectrum is shown on top. It possibly indicates a chemical shift in the threshold of C K in SiC. For the Si(100) substrate, the C K intensities were normalized to the respective Si $L_{2,3}$ intensities and absolute carbon coverages were determined using the empirical cross section obtained from the SiC standard. Quantitative REELS analysis indicated $5 \pm 2\%$ ML of carbon on the surface at room temperature immediately after sample insertion into the chamber. The onset of the (2×1) reconstruction occurred at ~ 405 °C.

function of time during a typical one-hour prebake, in order to determine carbon coverage and observe its removal during the prebake.

REELS data were first taken at room temperature. Subsequent data were collected at the prebake temperature at approximately 8-minute intervals. After a dozen or so measurements at the prebake temperature, the substrate temperature was ramped at a rate of 12 °C/minute until (2×1) reconstruction of the Si(100) occurred, as observed by RHEED at 400–430 °C. REELS spectra of the reconstructed surface and the carbon coverage was estimated. To minimize the effect of possible beam damage on measurement results, a new position on the sample was used for each subsequent measurement, for beam-induced hydrocarbon formation would introduce error. To assess the degree of typical C coverage non-uniformity on a given sample, REELS measurements were performed at room temperature on a number of positions (each ~ 2 mm apart) on a substrate. Fig. 3.7 illustrates the variation of C coverage with position on the wafer and indicates that the coverage varies by about 1.3% of a monolayer with measurement position.

Measurement of the time dependence of surface hydrocarbon contamination by REELS was initially attempted at the usual prebake temperature of 200 °C. However, we found that the hydrocarbon desorption occurred on a time scale much faster than the time scale of a REELS measurement (≥ 1 minute). Consequently, the measured C coverage dropped to undetectable levels after the initial measurement at room temperature. In fact, prebake temperatures as low as 150 °C yielded the same result. Figure 3.8 shows the time variation of C coverage during isothermal REELS measurements at 115°, and Figure 3.9 shows the time variation of C coverage during isothermal REELS measurements at 150° and 175°C. In the 115 °C graph, a gradual reduction of C coverage was measured during the first 30 minutes. At 150 °C and 175 °C the C coverage, while falling below our REELS detection limit in the first 10 minutes, increases and fluctuates sporadically at later measurement times (~ 50 minutes). As mentioned earlier, this variation in the hydrocarbon coverage is most likely due to outgassing of various components in the growth chamber which are heated during the sample prebake. In addition to the sample holder, we suspected that

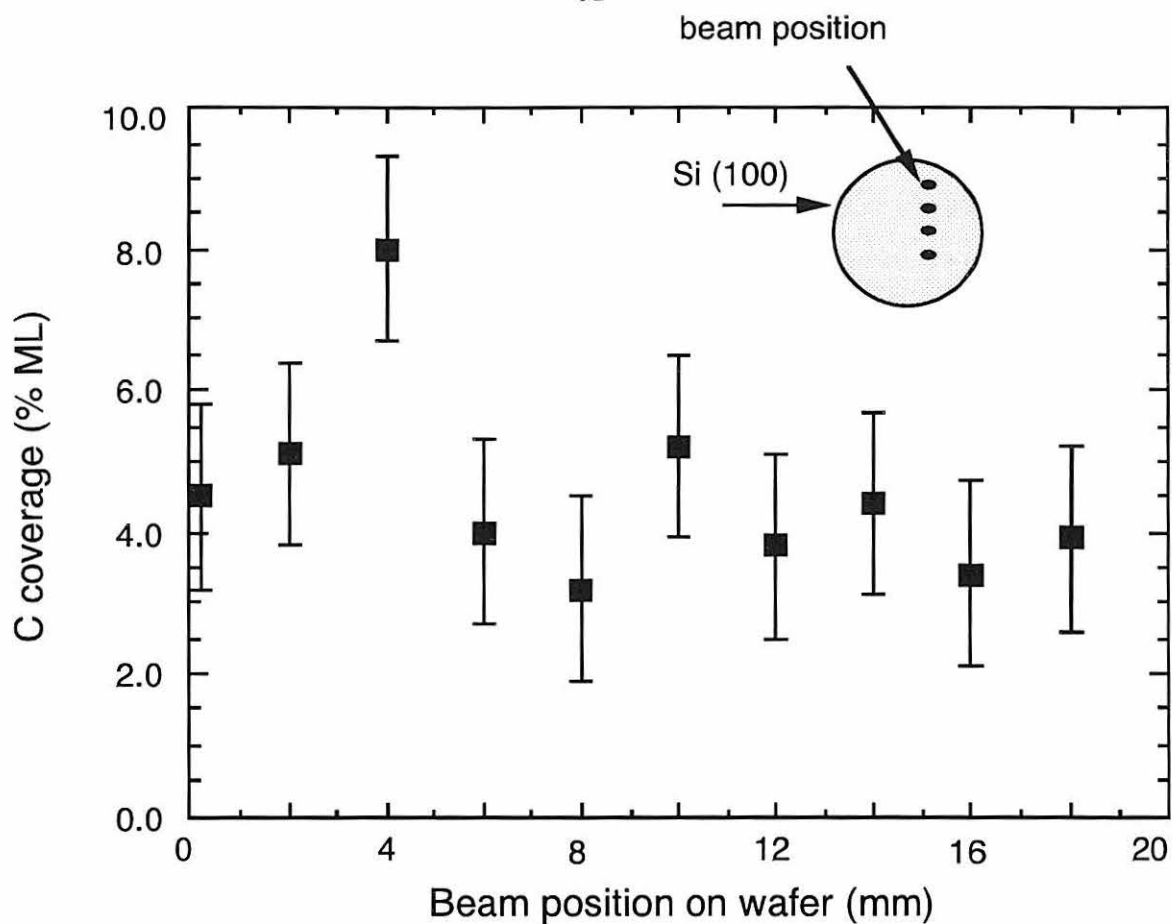


Figure 3.7: Typical carbon coverage on Si as a function of position on the wafer.

operation of filaments (e.g., in the ionization gauge, quadrupole mass spectrometer, and heater assembly) would contribute to hydrocarbon cracking and/or adsorption on the sample surface. However, REELS measurements made with filaments on and off (with the exception of the sample heater, which was left on) indicated no measurable effect by the filaments of the ion gauge and mass spectrometer. Thus the observed sporadic behavior of the C coverage is likely to be mainly due to the substrate holder. This is understandable because the substrate holder—and the heater behind it—are in much closer proximity to the sample surface than the other filaments.

It is important to note that for samples prebaked at any of the temperatures chosen for REELS measurement, the carbon coverage is always negligible at 400 °C (see Figures 3.8 and 3.9). Thus a prebake at 115 °C for one hour is equally effective in removing physisorbed hydrocarbons as a one-hour prebake at 200 °C, which is often

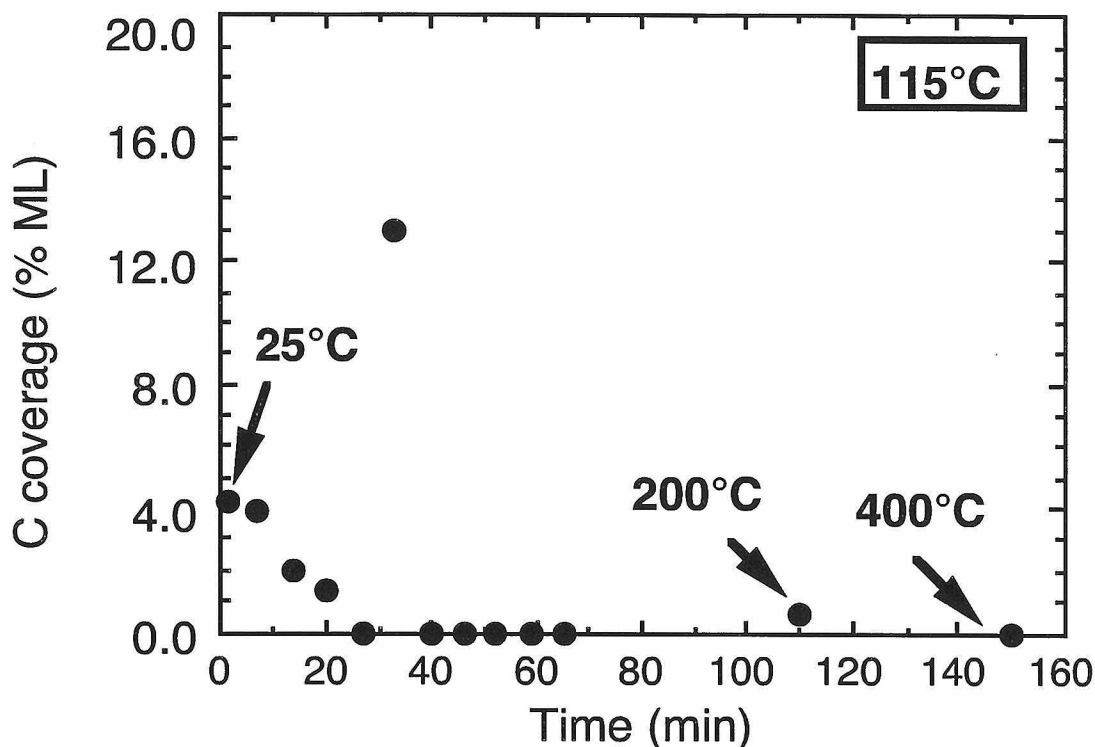


Figure 3.8: Time dependence of the carbon coverage on Si surfaces at 115 °C.

cited in the recent literature as a “good” prebake temperature.

3.4 Discussion

It is difficult to generalize about hydrocarbon desorption mechanisms because these are in principle dependent upon hydrocarbon structure and molecular weight, and because the relative abundance of different species depends on the cleaning and growth environments and cleaning solutions. Some observations can be made about hydrocarbon desorption from hydrogen-terminated silicon surfaces by quantifying time-dependent coverages, as we have done. The apparent activation energy for hydrocarbon desorption in our experiments is about 0.03 eV per hydrocarbon molecule ($= kT$, using $T = 115\text{ °C}$, or 388 K). This energy is much smaller than the energy required to break chemical bonds between H and Si (of the order of 2 eV/bond)[15], or between C and Si; this confirms that the hydrocarbons are in fact merely physisorbed on the silicon surface.

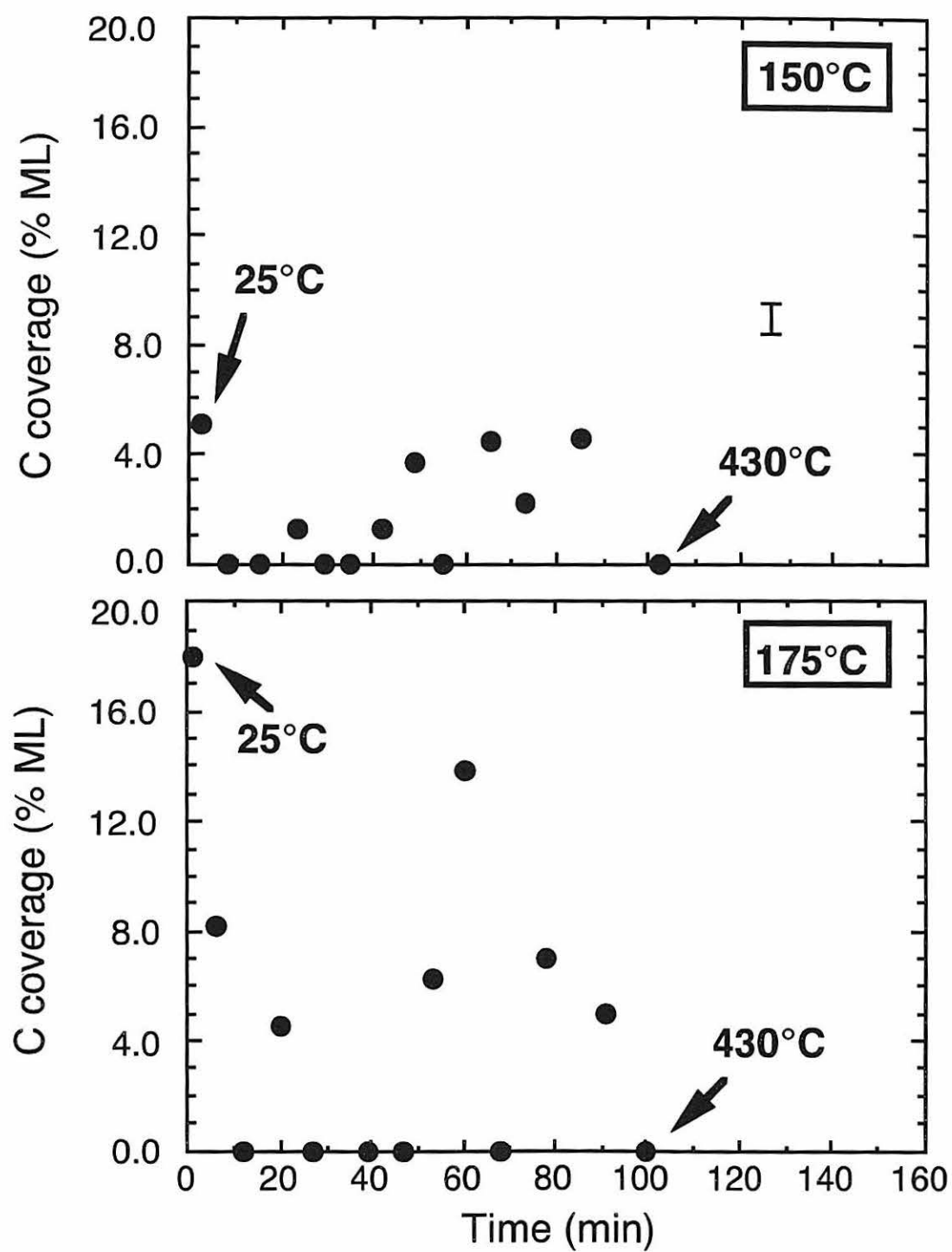


Figure 3.9: Time dependence of the carbon coverage on Si surfaces at 175 and 150 °C. While the carbon coverage may fluctuate at intermediate times of observation, it drops to undetectable levels at ~400 °C.

We were concerned about electron beam-induced damage to the hydrogen-terminated surfaces and made measurements to assess the degree of beam influence on the H—Si bond. Consecutive REELS measurements of carbon coverages were made for the same point on silicon substrates at room temperature with 30 keV electrons at 0.03 mA/cm² sample current density. We observed no change in carbon surface coverage after 20–60 minutes of irradiation. This is consistent with Auger spectroscopy studies of time evolution profiles of oxygen and carbon on H-terminated Si(100) surfaces, which reported an incubation period before C and O are detected on the Si(100) surface, which increases with increasing beam energy [16]. Our beam current density is lower than that of the cited work, and our irradiation times are lower by factors of 2–3. It was also reported that the cross section for electron beam-stimulated hydrogen desorption decreases by orders of magnitude with increasing electron energy. Given our higher incident beam energy of 30 keV, as opposed to 2–5 keV in AES measurements, and shorter irradiation times, it is not surprising that we do not observe significant beam-induced hydrocarbon desorption.

What about desorption of hydrocarbons due to core electron ionizations? REELS measurements on our Si(100) surfaces typically produced a relatively large Si $L_{2,3}$ core loss intensity. One may suspect that the ejection of an atomic electron due to ionization can cause desorption of adsorbed species. Auger spectroscopy studies of electron-stimulated desorption of deuterium from the Si(111) surface [17] for electron energies <1 keV found a stepwise increase in the desorption cross section at ~ 100 eV, which was attributed to Si L -shell ionization. The desorption efficiency was determined to be $\sim 10^{-3}$ eV. This value is very small and thus only a small fraction of core-level ionization is effective for electron-stimulated desorption. Again, in our REELS measurements our beam energy was much larger; and empirically we did not observe any hydrogen desorption as judged by our RHEED patterns which indicated our surfaces maintained a (1×1) structure for up to three hours of exposure to the incident beam, while low-temperature measurements were being obtained. It was not until they were heated to ~ 430 °C, at which point the normal transition from dihydride to monohydride termination occurred, that hydrogen desorbed.

3.5 Summary

We have performed quantitative REELS measurements on the surface concentration of common contaminants, namely carbon and oxygen, on Si(100) substrates in a molecular beam epitaxy chamber prior to film growth. From these experiments we have established the REELS detection limit for oxygen to be not more than 0.5 ML, and for carbon to be $(5 \pm 2)\%$ of a monolayer. Our time-dependent measurements of surface carbon coverage at various prebake temperatures indicate that desorption of physisorbed hydrocarbons is activated at ~ 115 °C, and that a one-hour substrate prebake at this temperature is sufficient to remove these hydrocarbons and render the surface atomically clean, and thus ready for epitaxy.

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Chapter 4 Investigation of Short-Range Surface Order With REELS EXELFS

4.1 Introduction

The growth of thin films by molecular beam epitaxy and *in situ* analysis has enabled synthesis of artificial structures with abrupt strain and composition profiles. Reflection high energy electron diffraction (RHEED) is well-suited to analysis of surface reconstructions, as discussed in the previous chapter, and gives qualitative information about surface roughness. However, with the advent of growth of ever more abrupt layers and metastable layers, a practical method for *in situ* analysis of local order as well as chemical composition is also desirable. A good example is the observation of stable surface reconstructions induced by epitaxial growth of thin layers of boron on Si(100) and Si(111) [1]. Thus, obtaining local order structure information would be useful in determining the mechanisms involved in the evolution of microstructure during the initial, critical stages of film growth.

In this chapter, REELS extended-edge energy loss fine structure (EXELFS) investigations of local order in Sn films on Si(100) and in Sn-Ge alloy films will be presented. Low-temperature ($\sim 330^\circ\text{C}$) epitaxy of Si on Si(111) with a thin mediating layer of Sn on the surface has prompted investigations of structure and dynamics of surfactants, such as the tin-induced atomic structure of the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ reconstructed surface [3]. Moreover, the zero energy band gap of α -Sn [4], which has a diamond cubic structure, has prompted investigations of α -Sn/Ge quantum-well structures. When alloyed with germanium, α -SnGe is predicted to have a direct band gap in the range of 0.0–0.55 eV for tin concentrations of 0.2–0.6 [5], making such an alloy potentially useful in infrared optoelectronic devices. From a fundamental standpoint, Sn films on Si and Sn-Ge alloys are good systems for EXELFS analysis

because the Sn $M_{4,5}$ edge energy loss cross section is relatively large. Previously, energy loss fine structure has been performed for epitaxial growth of Cu on Ag and was used to obtain information on strain relaxation during epitaxial growth [6]. Here we shall describe the use of similar methods to examine local order in semiconductor monolayer films and strained alloy layers.

4.2 Overview of EXELFS

The physical mechanism of EXELFS is analogous to the more well-known phenomenon of x-ray absorption fine structure (EXAFS). In both EXELFS and EXAFS, the probing beam is considered a quantum-mechanical wave, and the two phenomena are a diffraction effect in condensed matter. The description of EXELFS will closely follow that of EXAFS. EXAFS is well established in the biological, chemical and physical research communities and has proven to be a very useful analysis tool for probing local order structure.

4.2.1 Qualitative description

As discussed in Chapter 1, as an electron beam passes through a material, energy is removed from the beam by Compton scattering, heat transfer, x-ray fluorescence, and electron excitation and ionization. The attenuation of the incident beam by these processes is known as absorption, and is described by

$$I = I_0 e^{-\mu x} \quad (4.1)$$

where I_0 is the initial intensity, μ is the linear absorption coefficient, and x is the distance traveled in the material. If the incident electron energy is high enough to ionize atomic electrons of the material, the absorption spectra will show sharp jumps, or edges, corresponding to the ionization energies of these electrons. Upon first glance, the absorption coefficient decays exponentially, but with closer analysis one finds that it oscillates about the decaying exponential out to about 1000 eV above the edge (see

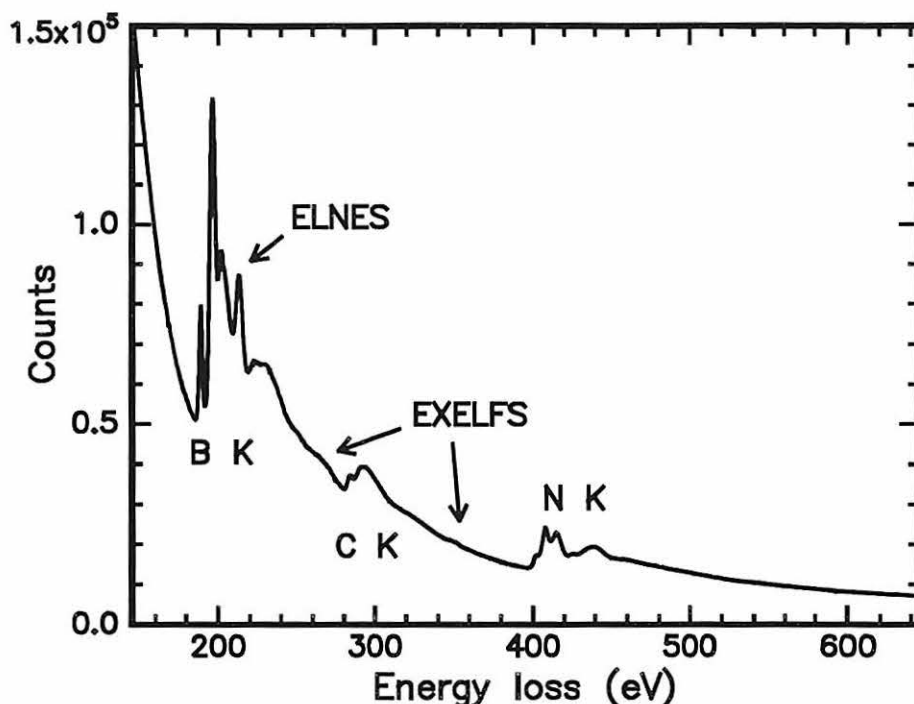


Figure 4.1: Schematic of fine structure oscillations in a typical energy loss spectrum. The features close to the atomic ionization threshold correspond to energy loss near-edge structure (ELNES), and the features further out correspond to the extended-edge energy loss fine structure (EXELFS). Data set from Gatan, Inc.

Fig. 4.1). The oscillations in the 100 eV or so above the edge are the near-edge energy-loss fine structure (NEELFS), which reflect the variations in the density of states above the Fermi level, and the remaining oscillations constitute the extended-edge energy loss fine structure. Both phenomena are characteristic of absorption spectra from condensed matter. We will focus on EXELFS in the discussion of this chapter.

The incident beam particles are treated quantum-mechanically as waves. When an incident electron (e.g., a RHEED electron) impinges on a solid surface and ionizes an atom (hereafter denoted as the “central” atom), the outward-traveling scattered electron wave encounters neighbor atoms and has a finite quantum-mechanical probability of being scattered back by the neighbors toward the central atom (see Fig. 4.2). The outgoing electron wave interferes with the sum of the incoming waves, and it is this interference that gives rise to oscillations in the observed scattering intensity at a

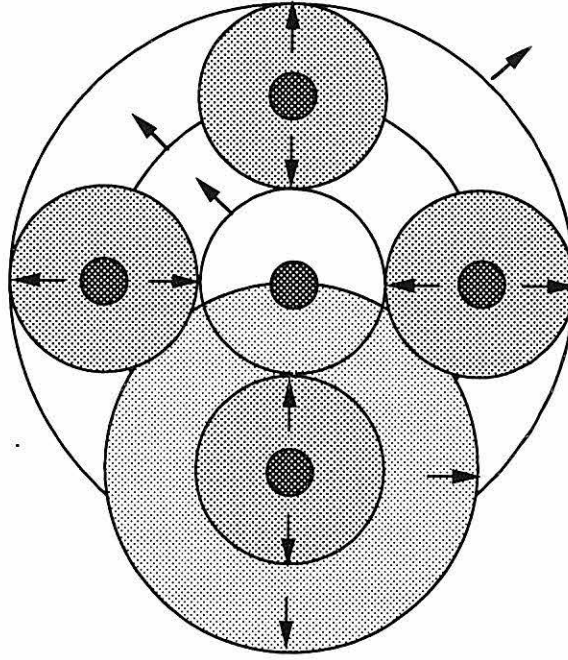


Figure 4.2: EXELFS can be understood as a quantum-mechanical interference phenomenon between the outgoing electron wave and the incoming waves scattered back toward the central atom by near neighbor atoms.

given energy loss. It is in this manner that EXELFS is unique to condensed matter, as it depends on the existence of shells of neighbor atoms at specific distances from the central atom. EXELFS is produced by the oscillation of the absorption coefficient due to neighbor atoms and is conventionally described mathematically by a function $\chi(k)$, the normalized absorption coefficient with respect to a free atom, for example, an atom in a dilute gas. Thus,

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}, \quad (4.2)$$

where μ and μ_0 are the condensed matter and free atom absorption coefficients, respectively.

The functional form of $\chi(k)$ can be arrived at from physical considerations. The oscillations are expected to be proportional to $\sin(2kR + \delta)$, where k is the wave number of an incident electron of rest mass m and R is the distance between the central and neighbor atoms, and δ is a phase shift consisting of two components:

$\delta(k) = \delta_l(k) + \phi(k)$, where δ_l is the shift due to the central atom and ϕ is the shift due to the backscattering atom. The amplitude for scattering is obtained from application of Fermi's Golden Rule for the rate of transition from the incident electron state Ψ_i to the final state Ψ_f , using the Born approximation in the matrix element calculation, so that Ψ_i and Ψ_f are both plane wave states. The scattering intensity is proportional to the number of backscattering atoms, N , and has a $1/r^2$ dependence. Thermal and static disorder can be accounted for by a probability distribution term $\exp(-2k^2\sigma^2)$, where σ^2 is the mean square deviation of an atom in the material from its equilibrium position and contains both static (temperature-independent) and dynamic (temperature-dependent) components. The electron wave interference can remain coherent as long as it does not undergo too many scattering events; this can be taken into account by a mean free path term $\exp(-2R/\lambda)$. Combining the physical features gives

$$\chi(k) = \frac{m}{4\pi\hbar^2k} \sum_j \frac{N_j}{R_j^2} f_j(k, \pi) \sin[2kR_j + \delta_j(k)] \exp(-2k^2\sigma^2) \exp(-2R_j/\lambda), \quad (4.3)$$

where the summation is taken over all coordination shells, i.e., all groups of neighbor atoms at equivalent distances R_j from the central atom.

4.2.2 Quantitative description

We shall consider some of the components of $\chi(k)$ in more detail. Some of this treatment will be familiar from the discussion of high-energy electron scattering in Chapter 1. The backscattering amplitude $f(k, \pi)$ results from application of Fermi's Golden Rule for the rate of the transition $|\Psi_i\rangle$ to $|\Psi_f\rangle$:

$$\Gamma = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f) \quad (4.4)$$

where $|\Psi_i\rangle$ is the initial state of the incident electron, $|\Psi_f\rangle$ is its final, outgoing wave function, $V_{fi} = \langle\Psi_f|V|\Psi_i\rangle$ is the matrix element connecting $|\Psi_i\rangle$ and $|\Psi_f\rangle$, and $\rho(E_f)$

is the density of final states. Here, the interaction potential is Coulombic:

$$V(r) = \frac{Ze^2}{|\mathbf{r}|} - \sum_{i=1}^Z \frac{e^2}{|\mathbf{r} - \mathbf{r}_i|}. \quad (4.5)$$

In order to simplify the matrix calculation, we use the Born approximation, which can be employed if the scattering potential is weak or if the incident electron has a large enough energy such that $(\mathbf{k} - \mathbf{k}_f) \ll 1$, and the incident and scattered electron may be considered plane waves. Denoting $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ as the momentum transfer, V_{fi} becomes

$$V_{fi} = \left\langle \Psi_f \left| \int e^{-i\mathbf{q} \cdot \mathbf{r}} \frac{Ze^2}{r} dV \right| \Psi_i \right\rangle - \left\langle \Psi_f \left| \int e^{-i\mathbf{q} \cdot \mathbf{r}} \sum_{n=1}^Z \frac{e^2}{|\mathbf{r} - \mathbf{r}_n|} dV \right| \Psi_i \right\rangle. \quad (4.6)$$

The first term is zero due to orthogonality of $|\Psi_i\rangle$ and $|\Psi_f\rangle$. The second term gives

$$V_{fi} = \langle \Psi_f | e^{-i\mathbf{q} \cdot \mathbf{r}} | \Psi_i \rangle. \quad (4.7)$$

In the limit $\mathbf{q} \cdot \mathbf{r} \ll 1$,

$$V_{fi} \propto \langle \Psi_f | \mathbf{q} \cdot \mathbf{r} | \Psi_i \rangle, \quad (4.8)$$

corresponding to the dipole approximation.

The phase shift in the sine function contains a shift due to the central atom (δ_0 for outgoing s wave, δ_1 for outgoing p wave, etc.) and a shift due to the backscattering atom. Often the sinusoid argument is written as

$$\delta_j(k) = \delta(k) + \phi_j(k), \quad (4.9)$$

where $\delta_j(k)$ is the total shift, the sum of the central atom shift $\delta(k)$ and the neighbor atom contribution $\phi_j(k)$. Theoretical values of the phase shift may be calculated following the angular momentum selection rule $|\Delta\ell| = 1$. Often in practice the phase shift is treated as an unknown and is extracted from EXELFS data.

We will assume that the thermal vibrations induce a Gaussian distribution of

scatterer positions, $p(r) = \exp(-2k^2\sigma^2)$. The parameter σ^2 is the root-mean-square deviation of a scatterer from the equilibrium position and is temperature-dependent. It can be calculated using either the Debye or Einstein approximation for lattice vibrations. The Debye approximation is better than Einstein for primitive lattices and for second and higher coordination shells for nonprimitive lattices. The Einstein approximation is better than Debye for the first shell of nonprimitive lattices and for complicated structures such as large biological molecules or amorphous solids. In practice, the Einstein model is preferred over the Debye model because of its relative simplicity. In the Einstein model,

$$\sigma_j^2 \cong \frac{\hbar}{M_j\omega_j} \left(\frac{1}{\exp(\hbar\omega_j/k_B T) - 1} + \frac{1}{2} \right), \quad (4.10)$$

where M_j is the mass of the atom at distance R_j and ω_j is its vibration frequency. By contrast, in the Debye model,

$$\sigma_j^2 = \frac{\hbar}{2M_j} \int \rho_j(\omega) \coth \left(\frac{\hbar\omega}{2k_B T} \right) \frac{d\omega}{\omega}, \quad (4.11)$$

with

$$\rho_j(\omega) = \frac{3\omega^2}{\omega_D^2} \left[1 - \frac{\sin(\omega R_j/\nu)}{\omega R_j/\nu} \right], \quad (4.12)$$

where $\omega_D = k_B\theta_D/\hbar$, θ_D is the Debye temperature, $\nu = \omega_D/k_D$, $k_D = (6\pi^2 N/V)^{1/3}$, and V is the unit cell volume.

Lastly, we consider the lifetime of the outgoing electron wave. The hole created by ionization of the central atom is filled in a time of $\sim 10^{-15}$ second. The lifetime of the electron is limited by scattering from surrounding electrons and atoms. Interference between outgoing and backscattered wave can occur only if the two are coherent. The finite lifetime is treated phenomenologically with the mean free path term $\exp(-2R_j/\lambda)$.

4.2.3 Data processing

Because the EXELFS is a relatively small effect, large incident beam fluxes are needed for collecting sufficient amounts of data of good statistical quality. In the case of extended x-ray absorption fine structure studies, advances have been facilitated with the availability of synchrotron radiation sources. In the case of EXELFS, parallel data acquisition has been much more efficient than serial acquisition and has given data of high signal-to-noise ratio.

The first step in EXELFS data processing involves isolating the fine structure oscillations by subtracting the smooth background. This is usually done by fitting the pre-edge intensity with a power-law background AE^{-B} , and extrapolating this fit through the edge and extended region. However, because the EXELFS oscillations are so subtle, this functional form for the background fit is not adequate. Insufficient accurate background subtraction produces large-amplitude contributions in the low R region (0–2 Å) and may cause broadening and even shifts in the peaks corresponding to radial distances of near neighbors. To isolate the EXELFS, the conventional method is to make a least-squares polynomial spline fit to the data, and the function and its first derivative are matched at the knots where the polynomials meet [7]. The number of spline regions is variable, and a judicious choice of the number of regions and the energy positions of these regions will remove as much of the background as possible without removing the fine structure oscillations. Fig. 4.3 shows an example of a spline fit superimposed upon a core loss intensity.

The data must be transformed from energy to k -space, using the relation

$$E(k) - E_0(k) = \frac{\hbar^2 k^2}{2m_e}. \quad (4.13)$$

The value of E_0 is the edge threshold energy. The data are then Fourier-transformed to give a radial distribution function, $f(R)$ (also called a radial structure function):

$$|F(R)| = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} \chi(k) k^n e^{-2ikR} dk. \quad (4.14)$$

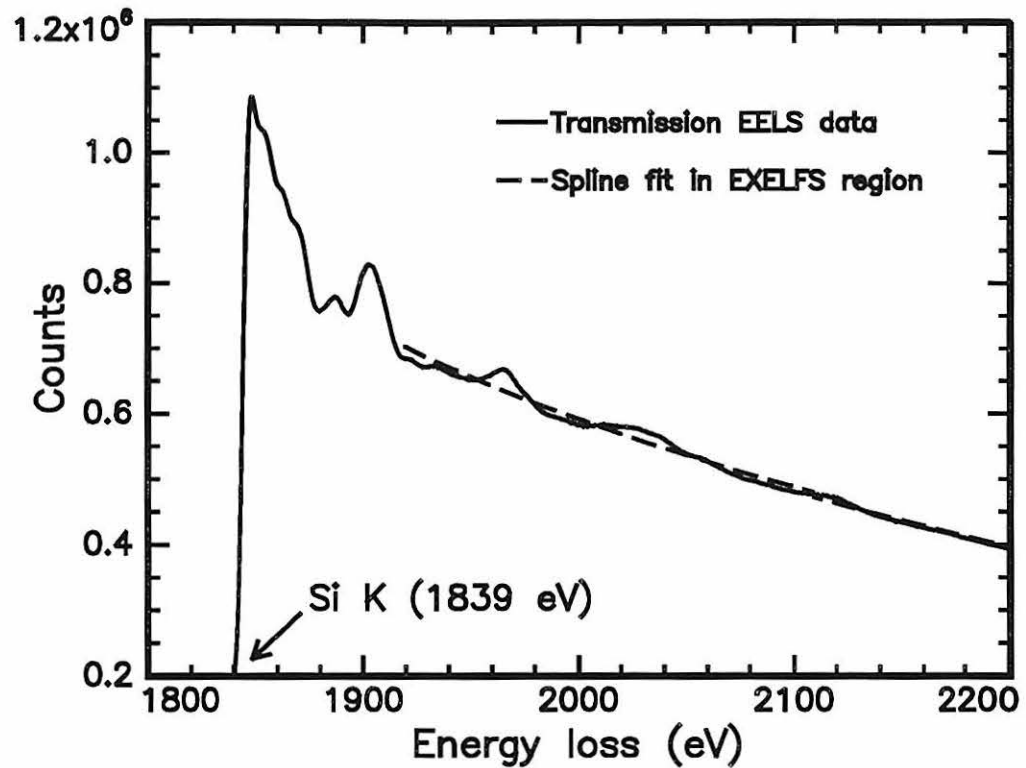


Figure 4.3: Example of a polynomial spline fit (dashed line) to a core loss intensity (solid line). This is a transmission electron energy loss spectrum from Si(100); the core loss (threshold at 1839 eV) exhibits both near-edge and extended-edge fine structure oscillations. The EXELFS region chosen was 1920–2265 eV, and two spline regions were used; the first region was fitted with a quadratic polynomial and the second region was fitted with a line. [Raw data was supplied courtesy of C. C. Ahn, Dept. of Materials Science, California Institute of Technology.]

Because the amplitude of $\chi(k)$ depends on k , in practice the $\chi(k)$ is weighted by a factor k^n ($n=1$ or 3) before Fourier-transforming, to give the oscillations roughly the same amplitude. The lower limit k_{min} of the transform is typically $\sim 2-3 \text{ \AA}^{-1}$ (where $k = 0$ corresponds to E_0) and the upper limit k_{max} is usually determined by the range of energies above the edge where the EXELFS is extractable above the noise, and is typically $10-15 \text{ \AA}^{-1}$. A window function with a gradual rolloff (e.g., a Gaussian with specified half-width) is employed to reduce effects of truncation ripple in the transform.

If the Fourier transform is done assuming a phase shift of zero, as in the expression above, the peaks in $|F(R)|$ do not correspond immediately to the crystallographic values, but must be corrected for the phase shift [8] using the relation

$$\delta_j(k) = \tan^{-1} \left[\frac{\text{Re } \chi(k)}{\text{Im } \chi(k)} \right] - 2kR_j. \quad (4.15)$$

The Fourier transform can also be done using calculated phase shifts [9], so that the number of unknown parameters to be determined by EXELFS analysis is reduced by one. Similarly, calculated scattering amplitudes may also be used.

Once $F(R)$ is obtained, a single peak can be isolated and inverse-transformed to determine the EXELFS due to a single coordination shell. Using this method for a number of peaks in $F(R)$, it is possible to extract the coordination numbers around each type of absorbing atom, the Debye-Waller $\exp(-2k^2\sigma^2)$ term due to vibrations of these atoms, the bond lengths and the mean free paths.

4.2.4 Problems and their resolutions

The EXELFS technique seems simple enough. But does it give accurate determinations of structural parameters? Are the approximations made in arriving at the expression for $\chi(k)$ valid in all regimes (e.g., low k , high k) for all atomic systems? In the cases where theoretical amplitudes and/or phase shifts are incorporated into the data, what is the confidence level at which these values are transferable? In addition to these questions, the issues of multiple scattering and validity of the dipole

approximation are among the many that are still unresolved in the interpretation of EXELFS data.

Phase shift transferability

It would certainly be desirable to reduce the number of unknowns in the EXELFS data. If parameters such as scattering amplitudes and phase shifts of the elements were independent of their chemical environment in the condensed state, they could be measured and tabulated for all the elements and used in subsequent structural determinations of unknowns. This has in fact been done by Teo and Lee [10] for about half of the elements.

Regarding the phase shift, the most direct test of transferability is to determine the shift for an atom pair in a molecule of known interatomic distance, and then use it to determine R in another molecule containing the same atoms but in a different chemical environment. Citrin *et al.* [9] have done this with EXAFS data obtained from Br_2 and CBr_4 and their experimental value for the Br—Br distance in CBr_4 was in excellent agreement with the known distance in Br_2 . In view of these results, the concept of phase shift transferability appears to be a viable one.

A concern arises as to where the EXELFS oscillations actually start. Typically they are assumed to start ~ 30 eV above the absorption edge, but how good is this arbitrary assumption for various systems? It has been proposed [11] that E_0 , the energy origin, be treated as a variable parameter, its choice being governed by the criterion that the experimental and theoretical phase shifts (or shifts measured from some standard) match at $k = 0$, for example. The energy origin E_0 is expected to be sensitive to the charge state of the central atom. When the atom is ionized, the core hole that is created changes the atomic screening by the electrons. Due to Coulomb repulsion, the electrons rearrange themselves to the new potential, and in the process can also be excited. Thus it can be seen how these “charge transfer” effects can affect the phase shift: E_0 shifts because the ejected electron now shares energy with other excitations, whereas in the simpler view, the rest of the atomic electrons played no part. From this, it appears that phase shift nontransferability can be approximately

compensated for by an appropriate shift of E_0 . However, the charge transfer effect is different from coordination shell to coordination shell, which will produce errors in fine structure analysis unless E_0 is varied from shell to shell.

The most serious cause of nontransferability is the breakdown of the Born approximation. This produces large deviations in phase shift from theoretical values at low k . This is because with increasing k , the effective atom size decreases as the outgoing electron penetrates deeper into the atom before scattering. At low k , the effective atomic size is comparable to the interatomic distance, and the backscattering atom sees an outgoing spherical wave instead of a plane wave as is assumed in the Born approximation. Fortunately, this can also be partially remedied by a shift of E_0 . However, as is true for charge transfer effects, the best E_0 shift varies from shell to shell [12].

The above results imply that phase shifts are not strictly transferable, but can be used to reasonably correct for ionic effects and the breakdown of the Born approximation (also known as the “small atom” approximation), even though the latter is quite an appreciable effect.

Dipole approximation

As discussed in Chapter 1, the dipole approximation is generally a very good one for REELS. In practice, it is found that the main contribution to inelastic scattering comes from the dipole term, and higher-order transitions are in general detectable only when the dipole transition is forbidden or when the density of states is high for a multipole transition, as is true for the $s \rightarrow d$ transitions of the L_1 edge [13]. Natoli and Benfatto [14] have computed the GOS for the Si K edge as a function of q , and found that the main contribution ($> 90\%$) to the GOS comes from the dipole term. EXELFS studies performed by Disko [15] of the oxygen K edge in Al_2O_3 under conditions of both small and large momentum transfers yielded the result that the first two nearest neighbor distances were virtually identical in the two cases. This lends credibility to the use of the dipole approximation even when momentum transfers are large.

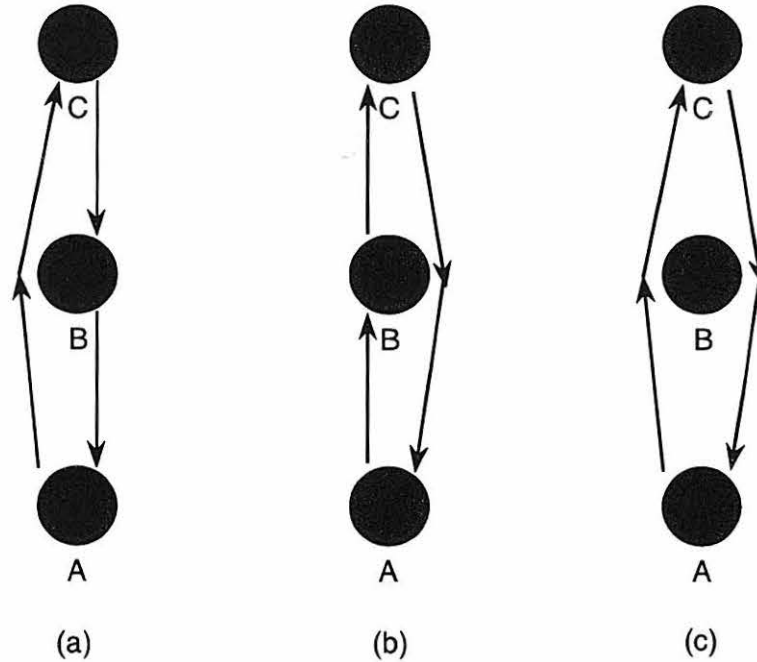


Figure 4.4: (a) Double scattering in which the intervening atom (B) scatters on the outward path of the electron. (b) Double scattering in which the intervening atom (B) scatters on the inward path of the electron. (c) Triple scattering, in which the intervening atom (B) scatters on both outward and inward paths of the electron.

Multiple scattering

The $\chi(k)$ expression operates under the assumption that the outgoing electron scatters backward only once from the surroundings before combining with the unscattered wave. This assumption is still valid in the presence of double scattering or multiple scattering as long as the amplitude and phase shift from these subsequent scatters is small compared to the initial scatter. Qualitatively, the amplitude for small angle scatters is much larger than for backscattering, so that double scattering is important relative to single scattering in the same shell. Generally, multiple scattering effects are small, except when one shell of atoms is directly shadowed by another shell, in which case multiple scattering effects are large, because of forward scattering (see Fig. 4.4), and can even change the phase of the shell [12]. In practice, multiple scattering effects are not important for second and third shells; however, multiple scattering in the second shell may be significant compared to single scattering from the third shell.

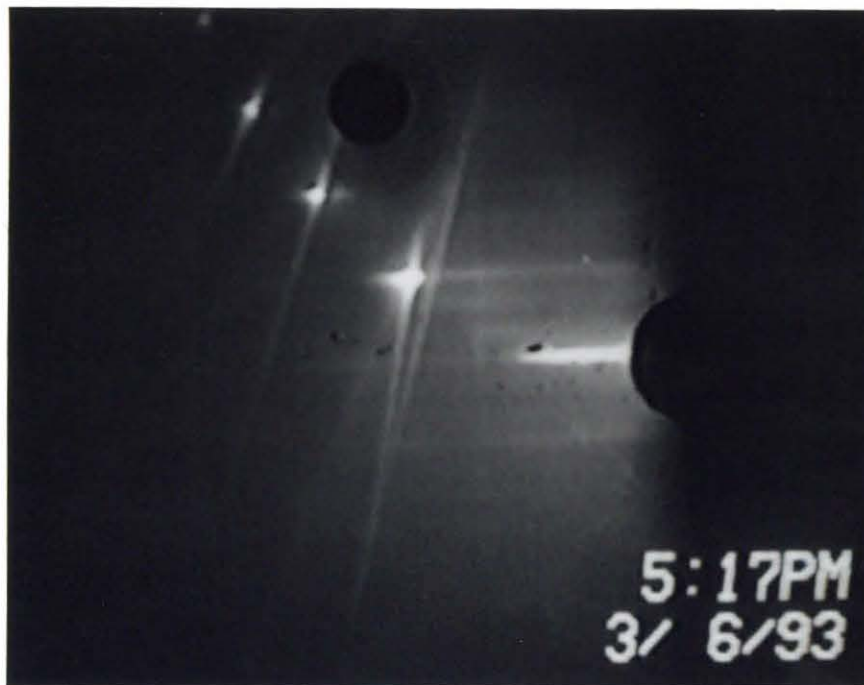


Figure 4.5: RHEED pattern from the Si(100) (3×1) surface. There are two faint one third-order Bragg rods between main Bragg rods.

4.3 Monolayer Sn films on Si(100)

Tin-induced reconstructions of the Si(100) surface have been previously investigated by Ueda *et al.* [16], who have observed (6×2), $c(4 \times 4)$, and (5×1) structures on clean Si(100) surfaces covered with thin layers of Sn. We have observed a new reconstruction, one with (3×1) periodicity as indicated by our RHEED data, on Si(100). The substrate was hydrogen-terminated via a hydrofluoric acid dip and prebaked *in situ* at 200 °C for one hour to desorb physisorbed hydrocarbons. Sn was then evaporated from a Knudsen-type effusion cell at a cell temperature of 1000 °C with a chamber base pressure of 5×10^{-10} Torr. The substrate temperature during growth was 200 ± 20 °C, measured by a thermocouple in contact with the back of the substrate holder. Samples were annealed at 550 °C for several minutes after Sn deposition, and the (3×1) reconstructions were observed at 150–170 °C (see Figure 4.5), after sample cooling.

To investigate further the nature of the reconstruction, we performed EXELFS analysis on this system, using the Sn $M_{4,5}$ edge intensity. The ionization cross section of Sn $M_{4,5}$ is relatively high, and the edge itself is well isolated from the nearest Si energy loss edge (i.e., Si K at 1839 eV) above the Sn $M_{4,5}$ threshold, making analysis relatively uncomplicated. The Sn M_2 , M_3 and M_1 edges, with thresholds at 756, 714, and 884 eV, respectively, are superimposed on the EXELFS analysis region for the $M_{4,5}$ edge, but these edges contribute incoherently with respect to EXELFS oscillations for the $M_{4,5}$ and thus have no effect on the analysis. While interpretation of oscillations in $M_{4,5}$ edges is not well developed for the $M_{4,5}$ edges here, the RDF yields fairly accurate near-neighbor distances, as previous work [17] has shown that the phase shift contributions from the central atom and the backscattering atom have opposite effects and tend to cancel each other.

Fig. 4.6 shows the EXELFS data region used and the $\chi(k)$ function obtained from a 1.9 ML coverage of Sn on hydrogen-terminated Si(100). We note that the signal-to-background ratio is rather small due to the nature of core losses in the high energy loss regime; however, clear oscillations are apparent. To isolate the EXELFS in our analysis, we have modeled the large plasmon background with a power law and performed a rough background subtraction. Then, an estimation of the purely atomic core loss component, through which the EXELFS oscillation occurs, was done using a cubic polynomial spline fit. We have performed the spline fit in two different ways: (1) requiring that the values at the spline region “knots” meet and that the spline function derivatives match at these knots; and (2) relaxing the constraint that the endpoints at spline region boundaries must meet, and merely requiring that the derivatives match. We have found that method 1 gives a smoothly varying $\chi(k)$, free of discontinuities that may otherwise be produced by a background subtraction; however, in some cases method 2 is better able to follow the slowly varying second-derivative maxima and minima in the background, and thus remove these low-frequency components from the data which do not contribute to the EXELFS. As an example, spline fitting to the 1.9 ML of Sn on Si(100) in these studies yielded no fine structure oscillations when method 1 was employed; however, when the derivative constraint was lifted,

the spline fit yielded the EXELFS oscillations in Figure 4.6.

Fourier transform of the $\chi(k)$ gives (without phase shift correction) a nearest-neighbor distance of $3.1 \pm 0.2 \text{ \AA}$ (see Fig. 4.8). We did not deconvolute effects of multiple inelastic scattering from this transform. The film is thin enough so that single scattering dominated. Furthermore, plasmon contributions reside primarily in the low k region; here, our Fourier transform window started at $\sim 9 \text{ \AA}^{-1}$ past the Sn $M_{4,5}$ threshold, well beyond the region where multiple scattering effects could become important. For electron scattering in the reflection geometry, these effects are larger than for the transmission geometry, thus broadening the nearest-neighbor peaks; however, the peak positions are not affected.

For purposes of comparison, we have also obtained EXELFS measurements from the Si $L_{2,3}$ core edge intensity from a hydrogen-terminated, unreconstructed (i.e., (1×1)) Si(100) surface annealed for two hours at 200°C to desorb physisorbed hydrocarbons (see Fig. 4.7). The resulting RDF from Si(100) is superimposed in Fig. 4.8 on the Sn/Si RDF, showing a deviation from the bulk Si—Si distance. For a Sn coverage of 1.9 ML, this radial probability function would represent a convolution of Sn—Si neighbors as well as Sn—Sn neighbors. A possible surface structure that is consistent with the measured coverage, the observed (3×1) periodicity and EXELFS-derived nearest-neighbor distance observed is a missing-row structure, in which the first monolayer of Sn is deposited on all Si surface sites, and the second monolayer of Sn is deposited so that there are two rows of Sn atoms for every three rows of Si atoms, as shown schematically in Figure 4.10. This structure may also indicate the beginnings of faceting of the adsorbed Sn layer, in agreement with recent scanning tunneling microscope (STM) observations of faceting of metal atoms on semiconductor surfaces [19]. A phase diagram illustrating the surface phases of Si(100) is shown in Figure 4.11.

It is worth noting that the Si(100) RDF of Figure 4.8 is consistent with the results of previous EXAFS and EXELFS studies of Si K edges [18], despite the differences in backscattering and phase shifts associated with the K and $L_{2,3}$ edges. Figure 4.9 shows the RDF resulting from EXELFS analysis we have performed for a Si K edge

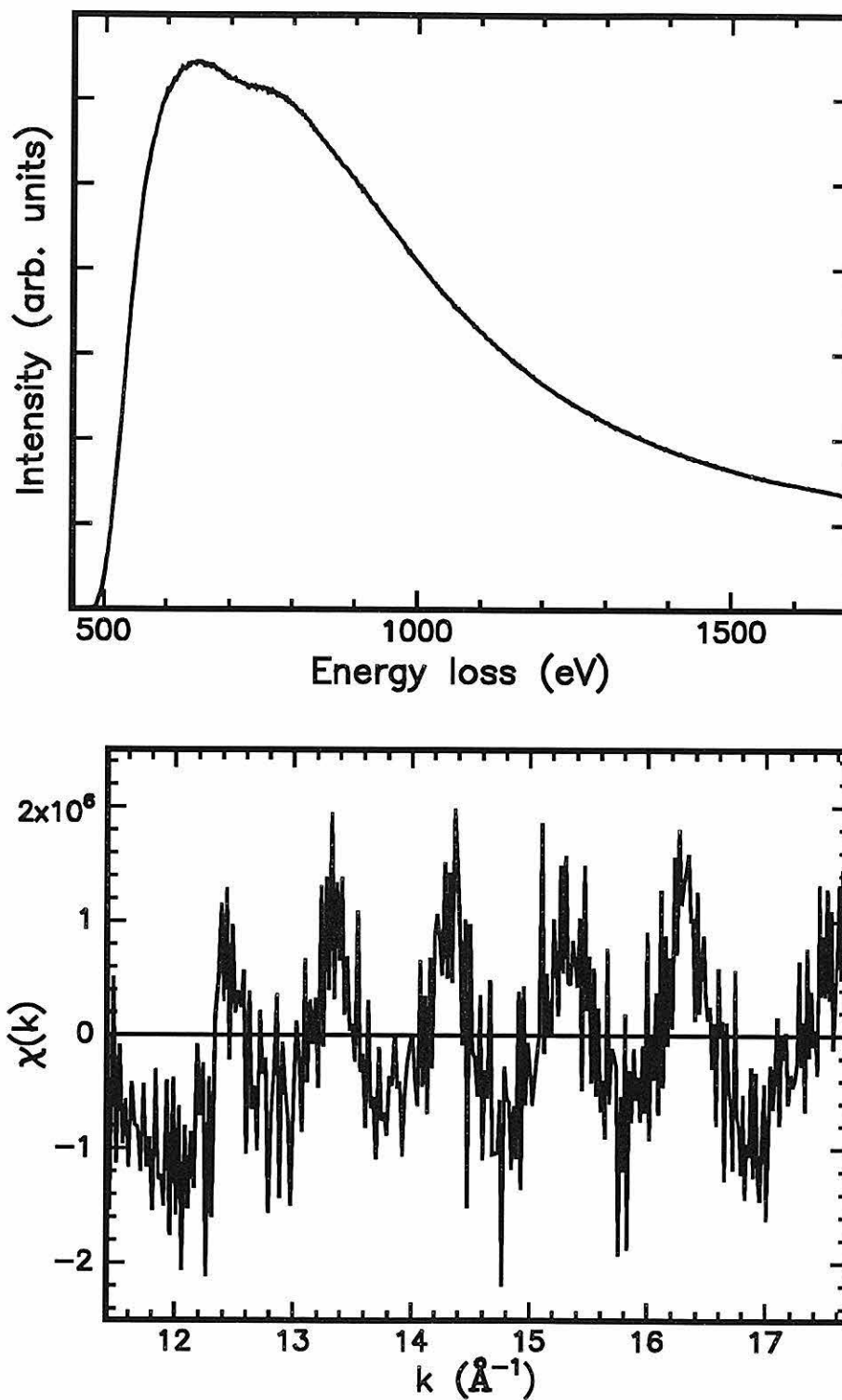


Figure 4.6: (a) The background-subtracted Sn $M_{4,5}$ core loss intensity obtained from 1.9 ML of Sn on Si(100). The data region used for EXELFS analysis is 800–1660 eV. (b) The $\chi(k)$ function obtained after spline fit background subtraction of data in (a).

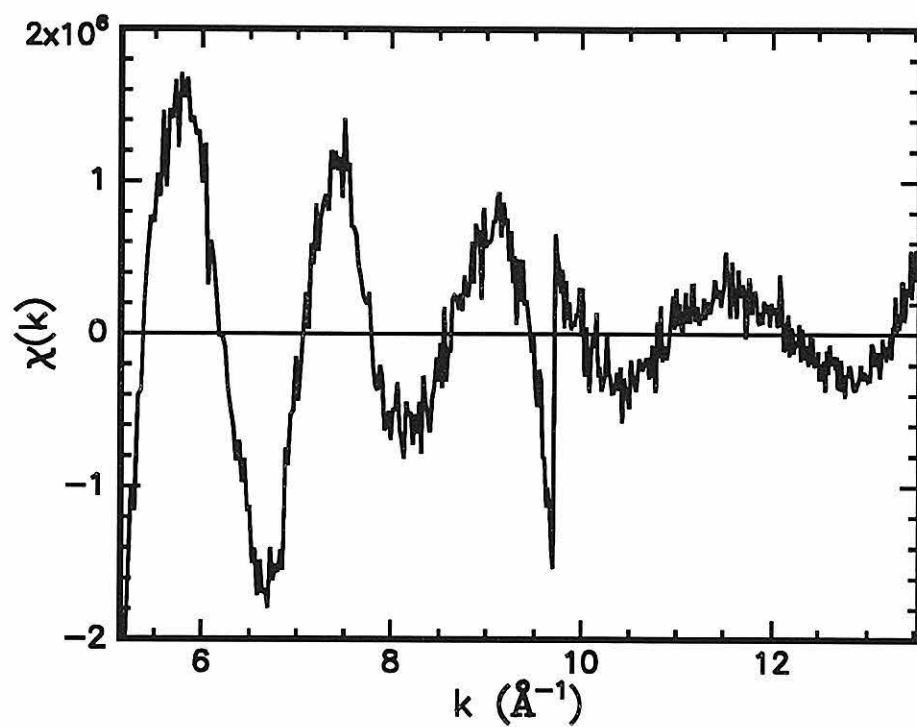


Figure 4.7: The $\chi(k)$ function obtained from the Si $L_{2,3}$ core loss intensity from bare hydrogen-terminated Si(100). The sharp discontinuity is a result of relaxing a knot constraint in the background subtraction.

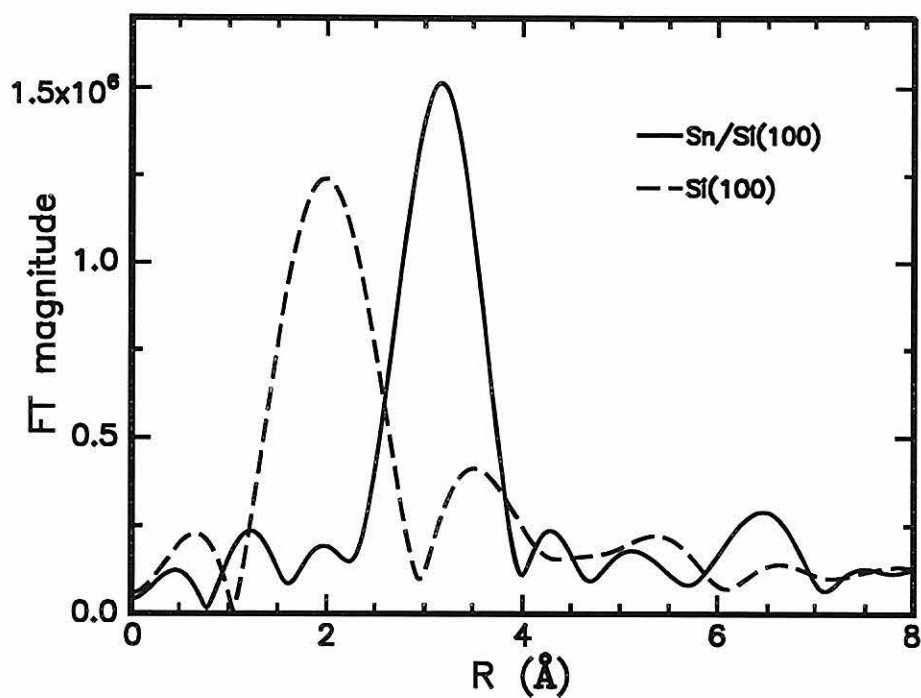


Figure 4.8: The radial distribution function of 1.9 ML Sn/Si(100) (solid line) with nearest neighbor at 3.1 Å, after Fourier transform of Fig. 4.6(b). Superimposed is the RDF of Si(100) (dashed line) with nearest neighbor at 2.0 Å. Neither RDF is phase shift-corrected.

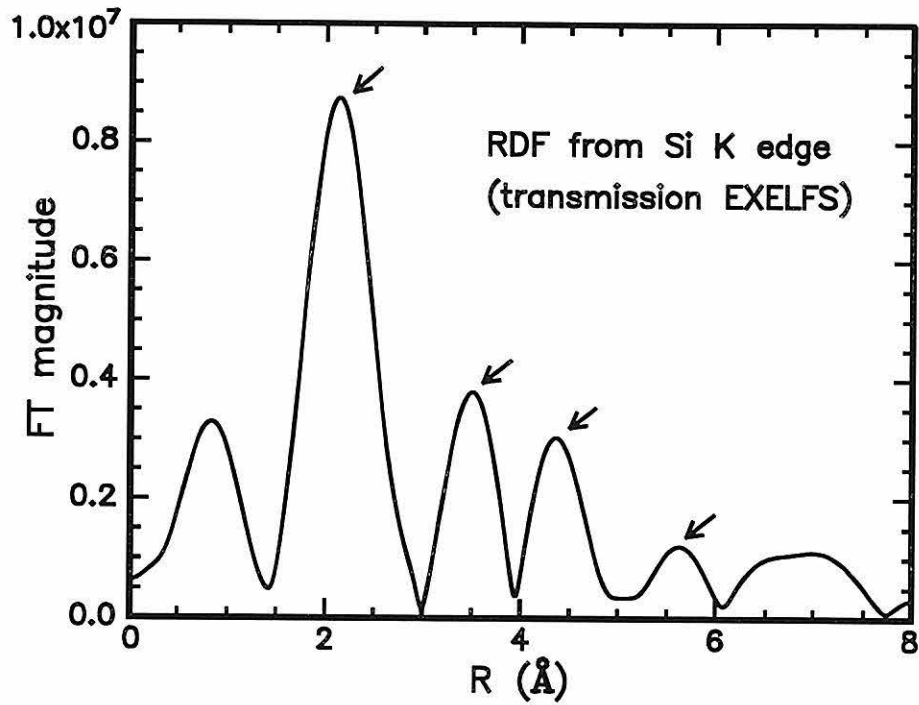


Figure 4.9: The radial distribution function of Si, derived from EXELFS analysis of the Si *K* core loss intensity from a transmission electron energy loss spectrum. The arrows denote near-neighbor distances of approximately 2.0 Å, 3.5 Å, 4.3 Å, and 5.6 Å, similar to the near-neighbor distances obtained from analysis of the Si *L*_{2,3} edge in REELS EXELFS (see previous figure).

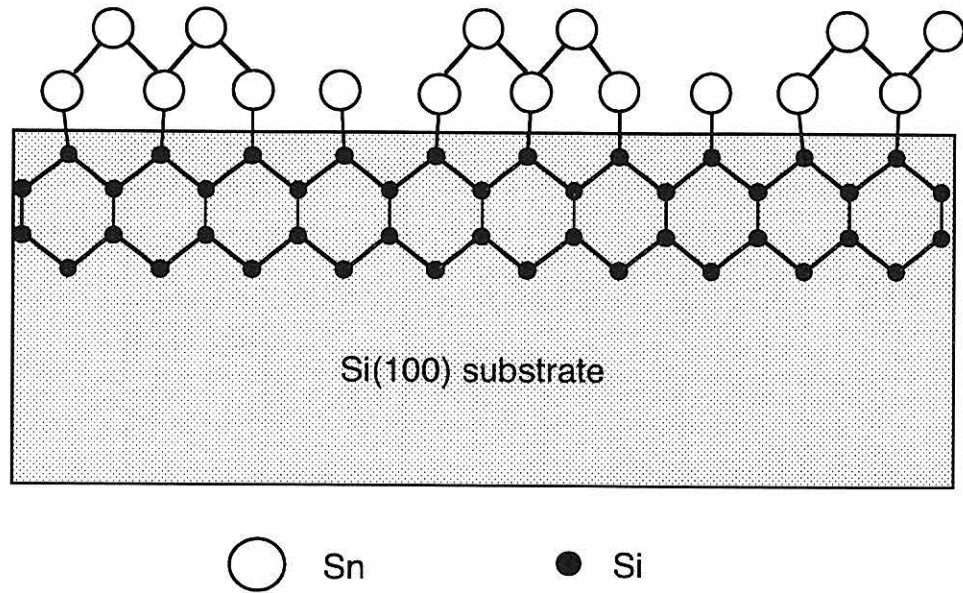


Figure 4.10: A possible structure for 1.9 ML Sn on Si(100) is the missing-row structure, in which the first monolayer of Sn is deposited so that there are two rows of Sn atoms for every three rows of Si atoms.

obtained by electron energy loss measurement in a transmission electron microscope. The nearest neighbor distances are in good agreement with those obtained by analysis of the Si $L_{2,3}$ edge.

4.4 SnGe alloys

In this section, REELS EXELFS analysis in determining short-range order in epitaxial SnGe alloys will be demonstrated. We have made REELS EXELFS measurements in the transmission electron microscope at room temperature on two such alloys. A strain-relieved 750 Å thick film of α -Sn_{0.2}Ge_{0.8} was grown at 120 ± 20 °C by Ar⁺ ion-assisted molecular beam epitaxy with ion energy of ~ 50 eV. The second sample was a 250 Å alloy of α -Sn_{0.01}Ge_{0.99} thermally grown at 150 ± 20 °C, a temperature sufficiently high so as to result in a small concentration of Sn islands segregated on the surface. For both films, Sn was evaporated from a Knudsen-type effusion cell and Ge from an electron beam evaporator. We did not observe any evidence of significant surface oxidation of the SnGe films, presumably because the incidence angle of the

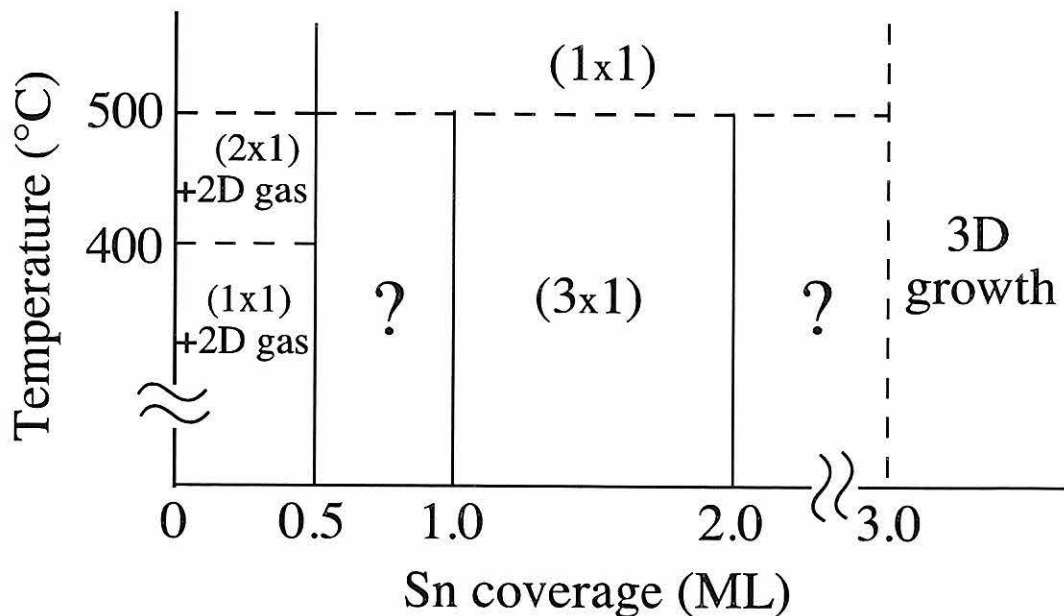


Figure 4.11: The surface phase diagram of Sn/H-terminated Si(100), showing the various Sn-induced reconstructions as a function of Sn coverage and temperature.

electron beam was such that it primarily probed the underlying film. We did not see any EXELFS contribution from thick, three-dimensional β -Sn islands in the second sample. This can be understood by considering that the Debye temperature of β -Sn is ~ 200 K (-73 °C), so that the room temperature thermal vibration amplitude would greatly reduce the β -Sn contribution to the EXELFS.

The EXELFS oscillations obtained from REELS spectra of these alloys are shown in Fig. 4.12, and the Fourier transforms of these $\chi(k)$ functions are shown in Fig. 4.13. The Sn in both alloys has a high probability of having Ge first-nearest neighbors in tetrahedral coordination, which is plausible because of the very small Sn concentrations. For the alloy with 20% Sn concentration (α -SnGe alloy I), the Sn atoms may be pictured as being surrounded by mostly Ge atoms (see Fig. 4.14), but with a Sn—Ge bond distance slightly larger than the Ge—Ge distance, which is expected, due to the larger Sn concentration in this strain-relieved epitaxial alloy. We found a Sn—Ge distance of 2.7 ± 0.2 Å. For the alloy with 1% Sn concentration (α -SnGe alloy II), we found a Sn—Ge distance of 2.4 ± 0.2 Å. For both samples, the distances of second- as well as first-nearest neighbors are in agreement with our model

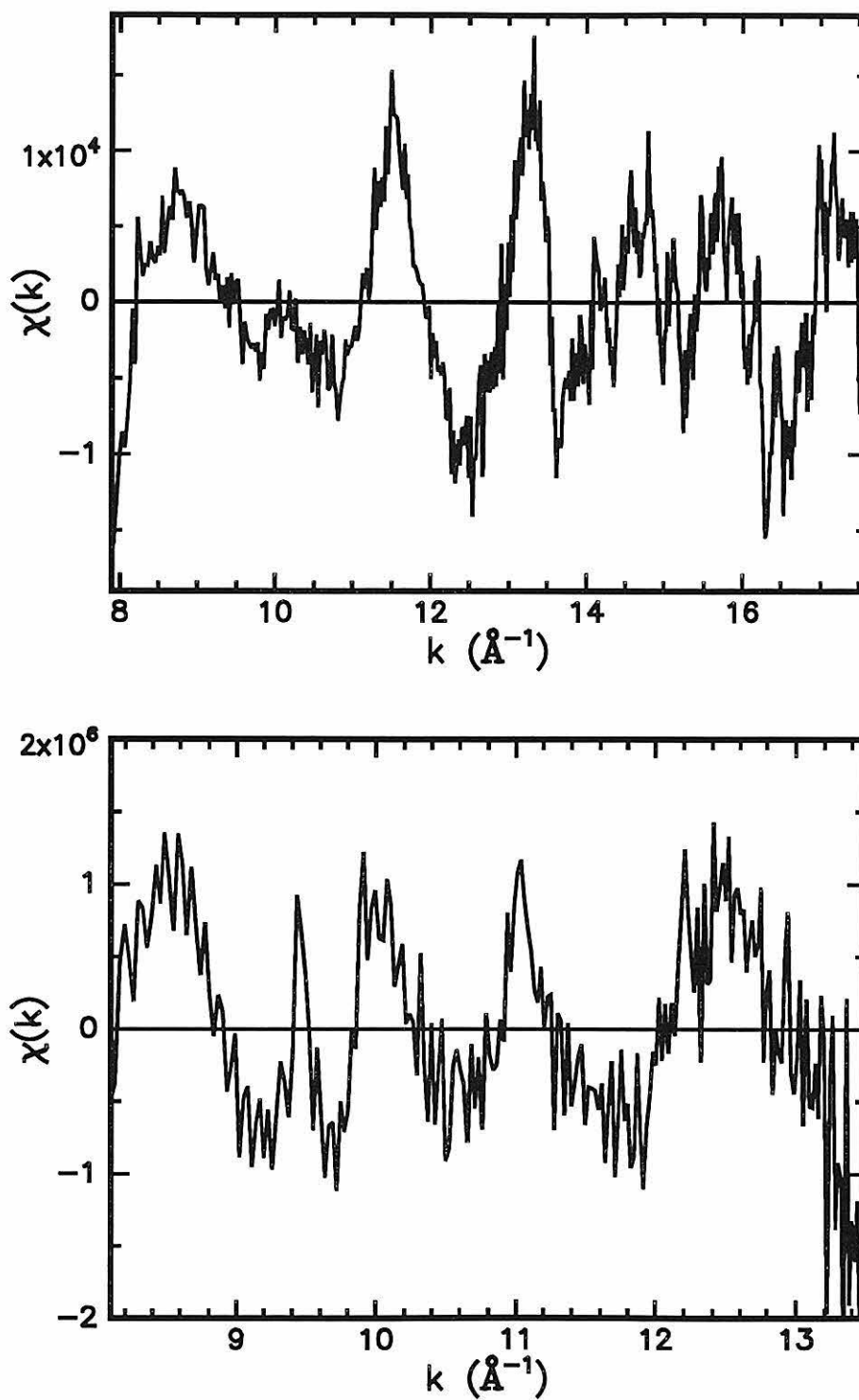


Figure 4.12: The $\chi(k)$ functions from Sn $M_{4,5}$ edges from (a) $\text{Sn}_{0.01}\text{Ge}_{0.99}$ and (b) $\text{Sn}_{0.2}\text{Ge}_{0.8}$.

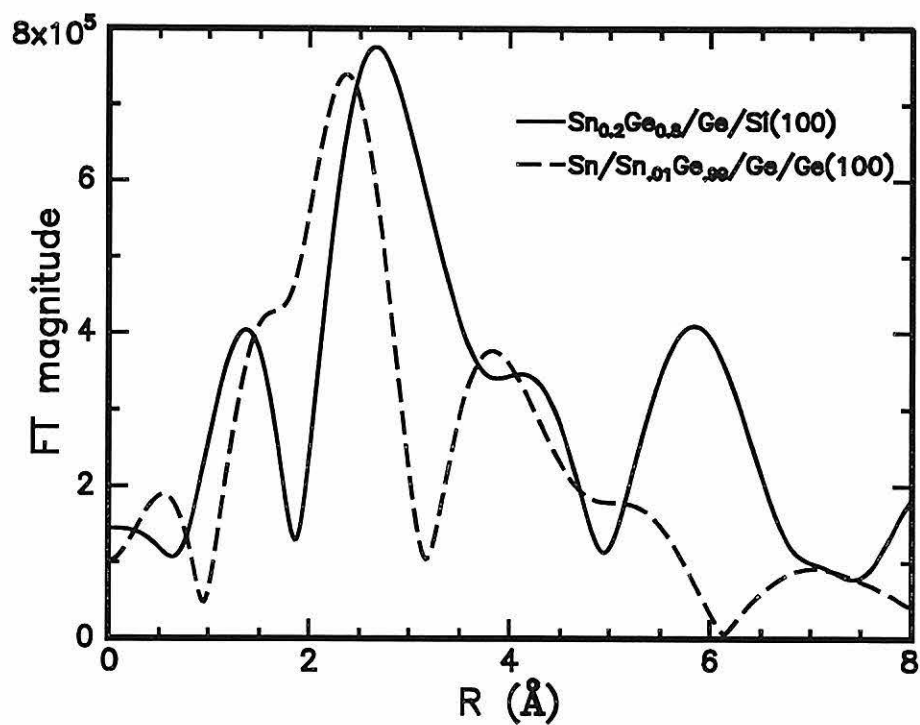


Figure 4.13: The radial distribution functions of $\text{Sn}_{0.2}\text{Ge}_{0.8}$ (solid line) with nearest neighbors at 2.65 and 4.1 Å, and $\text{Sn}_{0.01}\text{Ge}_{0.99}$ (dashed line) with nearest neighbors at 2.4 and 3.85 Å. Neither RDF is phase shift corrected.

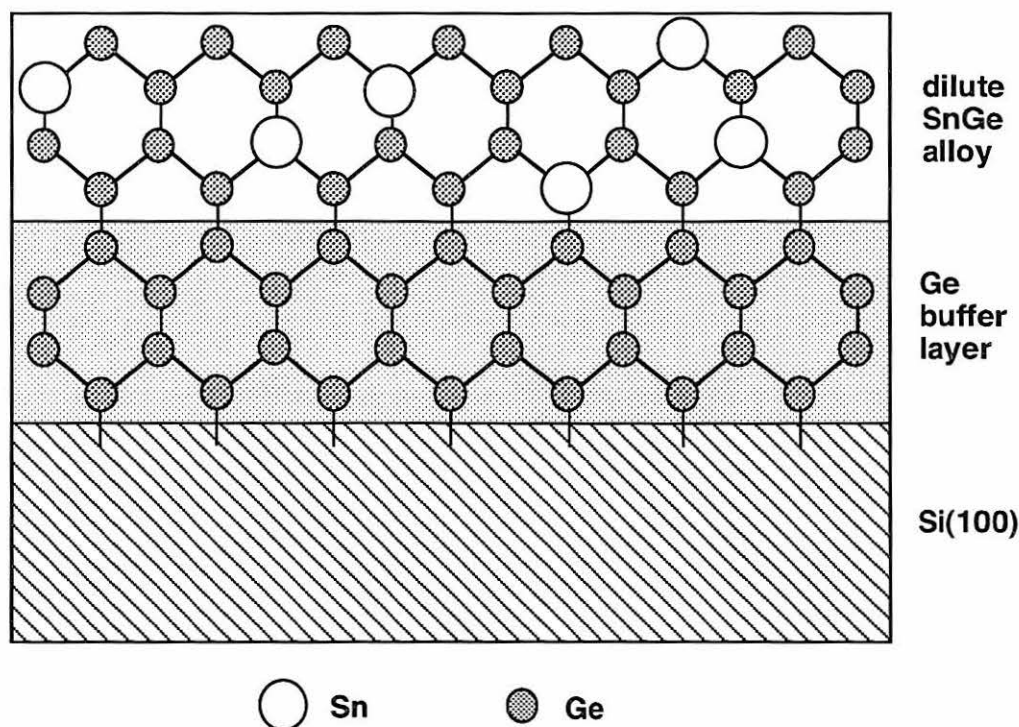


Figure 4.14: Schematic illustration of the structure of a dilute SnGe alloy, showing the environment of Sn atoms as being surrounded by mostly Ge atoms.

of Sn atom surroundings in dilute SnGe alloys. Our experimental findings of nearest-neighbor distances, along with nearest-neighbor distances for α -Sn, α -Ge, β -Sn, and α -Sn_{0.5}Ge_{0.5} in accordance with the virtual crystal approximation, are encapsulated in Fig. 4.15.

4.5 Summary

REELS EXELFS has been demonstrated for monolayer Sn films, epitaxial SnGe thin film alloys, and Si(100) surfaces. The first- and second-nearest neighbor distances in single crystals are consistent with previous transmission EXELFS and EXAFS data, and we have found that first- and second-nearest neighbor distances in SnGe alloys increase with Sn composition. REELS EXELFS is more difficult than transmission EXELFS due to effects of multiple inelastic scattering in the reflection geometry; however, the data rates obtained are comparable to those of synchrotron surface

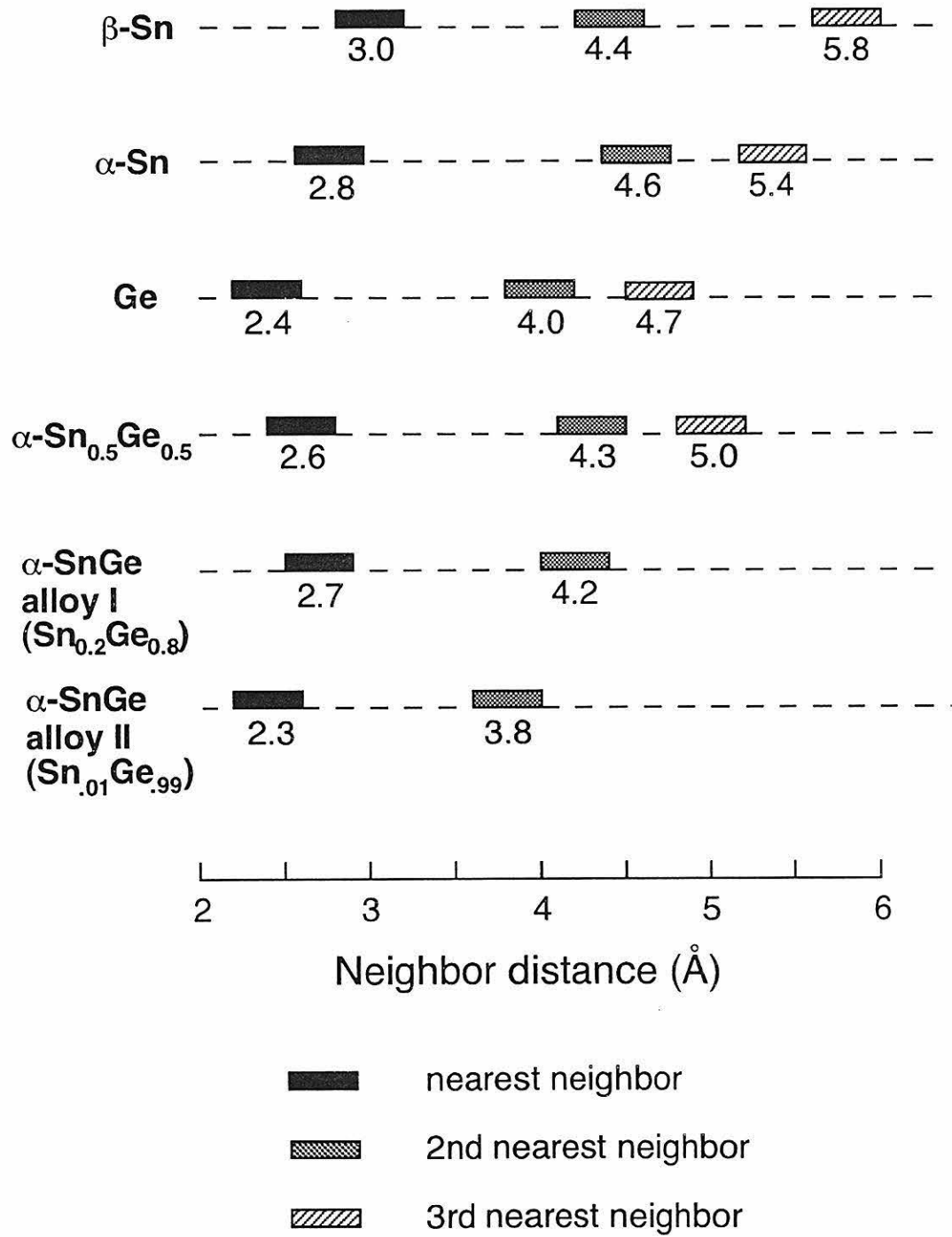


Figure 4.15: Nearest-neighbor distances of α -SnGe alloys I and II in this work, along with expected nearest-neighbor separations in α -Sn, α -Ge, β -Sn, and α -Sn_{0.5}Ge_{0.5} in accordance with the virtual crystal approximation.

EXAFS measurements and might be higher with parallel detection.

REELS EXELFS has been shown to be complementary to RHEED and REELS, allowing surface science measurements of long-range order (RHEED), long-range composition (REELS), and short-range order (EXELFS) to be obtained with a conventional RHEED system in a conventional molecular beam epitaxy growth chamber.

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Chapter 5 High-speed parallel-detection REELS and real time *in situ* monitoring

5.1 Introduction

We have demonstrated the versatility of REELS in the MBE chamber in providing useful information on surface chemical composition, long-range crystallographic structure, and local-order structure of various Group IV epitaxial semiconductor systems. All of the experiments described so far in this thesis were performed with an electron spectrometer operating in serial data acquisition mode, with the energy slit-scintillator photomultiplier tube detection described in Chapter 2. Although data rate is relatively high ($\sim$ few thousand counts per energy channel in a Si $L_{2,3}$ core loss), acquisition is very inefficient ($\sim 0.1\%$ of the scattered beam passes through the slit at any given time). We strive to achieve faster detection and higher efficiency which is capable of truly real-time composition analysis.

To provide motivation for fast detection, we consider that a typical large-range REELS scan (e.g., 0–1000 eV) takes almost a minute to collect; to obtain good signal-to-background levels adequate for extracting typical core losses it has been necessary to sum ~ 15 successive full-range scans, making the time scale of a REELS spectrum with very good quantitative alloy information about 15 minutes. This has not been satisfactory for measuring the time dependence of surface hydrocarbon concentration on a Si wafer at a prebake temperature of 200°C (discussed in Chapter 3); hence our reason for performing the time-dependent measurements at 115 °C, at which temperature the kinetics of hydrocarbon desorption have a time scale comparable to that of a REELS spectrum. In our REELS EXELFS measurements on SnGe alloys, it was necessary to collect core loss data continuously for four days in order to obtain the adequately large Sn $M_{4,5}$ and Si $L_{2,3}$ core loss intensities ($\sim 10^6$ counts each) needed

for EXELFS analysis. Although it is certainly a credit to REELS that it is able to provide virtually as much EXELFS information as obtained with surface EXAFS at synchrotron laboratories, clearly it is desirable to increase the REELS data acquisition rate and hence reduce acquisition time if REELS is to be useful for real-time monitoring. This would enable data acquisition to become more robust, as the shorter data collection time would make the detection system less prone to electrical noise (due to electronic interference of various components of the REELS instrumentation) and mechanical noise (e.g., vibrations due to pumps) which would produce artifacts in the spectra. From a more scientific perspective, faster detection would open new avenues of scientific investigation. Real-time monitoring of the surface of a growing film would enable studies of the kinetics of growth processes and the evolution of thin film microstructure. Time-dependent studies of phenomena in addition to hydrocarbon desorption would be possible. Ultimately, more practical goals such as precision alloy composition profile engineering may be possible with feedback from the monitoring system to the growth sources. This implies the capability for unprecedented levels of process control during molecular beam epitaxy.

Faster detection, obtained with parallel data acquisition, is in fact in widespread use in applications other than molecular beam epitaxy. Transmission electron microscopes with EELS and energy-dispersive x-ray (EDX) capabilities conventionally are equipped with parallel-detection spectrometers, and in this mode are able to collect data in imaging mode as well as in spectrum mode. For example, biologists use parallel detection as a matter of course, because they must be careful to minimize the radiation dose (and therefore radiation damage) to biological specimens.

This chapter will describe the implementation of parallel-detection REELS, or PREELS, in an epitaxial growth chamber. We will show and discuss the results of preliminary measurements on the $\text{Ge}_x\text{Si}_{1-x}$ heterostructure system, and make comparisons of PREELS with serial REELS.

5.2 Instrumentation

5.2.1 Overview

Figure 5.1 shows a schematic diagram of the PREELS assembly and Figure 5.2 is a photograph of the assembly with the growth chamber onto which it is incorporated. The same magnetic prism spectrometer is used as for serial REELS, except that the slit assembly was removed in order to access the entire electron dispersion at the spectrometer exit. In the exit plane, the dispersion is a few $\mu\text{m}/\text{eV}$. For an energy loss range of 1000 eV the dispersion has a spatial extent of a few millimeters. A series of magnetic quadrupole lenses are employed to magnify the dispersion to a spatial extent of ~ 5.1 cm (2") over a travel distance of ~ 16.5 cm (6.5"). At the end of the 16.5 cm trajectory is a viewport with a phosphorescent screen placed in the window that images the dispersion. By means of a standard camera macro lens, the image is optically coupled to a CCD detector, and the intensity is digitized and saved to a computer file.

5.2.2 Magnetic quadrupole lenses

Because the spreading of fast electrons inside scintillator material is of the order of several microns [1], the electron dispersion with its spread of several $\mu\text{m}/\text{eV}$ cannot be immediately imaged at the spectrometer exit. Instead, magnetic quadrupole lenses are placed between the spectrometer exit and scintillator in order to magnify the dispersion, resulting in an image on the phosphor screen with a spatial extent of ~ 5.1 cm (2") and a dispersion of ~ 10 $\mu\text{m}/\text{eV}$ (for an energy loss range of 500 eV), satisfactorily larger than the spreading in a scintillator due to multiple scattering.

The configuration of three quadrupole lenses has previously been developed [2] for parallel electron energy loss spectroscopy in the transmission electron microscope. In the magnetic lens system presented here (a photograph of which is shown in Figure 5.3), the sextupole lens is used to correct second-order aberrations at the spectrometer exit and plays no role in expanding the electron dispersion. Of the three quadrupoles,

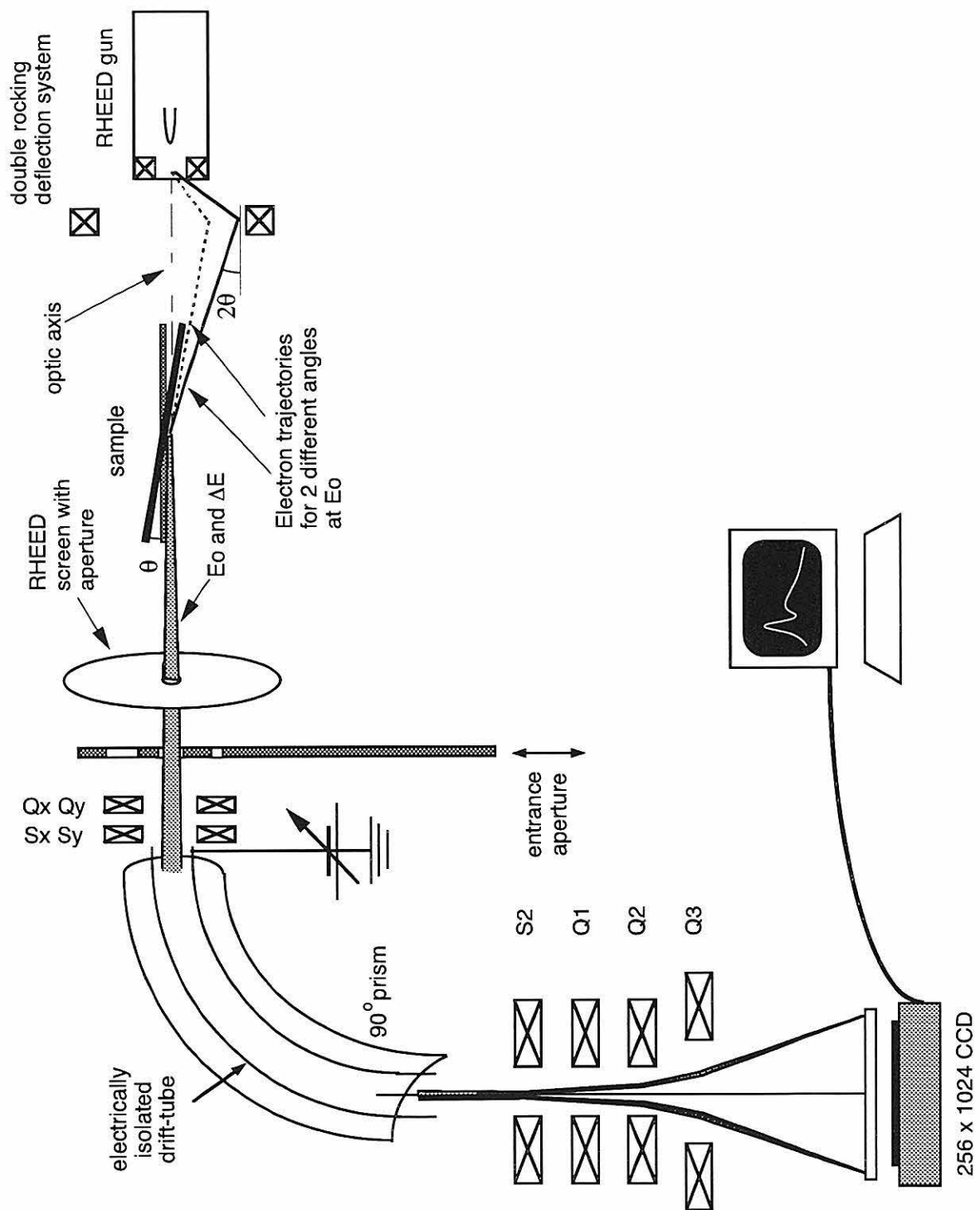


Figure 5.1: Schematic illustration of the parallel REELS assembly.

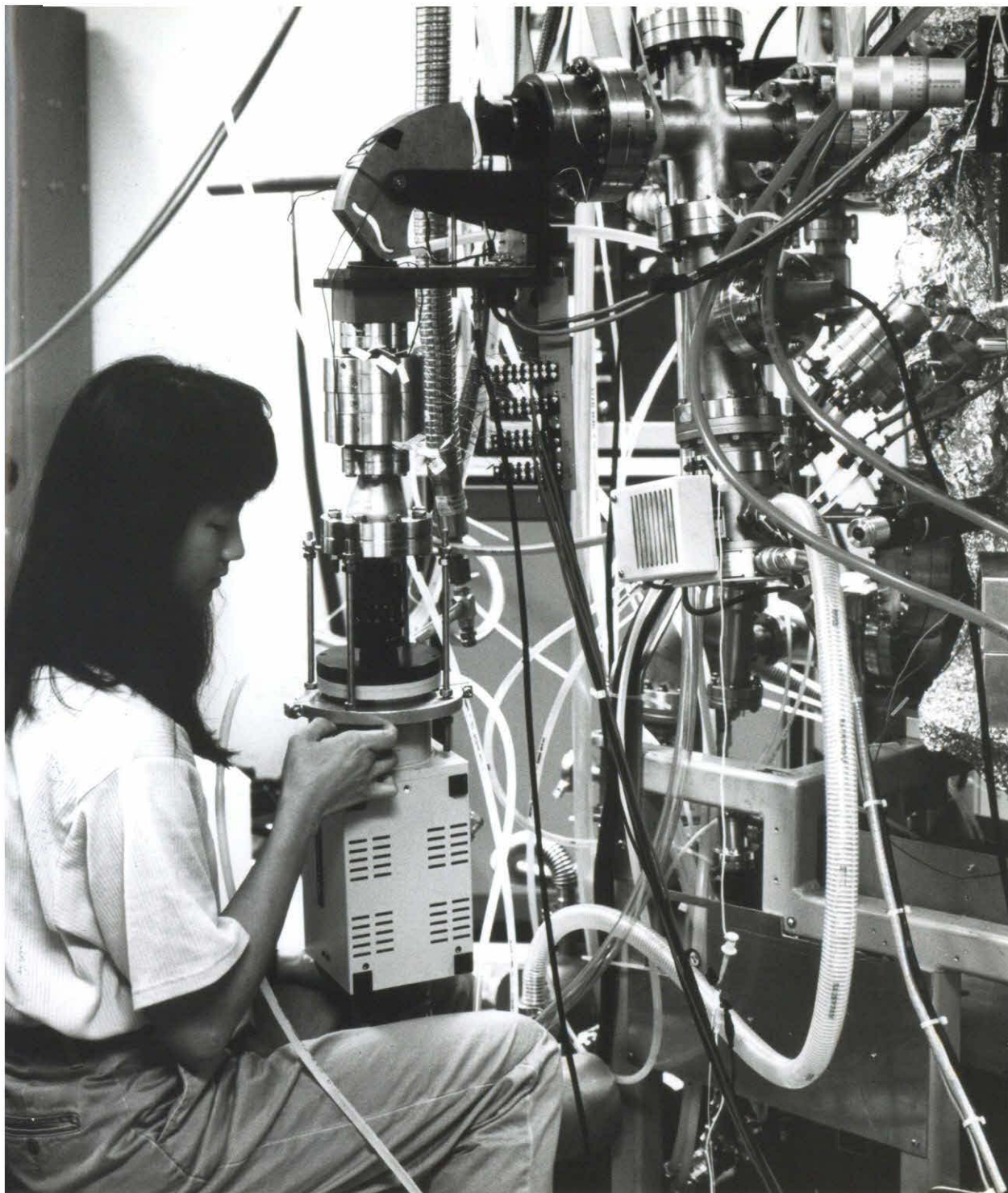


Figure 5.2: Photograph of the parallel REELS instrumentation and the growth chamber onto which it is incorporated.



Figure 5.3: Photograph of the magnetic lens system employed in the parallel REELS assembly. The coils of the sextupole lens are visible.

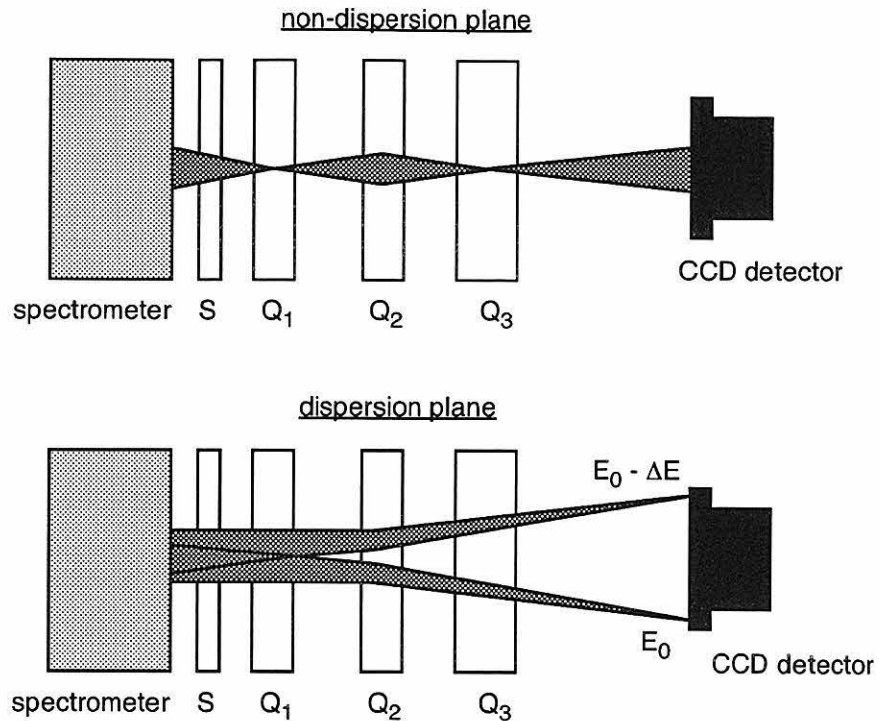


Figure 5.4: Schematic diagram illustrating the magnifying action of the quadrupole lenses. Diagram adapted from a similar one in Reference 2.

Q_1 acts as a focusing lens for the dispersion. Q_2 expands the width of the dispersion, and Q_3 performs the actual expansion in the dispersing direction, as shown in Figure 5.4. Indeed, it is an advantage of using quadrupole lenses that the dispersion can be magnified in two perpendicular directions independently, enabling magnification of the dispersion but keeping its width unaffected. This is desirable especially for directing the dispersion onto a one-dimensional detector array. For a two-dimensional array it would also be desirable to keep the dispersion width small, so that it is incident upon a minimum number of array elements and thus reduces uncertainties in signal magnitude due to pixel-to-pixel gain variations.

5.2.3 Phosphor screen

The fluorescent screen used to image the electron dispersion is a P-20 phosphor (cerium-doped yttrium vanadate) coating on a leaded glass (i.e., x radiation-shielding) substrate. It is used as a transmission screen, in which electrons impinge on the

“front” surface (the coated surface) and light is collected from the “back” surface. The front of the glass substrate is coated with a thin ($\leq 1 \mu\text{m}$) coating of aluminum in order to prevent electrostatic charging; the $\sim 25 \mu\text{m}$ thick phosphor is then coated on top of the aluminum layer.

Use of a fluorescent screen converts the electron dispersion to green photons before the signal enters the detector. This is known as the indirect exposure mode and reduces electron irradiation damage to the detector.

5.2.4 Optical lens

Optical coupling of the dispersion image on the phosphor screen to the detector is achieved using a standard camera lens with a numerical aperture of 1.8, interfaced to the detector with a C mount adapter flange. Current magnification is about 4:1. Use of an F mount (bayonet-type) is also possible and, with the larger diameter of the F mount aperture relative to the C mount, may alleviate vignetting problems in imaging the dispersion onto the detector.

5.2.5 CCD array detector

The detector used in our parallel REELS measurements is a state-of-the-art area-array charge-coupled device (CCD) detector, which is capable of ultra-high dynamic range (18 bit, i.e., $\sim 262,000:1$) sensitivity and rapid readout rates while maintaining very low noise levels. The sensing object is an array of silicon CCDs. This array of charge-coupled pixels is arranged in 1024 columns, with 256 pixels in each column. Photons striking the array generate charge in the photosites (pixels). Charge is collected over a certain exposure time, the amount of charge in each pixel being proportional to the amount of light striking it; then the accumulated charge per pixel is transferred one by one by means of shift registers to the video output of the CCD chip (see Figure 5.5). In the data acquisition mode we have chosen to use, the signal in each column of 256 pixels is summed to give the total charge in those pixels. The video signal is amplified and transformed to digital format using an analog-to-digital converter

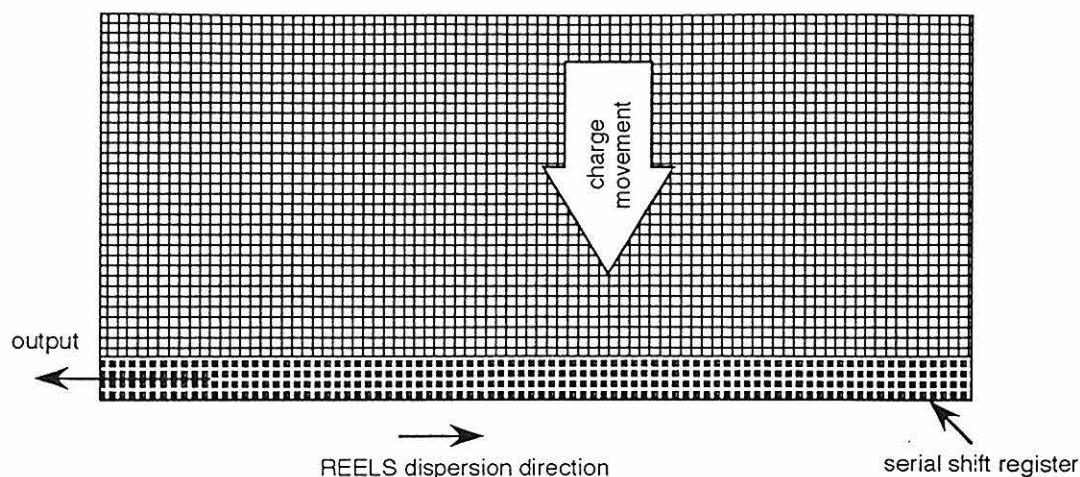


Figure 5.5: Schematic of the 256×1024 element CCD array in our parallel REELS system. Each pixel measures $19 \mu\text{m} \times 19 \mu\text{m}$, giving a total chip area of $4.86 \text{ mm} \times 19.45 \text{ mm}$.

(all within the detector housing) and the digital information is relayed by means of a fiber optic cable to a computer where it is processed for display (onto a monitor), manipulation, and storage to a disk file.

5.3 Parallel REELS data processing

As-recorded spectra in the multichannel analyzer of the parallel-detection system cannot be immediately interpreted to obtain meaningful information. The data contain several features that are common to all data recorded from array detectors. The individual pixels produce a “dark” current due to thermal leakage which contributes to the background in the recorded spectrum. This dark current may also possess some pixel-to-pixel variation due to small differences between individual array elements. The background due to dark current is subtracted from the data spectrum using a “dark current spectrum,” i.e., a spectrum recorded without a sample signal, but under the same experimental conditions (for example, temperature and exposure time) as used for recording the sample spectrum.

Another feature of parallel-recorded spectra is that due to small defects in the pixel elements, the charge generated for an equal amount of illumination may be

slightly different between individual elements. The solution to this is to record an “instrument response” spectrum using uniform illumination across the array, and use the response spectrum to normalize sample spectra. Of course, the dark current is subtracted from the response spectrum before it is used to normalize sample spectra.

5.4 Overall energy resolution of parallel REELS

The energy resolution of serial-detection REELS was found to be ~ 7 eV, as discussed in Chapter 2. For parallel REELS, the extra instrumentation involved (i.e., magnetic lenses, scintillator, CCD detector) may affect the overall resolution.

The additional sextupole lens placed at the spectrometer exit serves to attempt to nullify any remaining second-order aberrations of the magnet that are not already compensated for by the built-in sextupole of the Gatan 607 prism. Thus this external sextupole lens does not degrade energy resolution (and may even improve it). The three quadrupole lenses do not have any sextupole moments and thus do not affect the second-order focusing properties of the spectrometer exit. Also, the quadrupoles do not introduce other aberrations, such as the spiral distortion produced by round lenses [2]. The quadrupoles are snugly fitted around the optic axis to ensure that the beam experiences the field exactly in their centers. In addition, to ensure that the fields are as uniform as possible and that every part of the dispersion is faithfully magnified, each coil of the quadrupoles (and of the sextupole) was carefully and compactly wound by machine with large gauge (26 AWG) magnet wire of square cross section, and is free of kinks and other non-uniformities. The variation in number of turns of magnet wire among different coils was $\sim 2\%$.

The scintillating screen can affect the energy resolution due to the lateral spreading out of generated photons. However, if the fluorescent coating is sufficiently thin, this will increase the chances that photons generated at the “back” surface of the coating will be at virtually the same lateral position as those generated at the “front” surface, where the incident electrons first strike. Our phosphor coating is ~ 25 μm thick. The lateral spread of 30 keV electrons inside this material is of the order of several microns

[1]. Considering that the pixel dimension of the CCD array is $19\text{ }\mu\text{m}$, the maximum spatial uncertainty of a photon generated inside the phosphor amounts to a spatial uncertainty of less than one pixel of the CCD. Thus the overall energy resolution is virtually unaffected by the spatial resolution of the phosphor.

With serial-detection REELS, the energy resolution of the spectrometer was in large part determined by the width of the energy-selecting slit. For most of our measurements we used a slit width which yielded an energy increment of $\sim 1.4\text{ eV/channel}$ in the multichannel analyzer. With PREELS, the energy-selecting slit is eliminated and the energy increment per channel can be made arbitrarily small by increasing the electron dispersion with the quadrupole lenses. Our CCD detector has the property that when a $10\text{ }\mu\text{m}$ spot is focused onto the center of a single pixel, more than 85% of the charge remains in that pixel; thus the spatial resolution of the CCD array is measured to be about one pixel. Our preliminary measurements on the zero loss and first surface plasmon in silicon suggest an energy increment of $12\text{ eV}/11\text{ pixels}$, or $\sim 1.1\text{ eV/pixel}$, slightly better than that obtained with serial REELS. Thus, the parallel setup gives an energy resolution virtually the same or slightly better than that obtained with serial REELS, which is $\sim 6\text{--}7\text{ eV}$.

5.5 Real-time monitoring of the SiGe heterostructure system

In order to assess the viability of the parallel REELS technique in the growth chamber, we chose to study the $\text{Ge}_x\text{Si}_{1-x}$ alloy system, on which there are serial REELS measurements for purposes of comparison.

5.5.1 Experimental

A heterostructure of $\text{Ge}_x\text{Si}_{1-x}$ of graded composition (see Figure 5.6) was fabricated in a cryopumped MBE chamber with a base pressure of $5 \times 10^{-11}\text{ Torr}$. Pressure rose to $\sim 10^{-8}\text{ Torr}$ during film deposition. PREELS spectra were obtained during growth

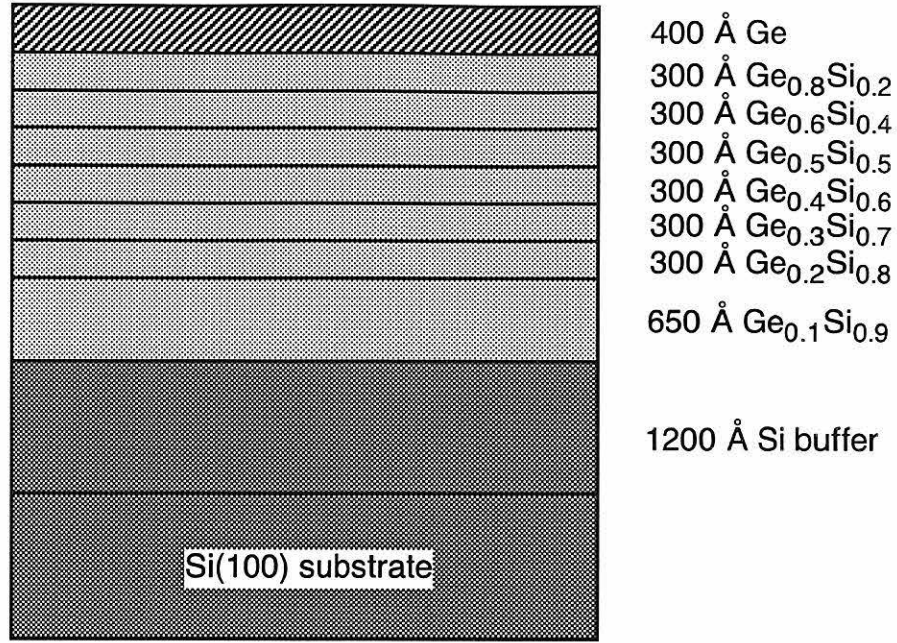


Figure 5.6: Schematic illustration of the $\text{Ge}_x\text{Si}_{1-x}$ heterostructure studied with parallel-detection REELS.

of each layer of the heterostructure. The RHEED beam incidence angle was $\sim 1.5^\circ$ and a Bragg reflection was analyzed by the spectrometer. The RHEED pattern was monitored continuously during the heterostructure growth. Figure 5.7 is a photograph of the RHEED pattern taken during the midst of alloy deposition.

The electron dispersion which was imaged onto the CCD array detector is shown in Figure 5.8. The band structure comprises the zero loss and first and second plasmon peaks in silicon. Farther out, the intensity decays and becomes invisible to the unaided eye. The Si $L_{2,3}$ core loss is not visible by eye.

Figure 5.9(a) and (b) show the background-subtracted Ge $L_{2,3}$ core loss intensity for several $\text{Ge}_x\text{Si}_{1-x}$ alloys of the heterostructure, for which data acquisition times were 2 seconds and 20 seconds, respectively. It is notable that the Ge $L_{2,3}$ edge is clearly visible in a $\text{Ge}_x\text{Si}_{1-x}$ alloy with a 2-second acquisition time. Although the signal-to-noise ratio is low in this scan, the figure shows a clear trend in the increase of the core loss signal as the Ge concentration increases in successively grown alloy layers of the heterostructure. The 20-second scan shows a marked increase in the signal-to-noise ratio.

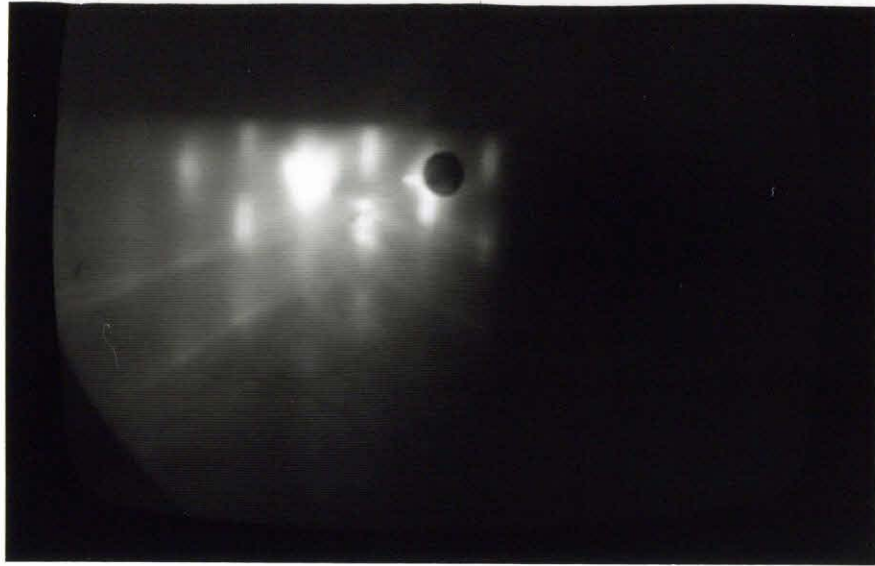


Figure 5.7: Photograph of RHEED pattern during $\text{Ge}_x\text{Si}_{1-x}$ heterostructure growth.

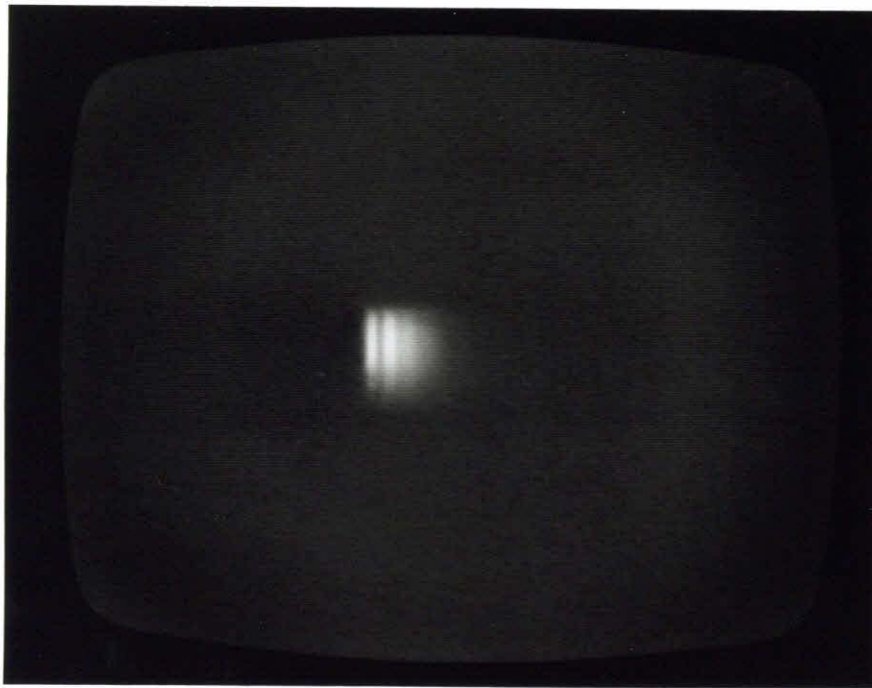


Figure 5.8: Photograph of electron dispersion representing the energy loss spectrum of a $\text{Ge}_x\text{Si}_{1-x}$ alloy. The bright bands are the zero loss and first two plasmons in silicon.

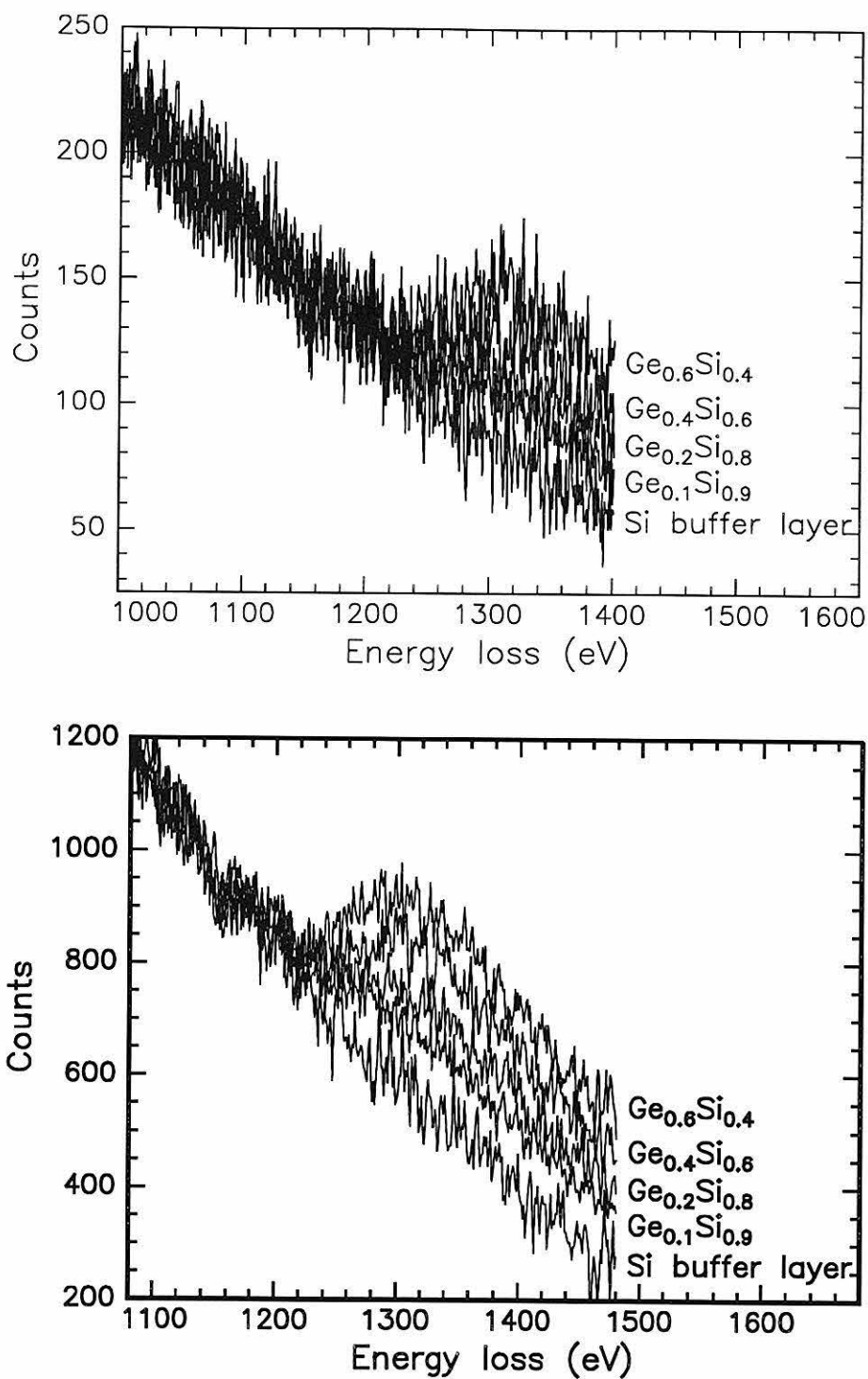


Figure 5.9: Background-subtracted Ge $L_{2,3}$ core loss intensities for several $\text{Ge}_x\text{Si}_{1-x}$ alloys of various compositions in a composition-graded SiGe superlattice, measured with parallel detection REELS. Data were obtained with 2-second (top) and 20-second (bottom) acquisition times.

5.5.2 Discussion

The core loss data shown imply a major advance in the ability to do real-time analysis during growth using PREELS. Previous REELS work performed with serial detection on $\text{Ge}_x\text{Si}_{1-x}$ alloys of various compositions (see Chapter 2) yielded Ge $L_{2,3}$ core loss intensities of the same signal-to-noise ratio, but acquisition time was, under favorable conditions, about 50-90 times longer, and often several hundreds of times longer. In the present system, data acquisition is expected to take at most a few seconds even for collecting spectra of core losses with very small cross sections.

We have found the PREELS sensitivity to be extremely high. Preliminary calculations on the electron-photon conversion efficiency to be ~ 4000 photons per incident electron. The detector, with a dynamic range of 262,000:1, is easily saturated when exposed to moderate room lighting. Wrapping the detector with aluminum foil during data collection is effective in completely blocking out ambient light. Another great triumph for PREELS is the fact that data collection is surprisingly stable in the presence of ambient AC noise sources, e.g., pumps, power supplies, etc., which have plagued our serial REELS measurements. PREELS spectra obtained with the substrate heater on and off were virtually identical, even though the AC current-driven heater coil caused significant 60 Hz oscillation of the RHEED pattern. Furthermore, the system is oblivious to mechanical vibrations at ~ 1 Hz of non-negligible amplitude of the cryopump pumping at 4000 liters/sec. This may in part be due to the rigid mechanical coupling of the CCD detector to the rest of the parallel REELS assembly (as shown in Figure 5.2). Of course, accurate focusing of the spectrometer plays a large part as well.

In conclusion, the implementation of parallel-detection REELS has in its preliminary experiments proven to be a success. The tremendous decrease in data acquisition time, stability against mechanical and electromagnetic noise, superior detective quantum efficiency, high dynamic range, and potential for EELS mapping make this system a remarkable diagnostic tool for real-time monitoring of novel and exotic processes (e.g., EXELFS) in the MBE environment. Ultimately, this system will have

the ability to automatically provide feedback to the growth sources to modify deposition parameters when necessary, making RHEED/PREELS a powerful diagnostic tool and process controller which will make numerous scientific contributions to the practice of *in situ* surface analysis during molecular beam epitaxy.

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Appendix A. Details of the serial REELS instrumentation

This appendix will discuss the more technical aspects of the important components of the serial-detection REELS system, and will include comments on the performance and user-friendliness of these components. Schematic drawings are provided at the end of the appendix to further elucidate the discussions.

Chamber

The REELS chamber was custom-designed and constructed of 304 stainless steel by Huntington Laboratories, Inc. (Mountain View, CA). All joints were UHV-welded. The diameter of the chamber body is 16". The three biggest ports were designed to accommodate the sample manipulator (top port), source flange and ion pump. Two ports directly opposite each other on the chamber body accommodate the RHEED gun and spectrometer assembly. The other ports were used for the sample load lock assembly, linear motion feedthroughs, electron beam evaporator, and viewports. The chamber was bolted to a heavy-duty metal table via an aluminum plate and cylindrical standoffs as an earthquake precaution. A disadvantage of this is that in this manner the chamber was mechanically rigidly coupled to the entire building, and measurements were occasionally prone to mechanical vibrations from building construction activity occurring several hundred yards away. However, perhaps more serious than mechanical noise was electromagnetic interference from the various AC sources nearby. The serial REELS detection system seemed very prone to electromagnetic interference not only from other instrumentation within the room, but also from next door.

RHEED gun

The RHEED gun used in all experiments performed for this thesis is a Thermionics Laboratory, Inc./Vieetech (Hayward, CA) Model VE-052, operating at a maximum accelerating voltage of 30 kV and a maximum emission current of $\sim 100 \mu\text{A}$. The electron source is a tungsten hairpin-type filament of 0.1 mm diameter producing electrons via thermionic emission. A beam spot size of $< 100 \mu\text{m}$ is obtained. Magnetic lenses steer the beam in the two directions (x , y) transverse to the beam direction; the z magnetic lens acts as a focusing lens. Operating pressure of this RHEED gun must be $\leq 10^{-6}$ Torr in order to prevent arcing of the filament. The power supply is a Model VP-052S with a stability of 0.005%.

In practice, the RHEED gun always operated with an emission current under $60 \mu\text{A}$; an approximate rule of thumb used was that the emission current (in μA) was about twice the accelerating voltage (in kV). Operation at emission currents higher than this often caused the power supply to trip.

Electron energy loss spectrometer

The spectrometer used is a Gatan Model 607 doubly focusing, second-order aberration-corrected magnetic sector with the dispersion plane oriented at 90° to the incident beam. By scanning the magnetic field inside the prism and using energy-selecting slits, electrons are sorted out according to their energies. A scintillator converts the electrons to photons and the signal is amplified by a photomultiplier tube and transferred to a multichannel analyzer.

The spectrometer is mounted behind the RHEED screen in the optical path of the scattered electrons. The beam enters the spectrometer through an entrance aperture which is of externally selectable size (1, 2, 3, and 5 mm available). A focusing coil assembly in front of the magnetic prism allows one to fine tune the magnet focus and provide corrections to second-order aberrations due to curvature of the magnet at the exit plane. The electrons then enter the magnetic prism. Electrons of the same energy

are brought to focus at a point on the energy-selecting slit by the combined effects of the focusing coils and the prism. Due to the different trajectories of electrons of different energies, the scattered beam is dispersed in space, the dispersion being $\sim 2 \mu\text{m}/\text{eV}$.

The focusing coil assembly consists of (1) a quadrupole magnet (X) which focuses electrons of the same energy into a short line at the exit slit; (2) a quadrupole magnet (Y) which rotates the line focus produced by the X quadrupole so that it lies parallel to the line of the slit; and (3) a sextupole magnet (θ) which attempts to correct for the second-order aberrations of the prism. The combined action of the focusing coils and prism give an energy resolution at the exit of the prism which is virtually identical to the energy resolution at the entrance, i.e., the spectrometer does not degrade the energy resolution of the detection system.

The scintillator is made of NE160; it is “fast,” meaning it has a very short ($\sim$ tens of nanoseconds) decay time and can handle large electron arrival rates. The photomultiplier tube (PMT) is a Hamamatsu R329-01 which is capable of counting single electrons up to a rate of $\sim 10^7/\text{sec}$. Additional advantageous features of the Gatan 607 include the fact that the drift tube is electrically isolated, allowing for operation in voltage scan mode; the energy-selecting slit is adjustable from 0–100 μm ; and small coils are provided inside the prism to generate a magnetic field to compensate for AC stray magnetic fields at mains frequency.

Sample manipulator

The sample manipulator used in the serial-detection REELS setup was a ISA RIBER Model PMR, consisting of translation tables with vernier controls for x , y and z motion, and a rotary motion feedthrough for sample tilting. A motor is attached to provide for sample rotation.

The substrate holder is held to the manipulator by a bayonet-type mount. It was necessary for us to design and construct a bushing and attach it to the sample transfer rod to hold the substrate block while guiding it into place on the manipulator. We

fabricated a bushing of aluminum. Sample transfer was generally time-consuming, because the normal to the sample mount face on the manipulator is not parallel to the transfer rod, but instead made an angle of $\sim 30^\circ$ with the transfer rod. Because of the limited view of the chamber interior from the available viewports, it was difficult to align the sample mount and transfer rod assembly and engage all three bayonets simultaneously into the slots of the sample mount.

Source flange and cooling shroud

The source flange was custom-designed to accommodate up to five evaporation sources and includes a cooling shroud for either water- or liquid nitrogen cooling. The five ports are 2.75" in diameter and arranged in a square array on a 10" flange, with one port in the center. The focal distance in our source flange is 8". Each port is equipped with its own shutter, manipulated by a pneumatic linear motion feedthrough with a 2" full extension. The cooling shroud is attached to the source flange via the pipe assembly (for supply and return of cooling medium), directly welded onto the source flange and cooling shroud. The pipes were designed to be coaxial for better thermal isolation, which would be especially important for liquid nitrogen cooling.

Effusion cell and electron beam evaporator

The effusion cell used was a EPI Knudsen-type cell, with a 10cc capacity pyrolytic boron nitride (PBN) crucible. The filament is noninductively wound tantalum wire, with PBN insulators. Layered tantalum foil serves as heat shielding. A standard W5%Re vs. W26%Re thermocouple measures the temperature of the crucible, which may be maintained at a maximum of $\sim 1200^\circ\text{C}$.

We found that water cooling worked better than liquid nitrogen cooling for the effusion cell. Non-uniform heating and subsequent local evaporation of liquid nitrogen within the cryoshroud resulted in local hot spots on the PBN crucible, causing a crucible to crack on one occasion.

The electron beam evaporator used was a Thermionics Laboratory, Inc. (Hayward, CA) Model 100-0011 rod-fed e-gun. The power supply (Model 150-0030) provides a constant output voltage of 4 kV and electron emission current of 0 -750 mA, yielding a maximum output power of 3000 Watts. The gun allows for continuous source material feeding and various tilting angles other than horizontal, making it advantageous to crucible e-guns. Water or liquid nitrogen cooling with a flow rate of ≥ 0.5 gallon/minute prevents excessive heating of the e-gun and its housing. Best performance is obtained when operating the gun at pressures $< 10^{-5}$ Torr.

We have successfully used this e-gun to evaporate silicon. High-purity (99.999%) silicon rods (1/4" diameter, 4" long) were commercially purchased from ESPI, Inc. (Agoura Hills, CA). We also obtained boron rods ($\sim 1/8$ " diameter, 4" long); however, these were brittle and not as robust as the silicon rods, presumably because boron is very difficult to form into rods. The surfaces of the boron rods were rough (unlike the smooth surfaces of the silicon rods) and resembled twigs. Evaporation of silicon using an emission current of 250 mA yielded a growth rate of approximately 15 Å/min with a source-substrate distance of 10". We found that growth is least prone to contamination when the electron beam current is such that only the interior, and not the perimeter of the rod diameter, is completely melted. Presumably, this prevents incorporation of contaminants from nearby e-gun surfaces. Using a homemade mirror assembly which we inserted into the e-gun housing in order to view the rod during growth, we were able to observe the rod while increasing the electron current from zero until the melt glowed orange in most of its interior.

Initial problems we had with this Thermionics e-gun included the fact that the linear motion feedthrough which advances the source rod did not provide enough travel distance. We were able to advance only about 0.75" of a 4" rod. We designed and fabricated an adaptor dummy rod that attached to the linear motion feedthrough and provided the extra travel needed to advance the entire source rod.

RHEED screen

The RHEED screen, of 3.7" (9.4 cm) diameter and 0.063" (1.6 mm) thickness, was fabricated of aluminum 6061, then polished (180 grit). The circular aperture through which the scattered RHEED beam travels is a 7/32" (5.6 mm) through hole. Three 9/64" (3.6 mm) counterbored holes equally spaced on a 3.0" (7.6 cm) bolt circle were drilled for mounting the screen inside the chamber.

The phosphorescent coating was P-31 phosphor, with copper-doped zinc sulfide as the active ingredient. P-31 powder was obtained from USR Optonix, Inc. (Hackensack, NJ). The coating was laid on the circular aluminum plate by the settling of an emulsion of equal parts of P-31 and sodium silicate (sodium metasilicate, pentahydrate) in deionized water. The sodium silicate acts as a binder to improve the adhesion of the P-31 to the metal plate. The plate was placed on an upside-down petri dish inside a 5-gallon capacity container with a spigot. The emulsion was very gradually drained out and the phosphor screen was allowed to dry overnight under a fume hood. The resulting coating was free of cracks visible to the eye, and fairly robust (as long as it did not come into contact with anything). A RHEED screen coated in this manner lasted typically about six months with no significant damage from electron irradiation.

Double rocking coils

As the incidence angle of the RHEED beam on the sample is increased, the scattered electrons stray further and further away from the optic axis of the energy loss spectrometer. This leads to beam focussing problems within the magnetic prism and to a degradation in energy resolution.

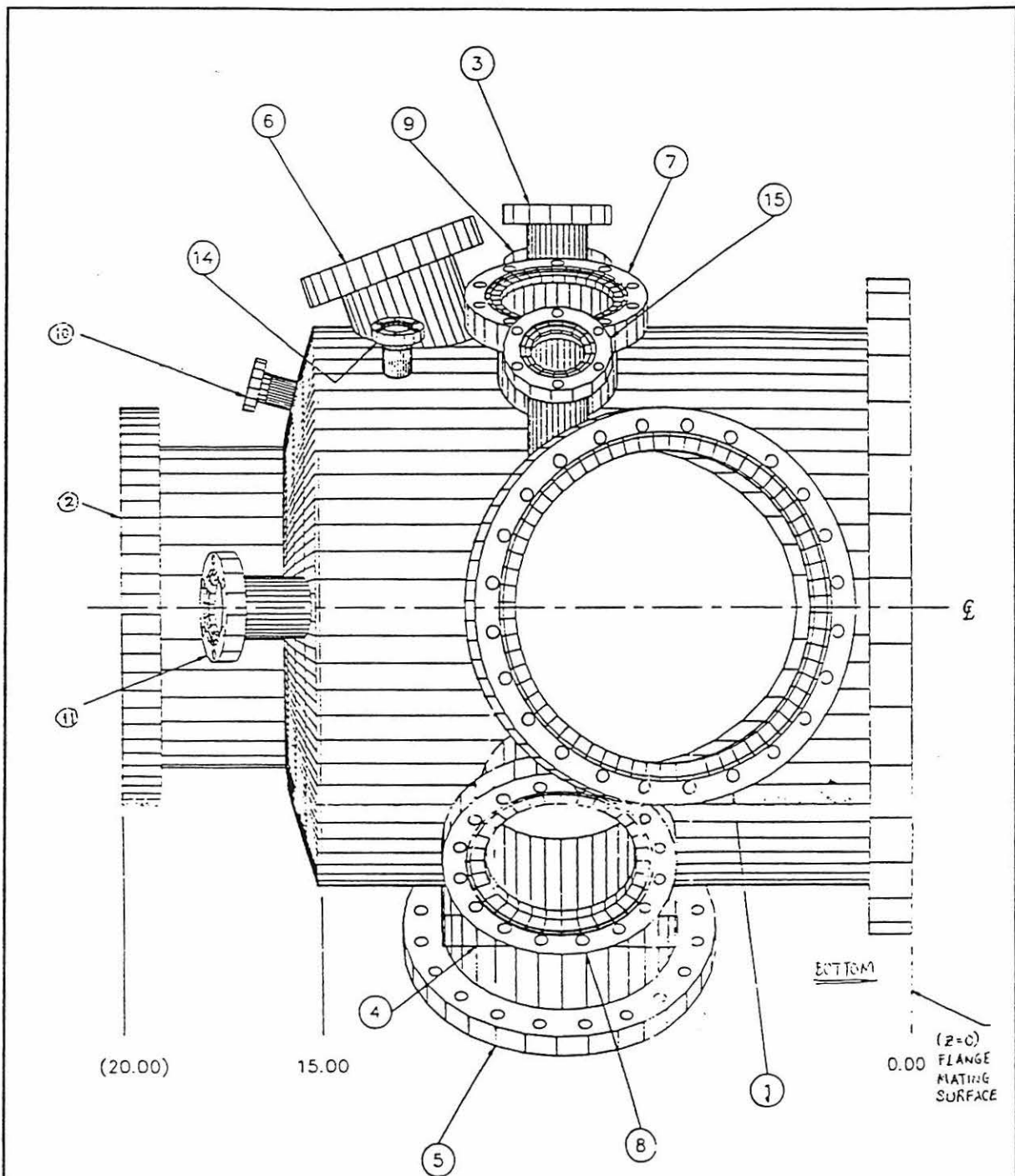
Our solution to maintaining adequate beam focus is to incorporate a second set of dipole magnet coils in the electron beam trajectory. The first set of dipole magnets (inside the RHEED gun assembly) steers the incident beam outward from the sample, and the second set of dipoles deflects the beam back toward the sample, providing

the advertised “double rocking.” A unique combination of sample tilt and double rocking deflections ensures that the scattered beam travels along the optic axis as it enters the energy loss spectrometer.

The implementation of the double rocking feature of the incident beam has significantly improved our energy resolution, as evidenced by observation of the low loss region of the energy loss spectrum. A zero loss and two plasmons (surface or bulk) are typically resolved in silicon samples. This had not been possible previously, except for very shallow incidence angles ($< 1^\circ$).

Differential pumping aperture

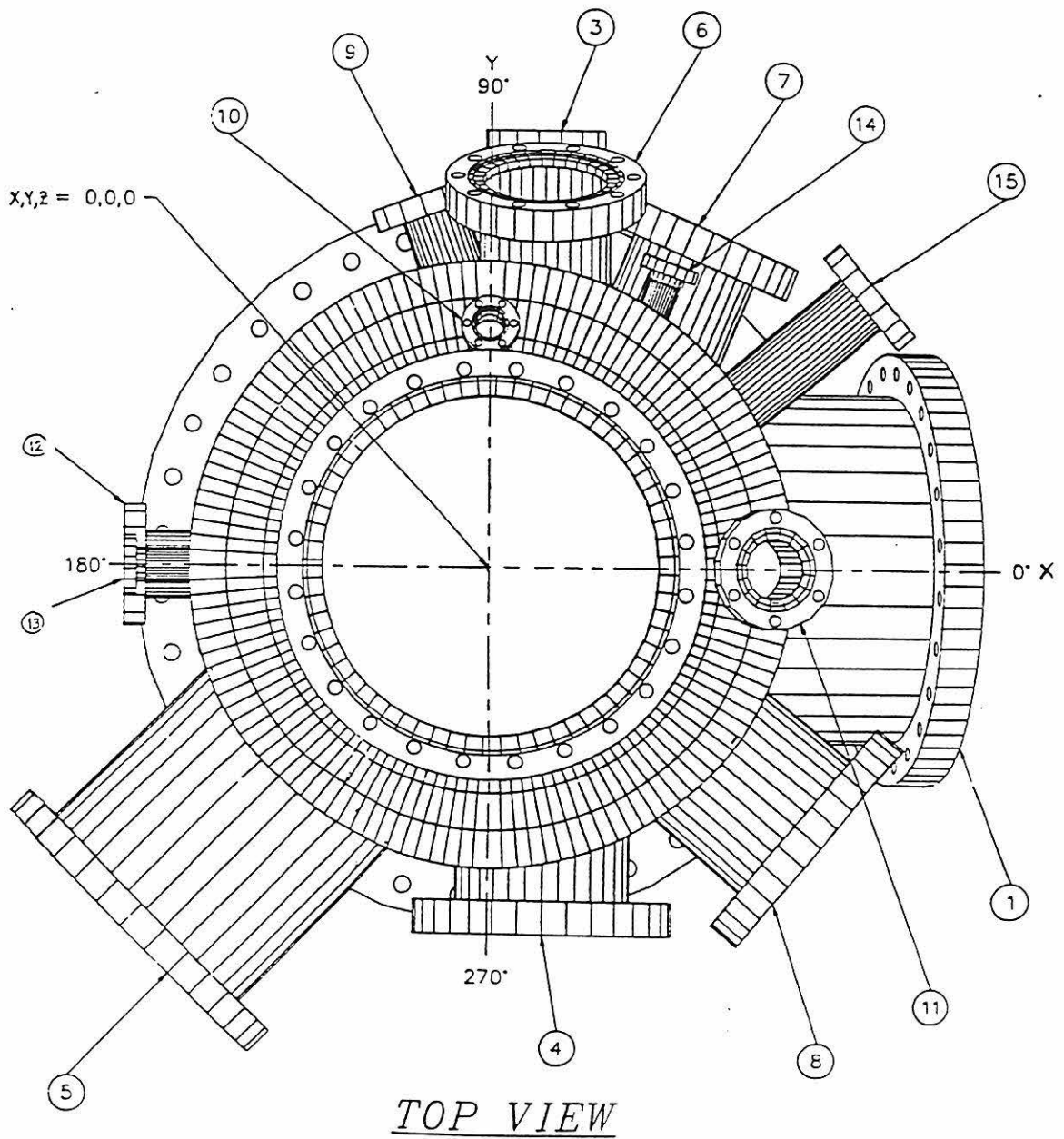
The Gatan energy loss spectrometer was developed for use in the transmission electron microscope; thus, it is not UHV-compatible. However, it was successfully interfaced to the UHV growth chamber by means of a differential pumping aperture of diameter ~ 6 mm and length ~ 0.75 ” (a circular hole drilled through the center of a standard 4.5” flange). The system was pumped with a mechanical pump, turbomolecular pump (50 liters/sec), titanium sublimation pump, and ion pump (400 liters/sec), giving an overall base pressure of typically 10^{-9} Torr.



All parts fabricated of 304
stainless steel

(Drawing courtesy of Huntington
Laboratories, Inc.)

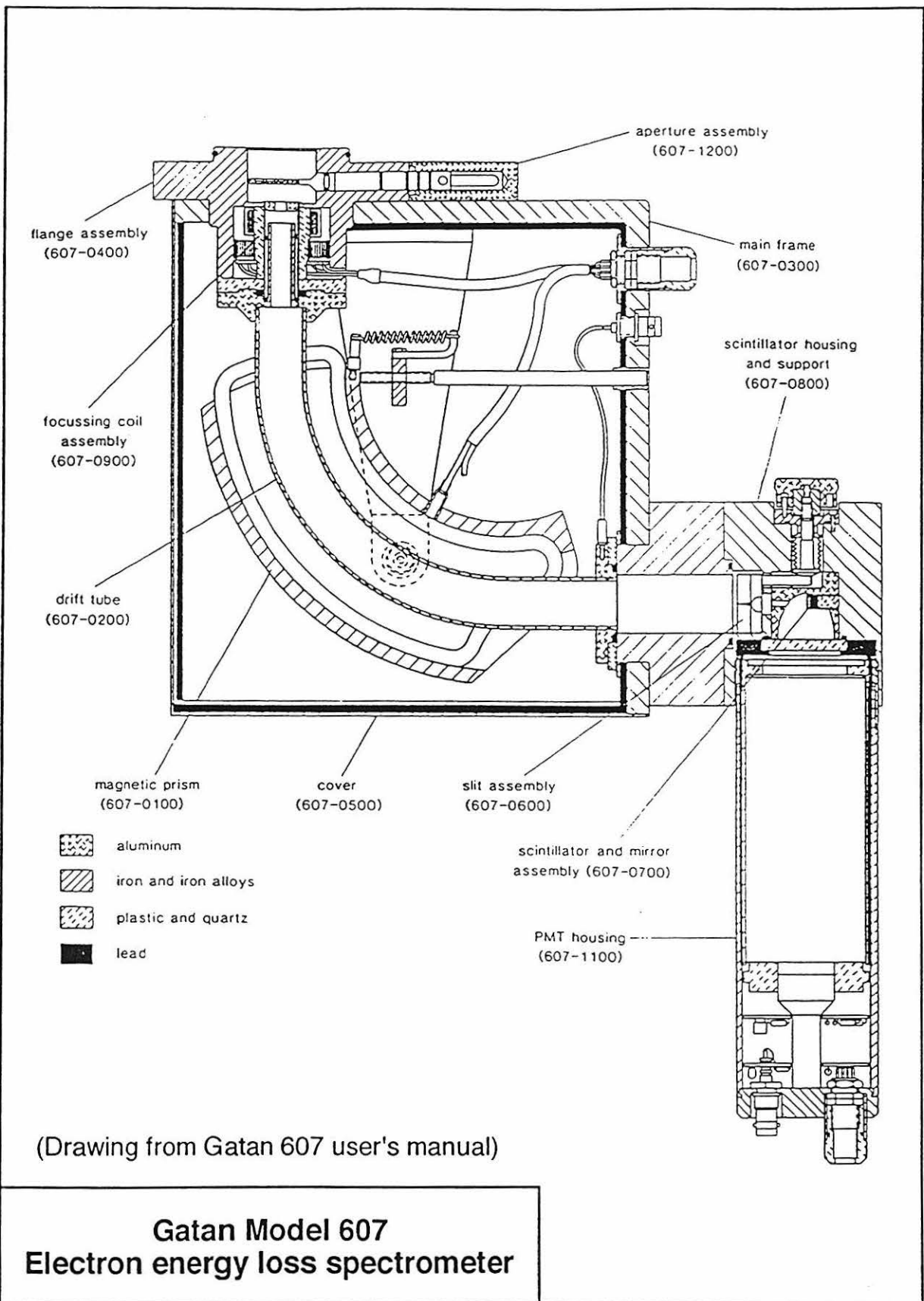
REELS chamber assembly
(4/16/91)

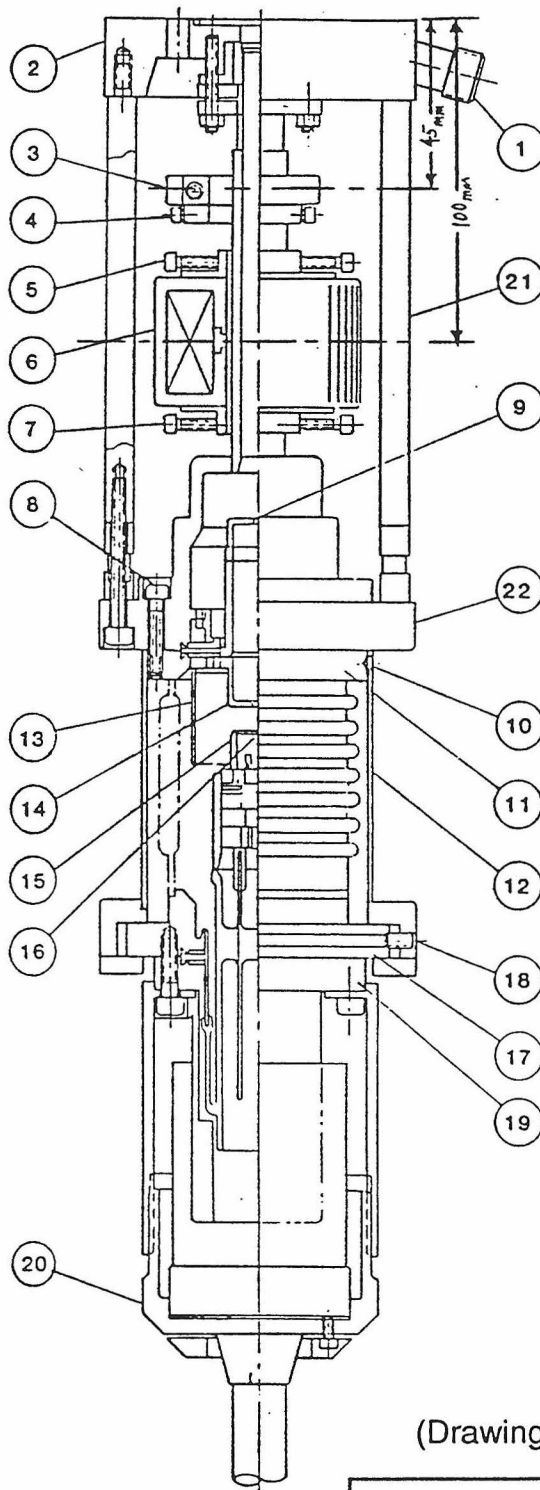


All parts fabricated of 304
stainless steel

(Drawing courtesy of Huntington
Laboratories, Inc.)

REELS chamber assembly
(4/16/91)

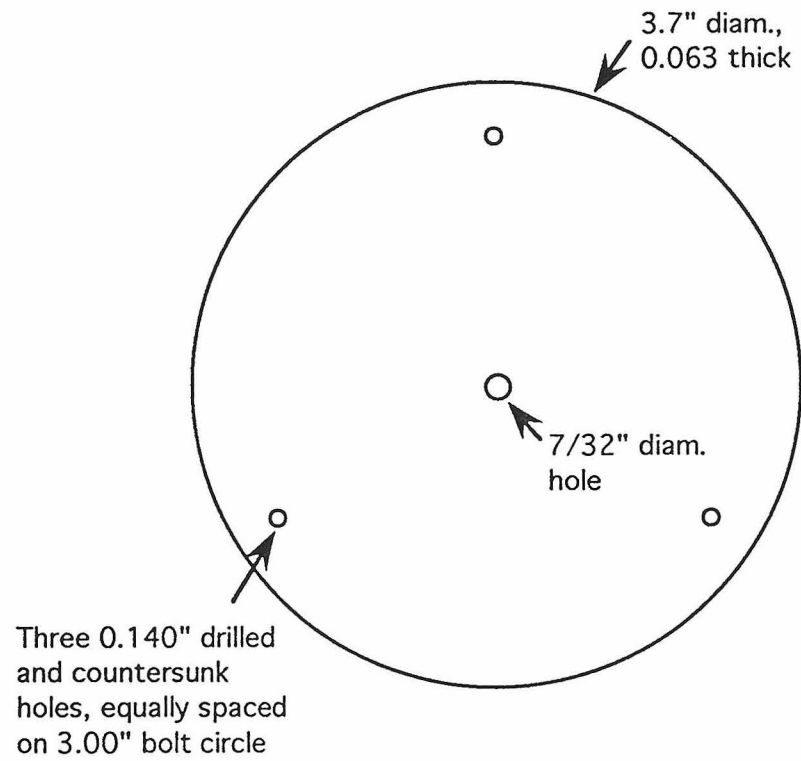




1. Lens coil connector
2. Chamber mounting flange
3. Deflection coil lens (X, Y)
4. Deflection alignment screws
5. Focus lens alignment screws (A)
6. Focus coil lens (Z)
7. Focus lens alignment screws (B)
8. Bellows flange screws
9. Beam aperture
10. Bellows cover screws.
11. Bellows flange
12. Bellows cover
13. Magnetic shield
14. Anode tube
15. Wehnelt cylinder
16. Filament location
17. Beam alignment flange
18. Beam alignment screws
19. Gun mounting flange
20. HV connector
21. 45 mm
22. 100 mm

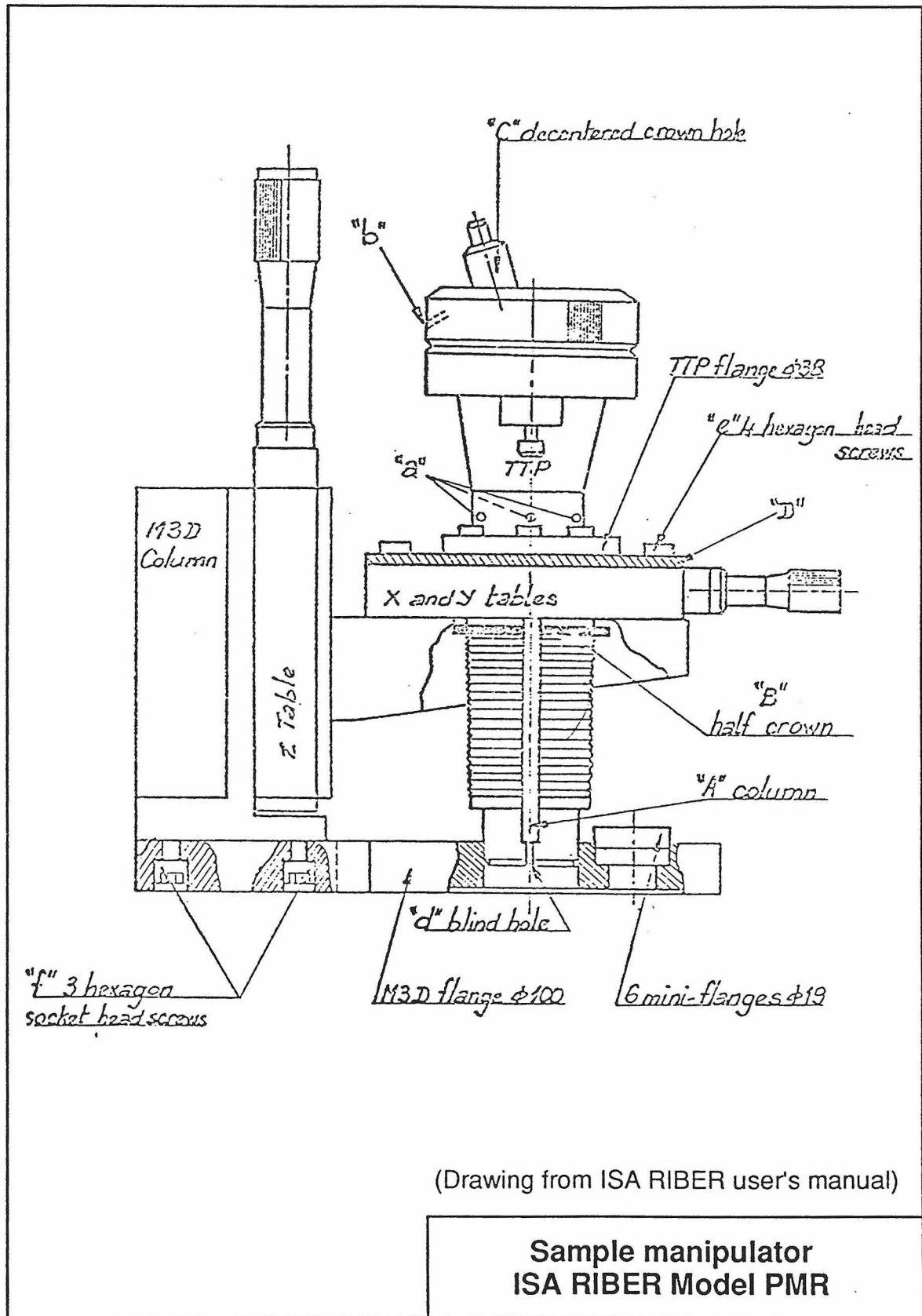
(Drawing from TLI/Vieetech user's manual)

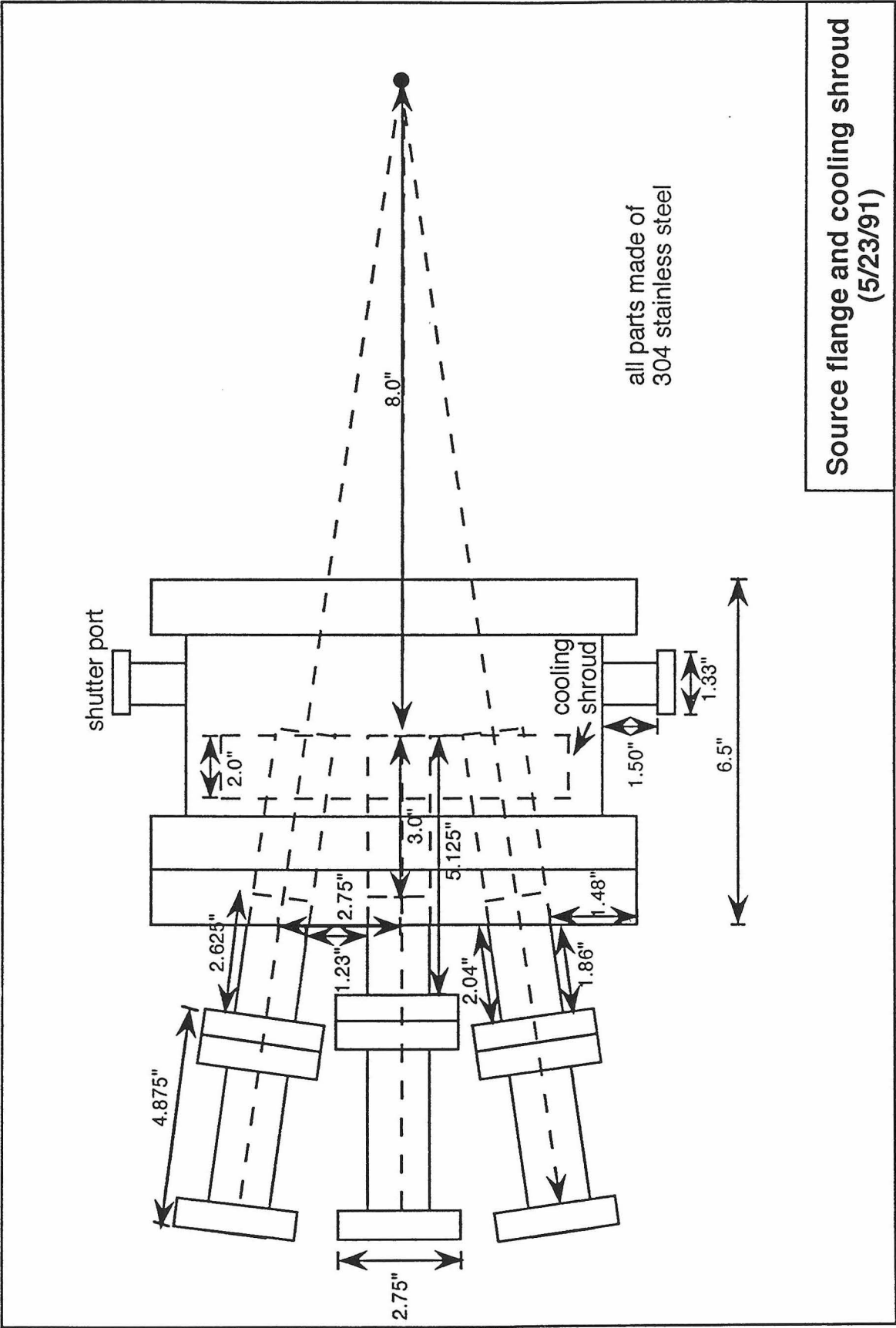
Model VE-052 RHEED gun
Thermionics Laboratory, Inc./Vieetech

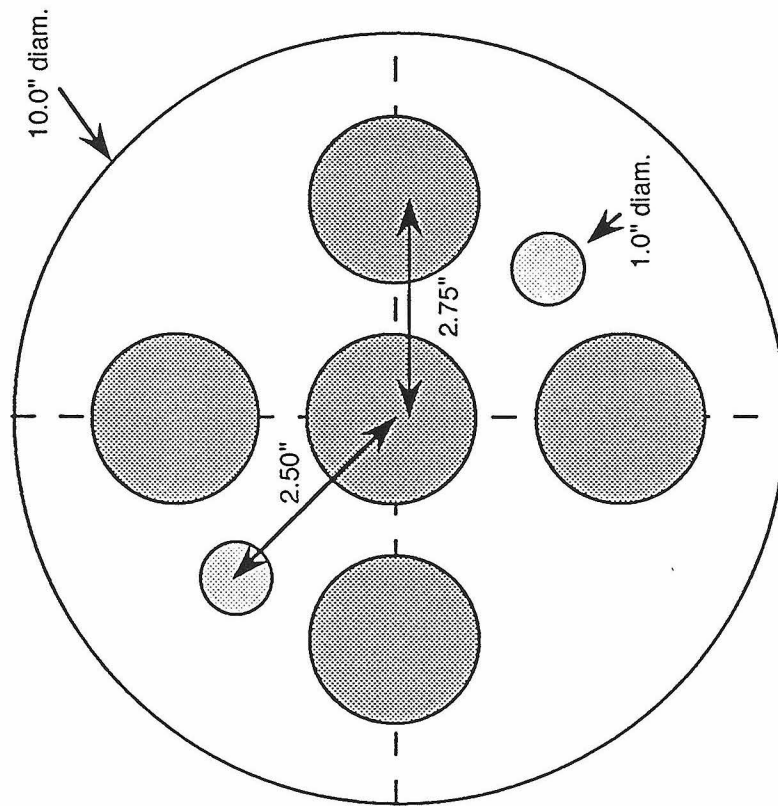


Material: Aluminum 6061

RHEED screen
(8/19/91)

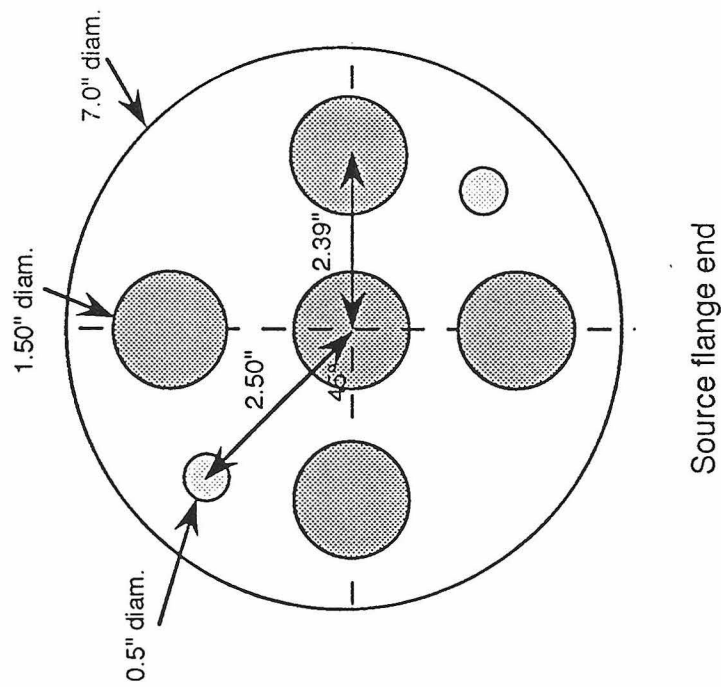




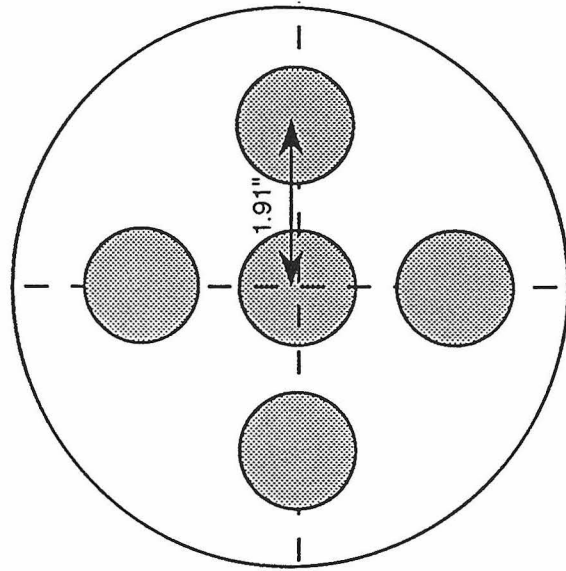


End view

Source flange
(5/23/91)

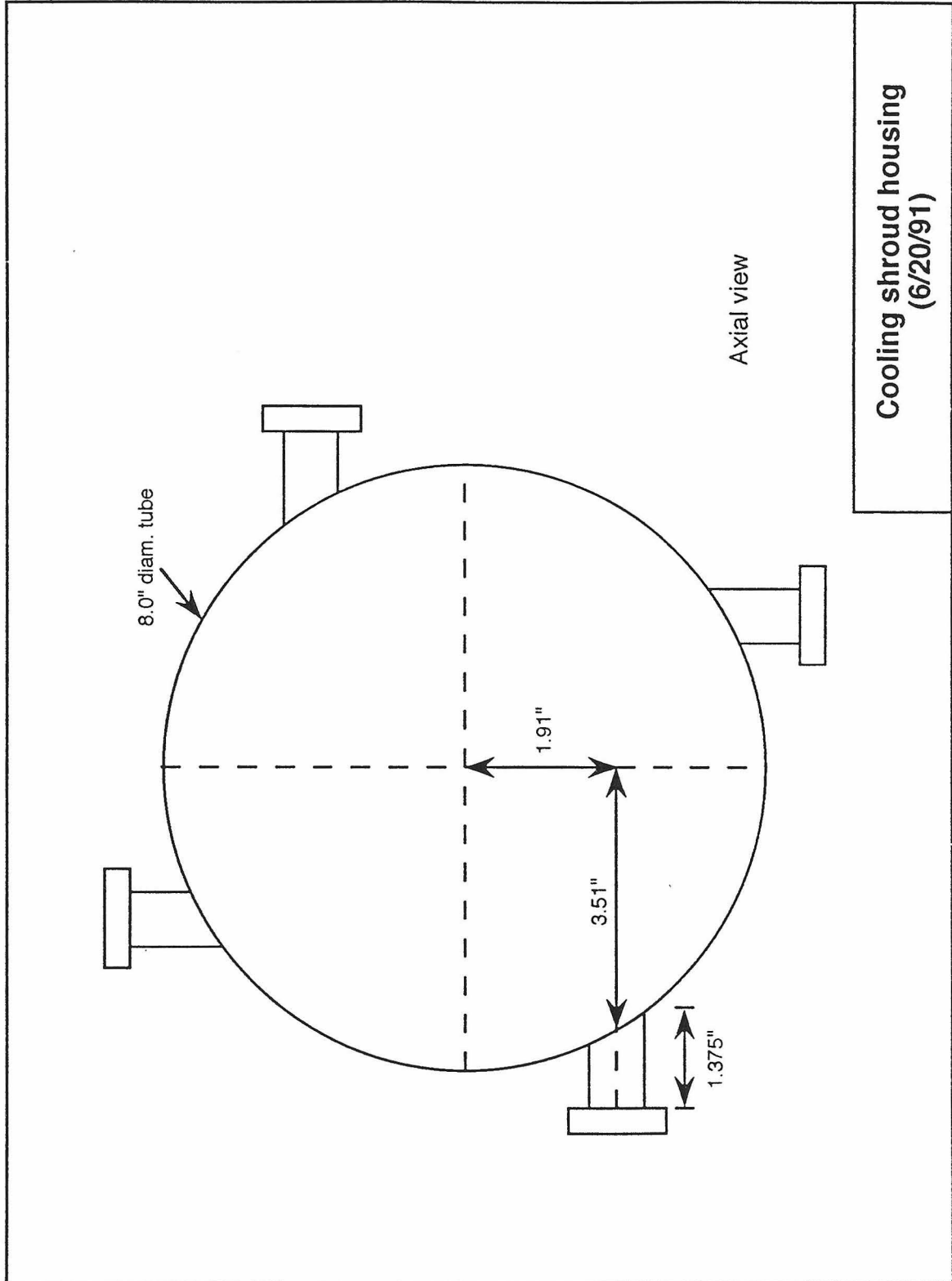


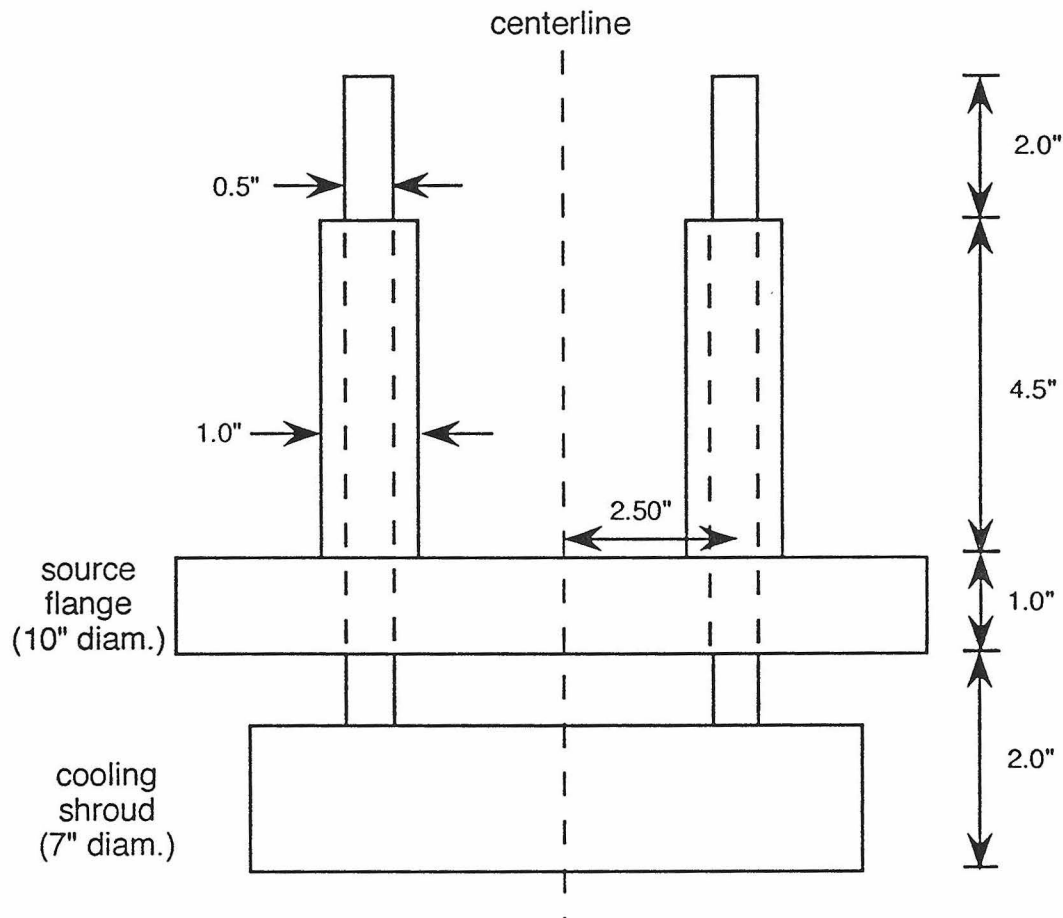
Substrate end



304 stainless steel, 1/16" thickness

Cooling shroud for source flange
(5/29/91)





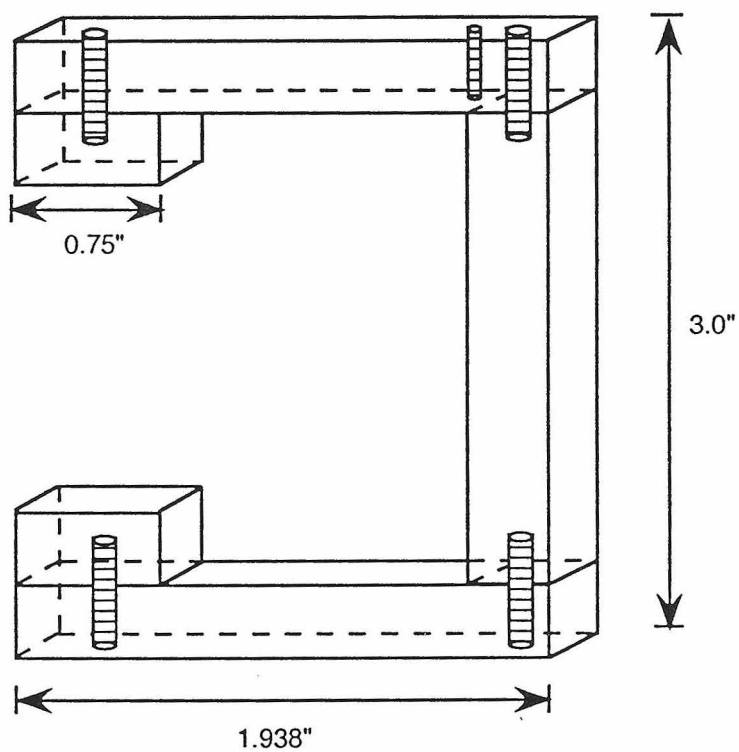
Wall thickness of pipes:
 ~0.065" (1" pipe)
 ~0.035" (0.5" pipe)

All components made of 304 stainless steel

Note: Effusion cell ports are not shown in this figure.

Side view

**Source flange/cooling shroud assembly
 (6/20/91)**

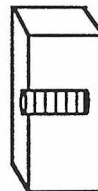


All pieces are fabricated of Permalloy
and have 1/4" square cross section

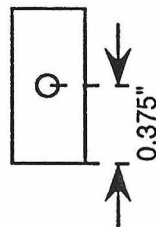
**Dipole magnets
(1/27/92)**

Part A

Fabricate 4 pieces. Drill and tap hole 3/16" deep for 4-40 flathead screw.

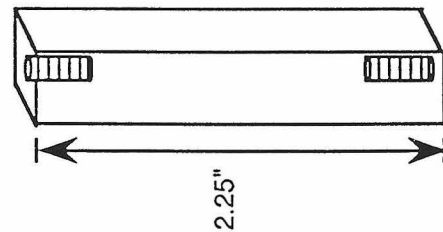


side view



top view

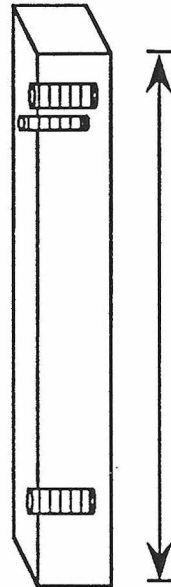
Part B



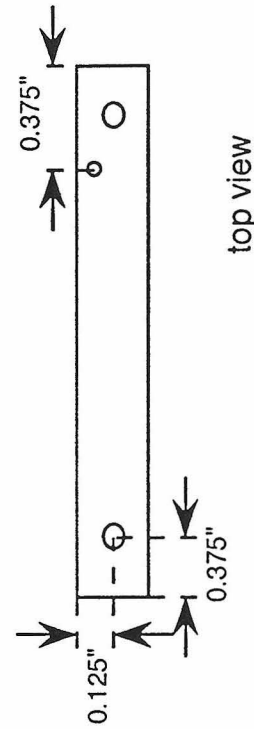
Fabricate 2 pieces. Drill and tap hole 1/4" deep for 4-40 flathead screw.

Part C

Fabricate 2 pieces with cross section 0.25" x 0.25" and 2 pieces with cross section 0.25" x 0.188". Drill and countersink two holes as shown for 4-40 flathead steel screws, plus a small hole (1/16" diam.) for 24 AWG magnet wire.



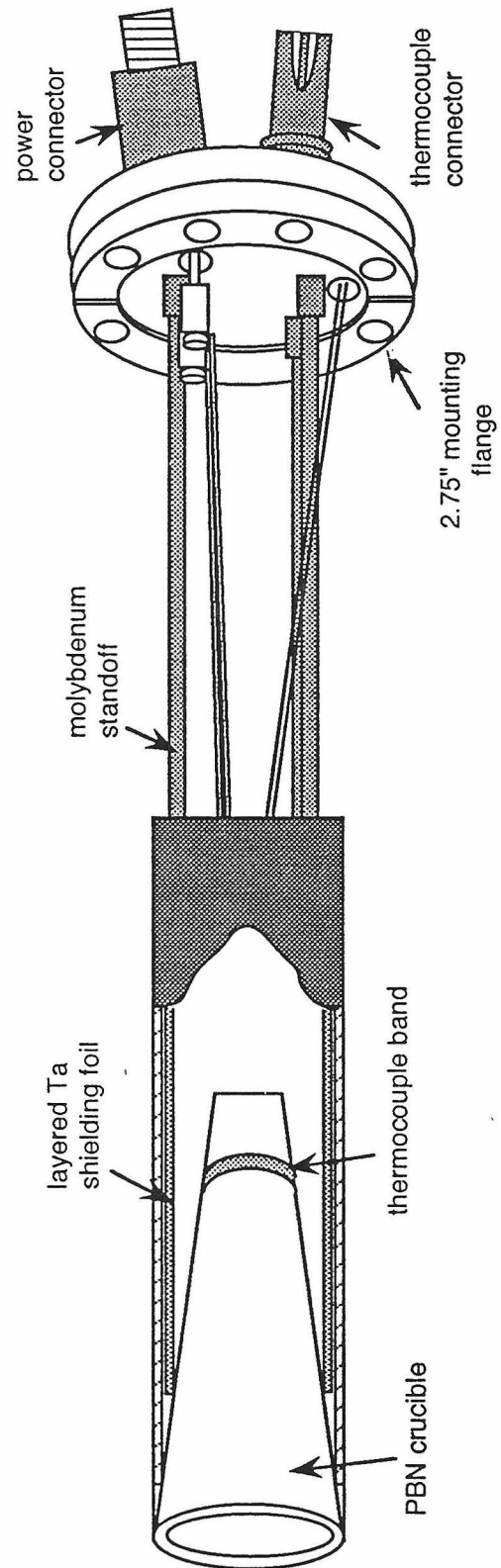
side view



top view

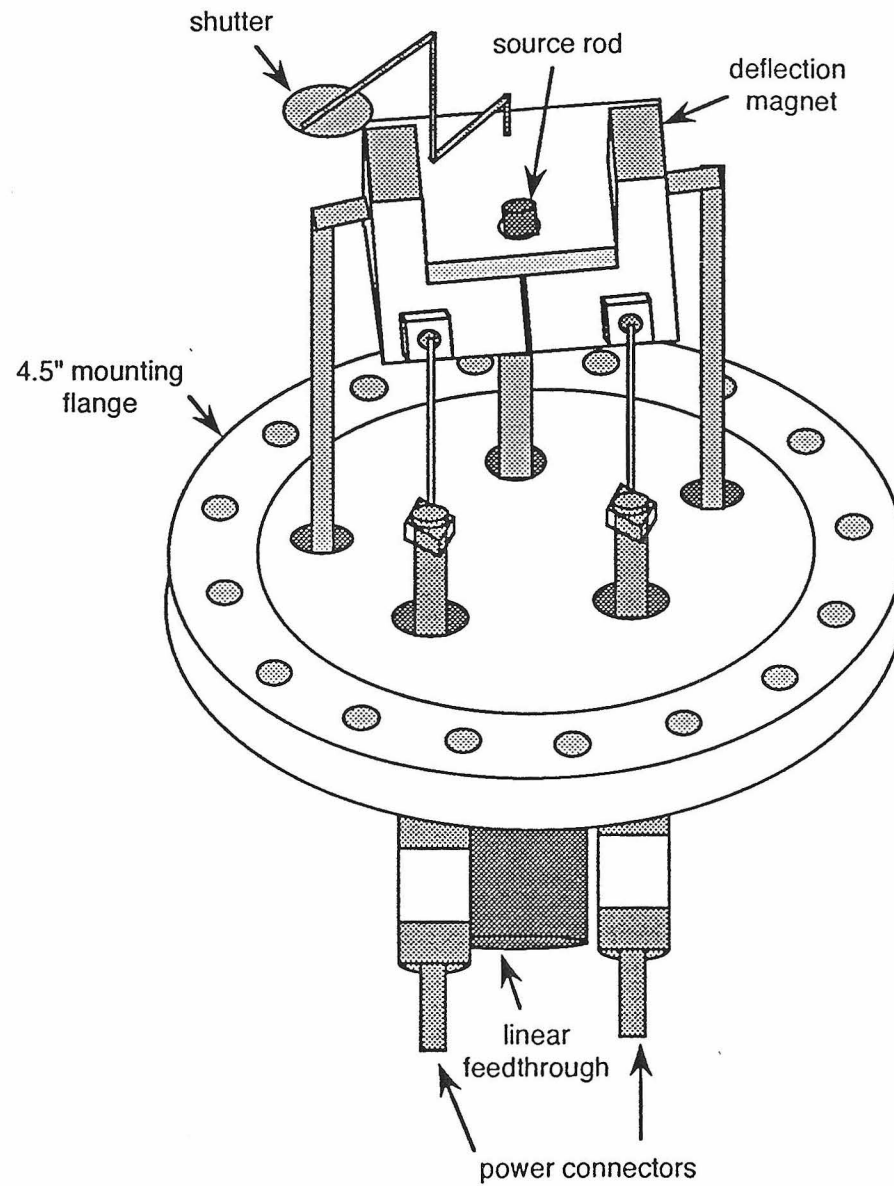
Exploded view

**Dipole magnets
(1/27/92)**



(Drawing adapted from EPI catalog)

EPI 10cc standard effusion cell



Model 100-0011

(Drawing adapted from Thermionics catalog)

Rod-fed electron beam evaporator

Appendix B. Source code for EXELFS analysis with relaxed knot constraints

This appendix includes the programs used in EXELFS analysis in this thesis. The conventional spline fit requirement of having the values of the data and their derivatives match at the knots proved to be too stringent in some of the data where the EXELFS oscillations were weak. This set of programs performs a spline fit with a relaxed knot constraint; i.e., that the values only, and not the derivatives, match at the knots.

All programs were written in Borland C++. A program called PREP.CPP takes a raw energy loss edge data file and prepares it for a spline fit. SPLFIT.CPP performs the spline fit, and FOURIER.CPP takes the Fourier transform of the edge data. Optional programs include TRUNCATE.CPP, which truncates $\chi(k)$ data according to user-specified limits of k before taking the Fourier transform; and SMOOTH.CPP, which smoothes $\chi(k)$ data in case it is noisy and will produce artifacts in the Fourier transform.

```
/* PROGRAM PREP.CPP
```

```
-----
This program takes an input file in EL/P format (long EELS header and
4096 counts values in 8-column format) and converts it into 2-column
format for EXELFS analysis. The header is completely stripped. User
provides high- and low-energy cutoff values for preparing the extended-
edge data. Output files are a .DAT file which includes the entire
background-subtracted edge (essentially the output of the EL/P program)
and a .EDG file which includes just the extended-edge data (this is the
file to use for subsequent EXELFS analysis).
```

```
*/
```

```
#include <iostream.h>
```

```
#include <fstream.h>
```

```
#include <sstream.h>
```

```
#include <iomanip.h>
```

```
#include <math.h>
```

```
#include <stdio.h>
```

```
#include <conio.h>
```

```
#include <string.h>
```

```
void plot(double xarray[], double yarray[], int Numpts);
```

```
main() {
```

```
clrscr();
```

```
char InputFileName[100];
```

```
char DataOutputFileName[100], EdgeOutputFileName[100];
```

```
cout<<"Please enter input file name (specify entire path): ";
```

```
cin>>setw(sizeof(InputFileName))>>InputFileName;
```

```
ostringstream(DataOutputFileName,sizeof(DataOutputFileName))<<InputFileName
<<ends;
```

```
int I=0;
```

```
while (DataOutputFileName[I] && DataOutputFileName[I]!='.') I++;
```

```
if (DataOutputFileName[I]=='.') DataOutputFileName[I]='\0';
```

```
ostringstream(DataOutputFileName,sizeof(DataOutputFileName),ios::app)<<".DAT"
<<ends;
```

```
ostringstream(EdgeOutputFileName,sizeof(EdgeOutputFileName))<<InputFileName
<<ends;
```

```
int J=0;
```

```
while (EdgeOutputFileName[J] && EdgeOutputFileName[J]!='.') J++;
```

```
if (EdgeOutputFileName[J]=='.') EdgeOutputFileName[J]='\0';
```

```
ostringstream(EdgeOutputFileName,sizeof(EdgeOutputFileName),ios::app)<<".EDG"
<<ends;
```

```

cout<<endl<<"Output files are "<<DataOutputFileName<<" and "
    <<EdgeOutputFileName<<endl<<endl;

/*
gets(InputFileName);
printf("As entered: %s\n", InputFileName);
int length=strlen(InputFileName);
if (strchr(InputFileName, '.')) {
    strncpy(DataOutputFileName, InputFileName, length-4);
    strncpy(EdgeOutputFileName, InputFileName, length-4);
    strcat(DataOutputFileName, ".DAT");
    strcat(EdgeOutputFileName, ".EDG");
    printf("\nOutput file names are %s and %s\n\n", DataOutputFileName,
        EdgeOutputFileName);
}
else {
    strcpy(DataOutputFileName, InputFileName);
    strcpy(EdgeOutputFileName, InputFileName);
    strcat(DataOutputFileName, ".DAT");
    strcat(EdgeOutputFileName, ".EDG");
    printf("\nOutput files are %s and %s\n\n", DataOutputFileName,
        EdgeOutputFileName);
}
*/

ifstream InputFile(InputFileName);
ofstream DataOutputFile(DataOutputFileName);
ofstream EdgeOutputFile(EdgeOutputFileName);

double CountsAtZero;
cout<<"Please enter the number of counts at energy zero (round ";
cout<<"down to\nnearest integer): ";
cin>>CountsAtZero;
cout<<"Counts at zero = "<<CountsAtZero;
float EnergyInc;
cout<<endl<<"Please enter the energy increment per channel (eV/ch): ";
cin>>EnergyInc;
cout<<"Energy increment = "<<EnergyInc;
float Low, High;
cout<<endl<<"Please enter the lowest energy value you wish to save: ";
cin>>Low;
cout<<endl<<"Please enter the highest energy value you wish to save: ";
cin>>High;
cout<<endl<<"Lowest = "<<Low<<endl<<"Highest = "<<High;
float E0;
cout<<endl<<"What is the threshold energy (in eV) of this edge? ";
cin>>E0;

```

```

cout<<endl<<"E0 = "<<E0;

if (!InputFile) {
    cout<<"Can't find input file";
}

// Skip through text header until last line of header (which starts with
// "EELS") is reached.
char Line[200];
do {
    char Letter;
    int i=0;
    do {
        InputFile.get(Letter);
        Line[i]=Letter;
        i++;
        cout<<Letter;
    } while (Letter!='\n');
} while (Line[0]!='E' || Line[1]!='E');

// Read in counts data. Ignore all values before CountsAtZero.
double TestCounts;
int ICountsAtZero=int(CountsAtZero);
do {
    InputFile>>TestCounts;
    cout<<endl<<TestCounts;
} while (int(TestCounts)!=ICountsAtZero);

cout<<endl<<"First value of Counts is "<<TestCounts;
// Use the second non-negative data value for energy zero.

// Determine how many data values to put into EdgeOutputFile.
int N;
N = int((High - Low)/EnergyInc) + 1;
cout<<endl<<"N = "<<N;

double Energy[900], k[900], Counts[900];

// Initialize all array elements to 0.
for (int p=0; p<900; p++) {
    Energy[p] = 0;
    Counts[p] = 0;
    k[p] = 0;
}

double mass=9.109534e-31;
double pi=3.14159265359;

```

```

double echarge=1.6021892e-19;
double hbar=6.626176e-34/(2*pi);
double constant;
constant = sqrt(2*mass)*sqrt(echarge)*1.0e-10/hbar;
cout<<endl<<"constant = "<<constant;

// Write Npts into output file:
DataOutputFile<<N<<endl;
EdgeOutputFile<<N<<endl<<E0<<endl<<EnergyInc<<endl<<Low<<endl<<High<<endl;

// Calculate energies and read in counts data until we reach Low.
cout<<endl<<"Starting to write to .DAT output file..."<<endl;
int q=1;
do {
    Energy[q] = E0 + (q-1)*EnergyInc;
    InputFile>>Counts[q];
    DataOutputFile<<Energy[q]<<"    "<<Counts[q]<<endl;
    q++;
} while (q<=int((Low-E0)/EnergyInc));

    // Nextra + N = Ntotal (Ntotal is the number of
int Nextra;                // points in the DataOutputFile).
Nextra = q-1;
cout<<endl<<"Nextra = "<<Nextra<<endl;
//cout<<".EDG file begins right after "<<endl;
//cout<<" "<<Energy[q]<<"    "<<Counts[q]<<endl;

cout<<"Starting to write to .EDG output file..."<<endl;

for (int s=(Nextra+1); s<=(Nextra+N); s++) {
    Energy[s] = E0 + (s-1)*EnergyInc;
    k[s] = constant*sqrt(Energy[s] - E0);
    InputFile>>Counts[s];
    // cout<<Energy[q]<<"    "<<NormEnergy[q]<<"    "<<k[q]<<"    ";
    // cout<<Counts[q]<<endl;
    DataOutputFile<<Energy[s]<<"    "<<Counts[s]<<endl;
    EdgeOutputFile<<k[s]<<"    "<<Counts[s]<<endl;
}

InputFile.close();
DataOutputFile.close();
EdgeOutputFile.close();
cout<<endl<<endl<<"Done!"<<endl;

plot(Energy, Counts, Nextra+N);

return 0;

```



```
}

/* int Channel=0;
do {
    InputFile>>Counts;
    if (!InputFile.eof())
        OutputFile<<Channel<<" "<<Counts<<endl;
    Channel++;
} while (!InputFile.eof()); */
```

```
/* PROGRAM SPLFIT.CPP
```

```
-----
This program does a polynomial spline fit of a data set Counts[1...900]
for a user-specified number of regions. The polynomial order for each
region is also user-specified. The FitOutputFile contains three columns
of data: (1) k[], (2) fit[], i.e., the calculated polynomials as a
function of k, and (3) chik[], the Counts data minus the polynomial
background, leaving the EXELFS oscillations. The NumOutputFile contains
the numerical results of the polynomial fit for each region.
```

```
*/
```

```
#include <iostream.h>
#include <fstream.h>
#include <iomanip.h>
#include <stdio.h>
#include <sstream.h>
#include <math.h>
#include <stdlib.h>
#include <conio.h>
#include <string.h>
```

```
//void plot(double xarray[], double yarray[], int Numpts);
```

```
int main() {
```

```
clrscr();
char InputFileName[100], OutputFileName1[100], OutputFileName2[100];
char OutputFileName3[100];
cout<<"Please enter your input file name (specify path): ";
cin>>setw(sizeof(InputFileName))>>InputFileName;

ostringstream(OutputFileName1,sizeof(OutputFileName1))<<InputFileName<<ends;
int I=0;
while (OutputFileName1[I] && OutputFileName1[I]!='.') I++;
if (OutputFileName1[I]=='.') OutputFileName1[I]='\0';
ostringstream(OutputFileName1,sizeof(OutputFileName1),ios::app)<<".FIT"<<ends;

ostringstream(OutputFileName2,sizeof(OutputFileName2))<<InputFileName<<ends;
int J=0;
while (OutputFileName2[J] && OutputFileName2[J]!='.') J++;
if (OutputFileName2[J]=='.') OutputFileName2[J]='\0';
ostringstream(OutputFileName2,sizeof(OutputFileName2),ios::app)<<".NUM"<<ends;

ostringstream(OutputFileName3,sizeof(OutputFileName3))<<InputFileName<<ends;
int K=0;
while (OutputFileName3[K] && OutputFileName3[K]!='.') K++;
```

```

if (OutputFileName3[K]=='.') OutputFileName3[K]='\0';
ostream(OutputFileName3,sizeof(OutputFileName3),ios::app)<<".COE"<<ends;

cout<<"Output files are: "<<endl<<OutputFileName1<<" ", "<<OutputFileName2
    <<"", and "<<OutputFileName3<<endl;

/*
gets(InputFileName);
int length=strlen(InputFileName);
char OutputFileName1[100];
char OutputFileName2[100];
OutputFileName1[0]='\0';
OutputFileName2[0]='\0';
if (strchr(InputFileName, '.')) {
    strncpy(OutputFileName1, InputFileName, length-4);
    strncpy(OutputFileName2, InputFileName, length-4);
    printf("\nCore file name is %s\n", OutputFileName1);
    strcat(OutputFileName1, ".FIT");
    strcat(OutputFileName2, ".NUM");
    printf("\nOutput file names are: %s and %s\n", OutputFileName1,
        OutputFileName2);
}
else {
    strcpy(OutputFileName1, InputFileName);
    strcpy(OutputFileName2, InputFileName);
    strcat(OutputFileName1, ".FIT");
    strcat(OutputFileName2, ".NUM");
    printf("\nOutput files are: %s and %s\n", OutputFileName1,
        OutputFileName2);
}
*/

ifstream InputFile(InputFileName);
if (!InputFile) {
    cout<<"Error: opening file";
}

int Npts;
InputFile>>Npts;
float E0;
InputFile>>E0;
float EnergyInc;
InputFile>>EnergyInc;
float Low, High;
InputFile>>Low;
InputFile>>High;
cout<<"N = "<<Npts<<endl;

```

```

cout<<"Energy increment = "<<EnergyInc;
cout<<endl<<"Low = "<<Low<<" "<<"High = "<<High<<endl;
double constant = 0.512314773;
//cout<<endl<<endl<<"Number of data points?"<<endl;
// Eventually, program will obtain N from output of PREP.

double k[900];
double Counts[900];

// Initialize all values of k and Counts to zero.
for (int a=0; a<900; a++) {
    k[a] = 0;
    Counts[a] = 0;
}
// Read input file data.
for (int i=1; i<=Npts; i++) {
    InputFile>>k[i]>>Counts[i];
}

int Nregions;
cout<<endl<<"How many spline fit regions do you want? ";
cin>>Nregions;

// Get the endpoints of the fit regions from keyboard.
double endpt[9]= {0,0,0,0,0,0,0,0,0};
for (int bee=1; bee<Nregions; bee++) {
    cout<<"Enter the high endpoint of region "<<bee<<" (in eV): ";
    cin>>endpt[bee];
}

// Calculate the number of data points in each fit region.
int N[10];
for (int dad=1; dad<Nregions; dad++) {
    if (dad==1)
        N[dad] = int((endpt[dad] - Low)/EnergyInc);
    else
        N[dad] = int((endpt[dad] - endpt[dad-1])/EnergyInc);
}
N[Nregions] = Npts;
for (int mom=1; mom<=(Nregions-1); mom++) {
    N[Nregions] = N[Nregions] - N[mom];
}
int Ntotcheck=0;
for (int test=1; test<=Nregions; test++) {
    Ntotcheck = Ntotcheck + N[test];
}

```

```

if (Ntotcheck!=Npts) {
    cout<<endl<<"Error!  The numbers of points of the regions don't add up!";
}

ofstream CoeffOutputFile(OutputFileName3);
CoeffOutputFile<<Nregions;

ofstream NumOutputFile(OutputFileName2);
NumOutputFile<<OutputFileName2<<endl<<endl
    <<"Total number of data points:  "<<Npts<<endl
    <<"Low = "<<Low<<"          "<<"High = "<<High<<endl
    <<"Energy increment is "<<EnergyInc<<" eV/channel"<<endl
    <<"There are "<<Nregions<<" spline fit regions."<<endl;

// Create vector of polynomial orders; create M, b, and sums arrays.
// Largest number of regions I'm providing for is 10.
// Largest polynomial order I'm providing for here is n=10.
// b will eventually be the solution array.
double M[10][11][11];
double b[10][11];
double sums[10][21];
int n[10]={0,0,0,0,0,0,0,0,0,0};
double c[10][11];
double fit[900];
double chik[900];
double sigma[900];
double chisquared;
for (int num=0; num<Nregions; num++) {
    cout<<endl<<"Order of polynomial "<<(num+1)<<":  ";
    cin>>n[num+1];
}

for (int dum=1; dum<10; dum++) {
    for (int hi=0; hi<11; hi++) {
        b[dum][hi] = 0;
        c[dum][hi] = 0;
        for (int bye=0; bye<11; bye++) {
            M[dum][hi][bye] = 0;
        }
        for (int hey=0; hey<21; hey++) {
            sums[dum][hey] = 0;
        }
    }

for (int w=0; w<900; w++) {

```

```

    fit[w] = 0;
    chik[w] = 0;
    sigma[w] = 0;
}

// This is the fitting routine.
int Ncurrent=1;
for (int reg=1; reg<=Nregions; reg++) {
    NumOutputFile<<endl<<endl<<endl;
    NumOutputFile<<"REGION "<<reg<<": (polynomial order = "<<n[reg]<<") "
    <<endl<<N[reg]<<" points, ranging from "
    <<k[Ncurrent]<<" to "<<k[Ncurrent+N[reg]-1]
    <<" (inverse angstroms)"<<endl<<endl;
    // Create sums array with dim=2n+1. sums[]=sums[reg][0...2n[reg]].
    cout<<endl;
    for (int d=0; d<=(2*n[reg]); d++) {
        // Sum the powers of k[i] over the N[reg] data points.
        for (int a=Ncurrent; a<(Ncurrent+N[reg]); a++) {
            if (k[a]==0) {
                if (d==0)
                    sums[reg][d] = sums[reg][d] + 1;
                else
                    sums[reg][d] = sums[reg][d];
            }
            if (d==0)
                sums[reg][d] = sums[reg][d] + 1;
            else
                sums[reg][d] = sums[reg][d] + pow(k[a],d);
        }
        cout<<sums[reg][d]<<" ";
        // Check values.
        // NumOutputFile<<sums[reg][d]<<" ";
    }

    // Assign the values of matrix M.
    cout<<endl<<"Coefficient matrix is:";
    NumOutputFile<<"Coefficient matrix is:";
    for (int g=1; g<=(n[reg]+1); g++) {
        cout<<endl;
        NumOutputFile<<endl;
        for (int h=1; h<=(n[reg]+1); h++) {
            M[reg][g][h] = sums[reg][g+h-2];
            cout<<M[reg][g][h]<<" ";
            // Print values to screen.
            NumOutputFile<<M[reg][g][h]<<" ";
            // Write M to output file.
        }
    }
}

```

```

    // Compute sums for b.
    cout<<endl<<"b = ";
    NumOutputFile<<endl<<endl<<"b = ";
    for (int f=1; f<=(n[reg]+1); f++) {
for (int m=Ncurrent; m<(Ncurrent+N[reg]); m++) {
    if (k[m]==0) {
        if ((f-1)==0)
            b[reg][f] = b[reg][f] + Counts[m];
        else
            b[reg][f] = b[reg][f];
    }
    else
        b[reg][f] = b[reg][f] + Counts[m]*pow(k[m],(f-1));
}
    cout<<b[reg][f]<<" "; // Print values to screen.
    NumOutputFile<<b[reg][f]<<" "; // Write b to output file.
}

    // Find the coefficients by Gaussian elimination.
    for (int j=1; j<=(n[reg]+1); j++) {
double Mtemp1 = M[reg][j][j];
b[reg][j] = b[reg][j] / M[reg][j][j];
cout<<endl;
for (int q=j; q<=(n[reg]+1); q++) {
    M[reg][j][q] = M[reg][j][q] / Mtemp1;
    cout<<M[reg][j][q]<<" ";
}
    cout<<" "<<b[reg][j];
for (int t=(j+1); t<=(n[reg]+1); t++) {
    double Mtemp2 = M[reg][t][j];
    b[reg][t] = b[reg][t] - M[reg][t][j]*b[reg][j];
    for (int p=j; p<=(n[reg]+1); p++) {
        M[reg][t][p] = M[reg][t][p] - M[reg][j][p]*Mtemp2;
    }
}
}

    // Print upper triangular matrix to screen.
    cout<<endl<<"Upper triangular matrix is:";
    NumOutputFile<<endl<<endl<<"Upper triangular matrix is:";
    for (int u=1; u<=(n[reg]+1); u++) {
cout<<endl;
NumOutputFile<<endl;
for (int v=1; v<=(n[reg]+1); v++) {
    cout<<M[reg][u][v]<<" ";
    NumOutputFile<<M[reg][u][v]<<" ";
}
}

```

```

cout<<" "<<b[reg][u];
NumOutputFile<<" "<<b[reg][u];
}

// Now we have the last coefficient; solve for the rest by back-
// substitution.
// Create coefficient array; c[reg][1]=c[reg]0, c[reg][2]=c[reg]1, etc.
cout<<endl<<"The coefficients for region "<<reg<<" are:";
NumOutputFile<<endl<<endl<<"The coefficients for region "<<reg<<" are:";
CoeffOutputFile<<endl<<N[reg]<<" "<<n[reg];
for (int r=(n[reg]+1); r>=1; r--) {
c[reg][r] = b[reg][r];
if (r==(n[reg]+1))
{}
else
for (int s=(r+1); s<=(n[reg]+1); s++) {
c[reg][r] = c[reg][r] - M[reg][r][s]*c[reg][s];
}
cout<<endl<<"c["<<reg<<"] ["<<r<<"] = "<<c[reg][r]; //Print to screen.
NumOutputFile<<endl<<"c["<<reg<<"] ["<<r<<"] = "<<c[reg][r];
CoeffOutputFile<<" "<<c[reg][r];
}

// Calculate the fit polynomials and write to output files.
chisquared=0;
for (int z=Ncurrent; z<(Ncurrent+N[reg]); z++) {
for (int zap=1; zap<=(n[reg]+1); zap++) {
if ((zap-1)==0)
fit[z] = fit[z] + c[reg][zap];
else
fit[z] = fit[z] + c[reg][zap]*pow(k[z],zap-1);
}
chik[z] = Counts[z] - fit[z]; // Background subtraction.
chisquared = chisquared + pow((Counts[z]-fit[z]),2)/Counts[z];
}
chisquared = chisquared/(N[reg]-n[reg]-1);
NumOutputFile<<endl<<"Chi-squared = "<<chisquared;
Ncurrent = Ncurrent + N[reg];
}

CoeffOutputFile<<endl<<endl<<Npts<<endl<<EnergyInc<<endl<<EO<<endl
<<constant<<endl;
for (int ph=1; ph<=Npts; ph++) {
CoeffOutputFile<<endl<<k[ph]<<" "<<fit[ph]<<" "<<chik[ph]
<<" "<<Counts[ph];
}

```



```

ofstream FitOutputFile(OutputFileName1);
FitOutputFile<<Npts<<endl<<EnergyInc<<endl<<EO<<endl<<constant<<endl;

// Weight the chik[] by a power of k if desired.
char answer;
int weightpower;
cout<<endl<<endl<<"Would you like to weight the chi by a power of k?  ";
cin>>answer;
if (answer=='n') {
    for (int pop=1; pop<=Npts; pop++) {
        FitOutputFile<<k[pop]<<"    "<<fit[pop]<<"    "<<chik[pop]<<endl;
    }
}
else {
    cout<<endl<<"What power of k?  ";
    cin>>weightpower;
    for (int wow=1; wow<=Npts; wow++) {
        chik[wow] = chik[wow]*pow(k[wow],weightpower);
        FitOutputFile<<k[wow]<<"    "<<fit[wow]<<"    "<<chik[wow]<<endl;
    }
}

InputFile.close();
CoeffOutputFile.close();
FitOutputFile.close();
NumOutputFile.close();

cout<<endl<<endl<<"Done!!"<<endl;

return 0;
}

```

```
/* PROGRAM FOURIER.CPP
```

```
-----
This program takes a file with chi(k) data and takes its Fourier
transform. Lower and upper limits of k and r can be chosen by the
user, and an optional windowing function (Gaussian or parabolic) is
available. The output file has the extension .RDF and holds the
Fourier transform magnitude values. User has the option of
correcting for phase shifts by inputting a phase shift file.
```

```
*/
```

```
#include <stdio.h>
```

```
#include <iostream.h>
```

```
#include <iomanip.h>
```

```
#include <string.h>
```

```
#include <strstream.h>
```

```
#include <fstream.h>
```

```
#include <math.h>
```

```
#include <conio.h>
```

```
//#define SWAP(a,b) tempr=(a);(a)=(b);(b)=tempr
```

```
void window(double array[], int index, int Npts);
```

```
void transform(double xdata[], double ydata[], double phases[], double
    newxdata[], double answer[], int Npts);
```

```
int main() {
```

```
clrscr();
```

```
char InputFileName[100], OutputFileName[100];
```

```
cout<<"Please enter your input file name (including path): "<<endl;
```

```
cin>>setw(sizeof(InputFileName))>>InputFileName;
```

```
ostrstream(OutputFileName,sizeof(OutputFileName))<<InputFileName<<ends;
```

```
int I=0;
```

```
while (OutputFileName[I] && OutputFileName[I]!='.') I++;
```

```
if (OutputFileName[I]=='.') OutputFileName[I]='\0';
```

```
ostrstream(OutputFileName,sizeof(OutputFileName),ios::app)<<".RDF"<<ends;
```

```
cout<<endl<<"Output file is "<<OutputFileName<<endl;
```

```
/*
```

```
OutputFileName[0]='\0';
```

```
if (strchr(InputFileName, '.')) {
```

```
    strncpy(OutputFileName, InputFileName, length-4);
```

```
    printf("\nCore file name is %s\n", OutputFileName);
```

```
    strcat(OutputFileName, ".RDF");
```

```
    printf("\nOutput file name is %s\n\n", OutputFileName);
```

```
}
```

```
else {
```

```

        strcpy(OutputFileName, InputFileName);
        strcat(OutputFileName, ".RDF");
        printf("\nOutput file is %s\n\n", OutputFileName);
    }
    */

    ifstream InputFile(InputFileName);
    ofstream OutputFile(OutputFileName);

    if (!InputFile) {
        cout<<"Can't find input file"<<endl;
    }

    double x[700], y[700], xconj[700], ftmag[700], phase[700];
    for (int i=0; i<700; i++) {                // Initialize all arrays.
        x[i] = 0.0;
        y[i] = 0.0;
        xconj[i] = 0.0;
        ftmag[i] = 0.0;
        phase[i] = 0.0;
    }

    // Read in input data.
    int N;
    double constant, E, Scrap;
    float E0, EnergyInc;
    //double Scrap;
    InputFile>>N>>EnergyInc>>E0>>constant;

    if (N>699) {
        cout<<"Too many points!  Modify code....";
    }

    for (int p=1; p<=N; p++) {
        //      InputFile>>x[p]>>Scrap>>y[p];
        InputFile>>x[p]>>y[p];
        //      cout<<x[p]<<"      "<<y[p]<<endl;
    }

    cout<<endl<<"N = "<<N<<endl<<"constant = "<<constant<<endl;
    cout<<"E0 = "<<E0<<endl<<"Energy increment = "<<EnergyInc<<" eV/channel";
    cout<<endl;

    char reply;
    cout<<"Would you like to correct for phase shifts?";
    cin>>reply;
    if (reply=='n')

```

```

    {}
else {
    char PhaseFileName[100];
    cout<<"Please enter the name of the input file with the phase data:"<<
    endl;
    cin>>PhaseFileName;
    ifstream PhaseData(PhaseFileName);
    for (int q=1; q<=N; q++) {
        PhaseData>>Scrap>>phase[q];
    }
}

cout<<endl<<"For windowing of the data, would you like";
cout<<endl<<" (1) a parabolic (""Welch"" ) window,";
cout<<endl<<" (2) a Gaussian window, or";
cout<<endl<<"          (3) a square window ?"<<endl;
int winindex;
cin>>winindex;

// Window the data.
window(y, winindex, N);

// In order to do the Fourier transform, put the data into every other slot
// in the chik[] array.
/*
for (int m=0; m<=((2*N)-2); m=m+2) {
    chik[m] = chiktemp[m/2];
}

E = pow((k[N-1]/constant),2) + E0;
for (int J=N; J<1024; J=J+2) {
    E = E + EnergyInc;
    k[J] = constant*sqrt(E-E0);
}
*/

int sign=0;
char answer;
cout<<endl<<"Are you doing a forward transform? ";
cin>>answer;
if (answer=='y')
    sign = 1;
else
    sign = -1;

double min, max;
if (sign==1) {

```

```

        cout<<endl<<"Please enter the range of r for which you want to do the ";
        cout<<"transform."<<endl;
        cout<<"r_min: ";
        cin>>min;
        cout<<endl<<"r_max: ";
        cin>>max;
    }
    else {
        cout<<endl<<"Please enter the range of k for which you want to do the ";
        cout<<"transform."<<endl;
        cout<<"k_min: ";
        cin>>min;
        cout<<endl<<"k_max: ";
        cin>>max;
    }

    double step=(max-min)/500.0;
    for (int v=1; v<=500; v++) {
        xconj[v] = min + (v-1)*step;
    }

    // Do the Fourier transform.
    cout<<endl<<"Doing the Fourier transform....";
    transform(x, y, phase, xconj, ftmag, N);
    cout<<endl<<endl<<"Fourier transform completed."<<endl;

    // Write results of Fourier transform into output file .RDF.
    cout<<endl<<"Writing results of transform into output file...";
    for (int w=1; w<=500; w++) {
        OutputFile<<xconj[w]<<"    "<<ftmag[w]<<endl;
    }

    InputFile.close();
    OutputFile.close();

    cout<<endl<<endl<<"Done!!"<<endl;

    return 0;
}

```

```

void window(double array[], int index, int Npts) {
    double weight[1024];
    for (int r=0; r<1024; r++) {
        weight[r] = 0;
    }
}

```

```

if (index==1) {                                     // Welch windowing routine.
    for (int s=1; s<=Npts; s++) {
        weight[s] = 1-pow((((s-1)-0.5*Npts)/(0.5*Npts)),2);
        array[s] = array[s]*weight[s];
    }
    cout<<endl<<"Parabolic windowing completed.";
}
if (index==2) {                                     // Gaussian windowing routine.
    float halfwidth;
    cout<<endl<<"For Gaussian windowing of your data, please enter the ";
    cout<<"half-width you\ndesire (in terms of fraction of total data ";
    cout<<"points):  ";
    cin>>halfwidth;
    double sigma;
    sigma = halfwidth/sqrt(2*log(2));
    sigma = int(sigma*Npts);                         // Convert sigma to units of channels.
    cout<<"sigma = "<<sigma<<" channels.";
    int gaussspace = 2*sigma;                        // This Gaussian falls to 0.018 at
    for (int p=1; p<=gausspace; p++) {               // 2*sigma.
        int mean = gaussspace;
        weight[p] = exp(-pow((((p-1)-mean)/sigma),2));
        array[p] = array[p]*weight[p];
    }
    for (int t=(gausspace+1); t<=(Npts-gausspace); t++) {}
    for (int u=(Npts-gausspace+1); u<=Npts; u++) {}
    int mean = Npts - gaussspace;
    weight[u] = exp(-pow((((u-1)-mean)/sigma),2));
    array[u] = array[u]*weight[u];
    }
    cout<<endl<<"Gaussian windowing of data completed.";
}
if (index==3)
    {}
}

```

```

void transform(double xdata[], double ydata[], double phases[], double
    newxdata[], double answer[], int Npts) {

```

```

    double Real, Imag;
    double delta;
    for (int s=1; s<=500; s++) {
        Real = 0.0;
        Imag = 0.0;
        for (int n=1; n<=Npts; n++) {
            if (n==1)

```

```

        delta = xdata[2] - xdata[1];
    else
        delta = xdata[n] - xdata[n-1];
    Real = Real + ydata[n]*cos(2*xdata[n]*newxdata[s]+phases[n])*delta;
    Imag = Imag + ydata[n]*sin(2*xdata[n]*newxdata[s]+phases[n])*delta;
    }
    answer[s] = sqrt(pow(Real,2) + pow(Imag,2));
}

}

/*
void dfour1(double data[], unsigned long nn, int isign) {
// Replaces data[1...2*nn] by its discrete Fourier transform, if isign is
// input as 1; or replaces data[1...2*nn] by nn times its inverse discrete
// Fourier transform if isign is input as -1. data is a complex array of
// length nn or, equivalently, a real array of length 2*nn. nn MUST be an
// integer power of 2 (this is not checked for).

unsigned long n, mmax, m, j, istep, i;
double wtemp, wr, wpr, wpi, wi, theta;    // Double precision for the trig
float tempr, tempi;                        // recurrences.

n = nn << 1;
j = 1;
for (i=1; i<n; i+=2) {                    // This is the bit-reversal section
    if (j>i) {                             // of the routine.
        SWAP(data[j], data[i]);           // Exchange the two complex numbers.
        SWAP(data[j+1], data[i+1]);
    }
    m = n >> 1;
    while (m>=2 && j>m) {
        j -= m;
        m >>= 1;
    }
    j += m;
}

// Here begins the Danielson-Lanczos section of the routine.
mmax = 2;
while (n>mmax) {                           // Outer loop executed (ln nn)
    istep = mmax << 1;                     // times.
    theta = isign*(6.28318530717959/mmax); // Initialize the trigonomet-
    wtemp = sin(0.5*theta);                // ric recurrence.
    wpr = -2.0*wtemp*wtemp;
    wpi = sin(theta);
}

```

```

        wr = 1.0;
        wi = 0.0;
        for (m=1; m<mmax; m+=2) {
            for (i=m; i<=n; i+=istep) {
                j = i + mmax;
                tempr = wr*data[j] - wi*data[j+1]; // This is the
                tempi = wr*data[j+1] + wi*data[j]; // Danielson-Lanczos
                                                    // formula.
                data[j] = data[i] -tempr;
                data[j+1] = data[i+1] - tempi;
                data[i] += tempr;
                data[i+1] += tempi;
            }
            wr = (wtemp = wr)*wpr - wi*wpi + wr; // Trigonometric
            wi = wi*wpr + wtemp*wpi + wi; // recurrence.
        }
        mmax = istep;
    }
}
*/

```



```
/* PROGRAM TRUNCATE.CPP
```

```
-----
This program takes a chi(k) data file and truncates it according to
specified k limits. The output file has an extension .TRF and is an
input file for the Fourier transform program FOURIER.CPP.
```

```
*/
```

```
#include <iostream.h>
#include <fstream.h>
#include <iomanip.h>
#include <stdio.h>
#include <sstream.h>
#include <math.h>
#include <stdlib.h>
#include <conio.h>
#include <string.h>
#include <sstream.h>
```

```
int main() {
```

```
clrscr();
```

```
char InputFileName[100], OutputFileName[100];
```

```
cout<<"Please enter your input file name (specify path):  ";
```

```
cin>>setw(sizeof(InputFileName))>>InputFileName;
```

```
ostringstream(OutputFileName,sizeof(OutputFileName))<<InputFileName<<ends;
```

```
int I=0;
```

```
while (OutputFileName[I] && OutputFileName[I]!='.') I++;
```

```
if (OutputFileName[I]=='.') OutputFileName[I]='\0';
```

```
ostringstream(OutputFileName,sizeof(OutputFileName),ios::app)<<".TRF"<<ends;
```

```
cout<<endl<<"Output file is "<<OutputFileName<<endl<<endl;
```

```
ifstream InputFile(InputFileName);
```

```
ofstream OutputFile(OutputFileName);
```

```
if (!InputFile) {
```

```
    cout<<"Error: opening file";
```

```
}
```

```
int Npts;
```

```
InputFile>>Npts;
```

```
float EnergyInc;
```

```
InputFile>>EnergyInc;
```

```
float E0;
```

```
InputFile>>E0;
```

```
double constant;
```

```

InputFile>>constant;

double kmin, kmax;
cout<<endl<<"What is the minimum value of k you wish to save? "<<endl;
cin>>kmin;
cout<<endl<<"What is the maximum value of k you wish to save? "<<endl;
cin>>kmax;

double k[1000], Fit[1000], Chik[1000];
for (int p=0; p<1000; p++) {
    k[p] = 0.0;
    Fit[p] = 0.0;
    Chik[p] = 0.0;
}

double Scrapk, ScrapFit, ScrapChik;
do {
    InputFile>>Scrapk>>ScrapFit>>ScrapChik;
} while (Scrapk<kmin);

int N=0;
do {
    InputFile>>k[N]>>Fit[N]>>Chik[N];
    N++;
} while (k[N-1]<kmax);
Npts = N;

OutputFile<<N<<endl<<EnergyInc<<endl<<E0<<endl<<constant<<endl;
for (int q=0; q<Npts; q++) {
    OutputFile<<k[q]<<"      "<<Fit[q]<<"      "<<Chik[q]<<endl;
}

InputFile.close();
OutputFile.close();

cout<<endl<<"All done!"<<endl;

return 0;
}

```

```
/* PROGRAM SMOOTH.CPP
```

```
-----
This program takes a chi(k) data file as the input and smoothes the
EXELFS data. User specifies how many times to do the smoothing.
Output file has the extension .SM and is ready for inputting in the
Fourier transform program FOURIER.CPP.
```

```
*/
```

```
#include <iostream.h>
#include <fstream.h>
#include <iomanip.h>
#include <stdio.h>
#include <strstream.h>
#include <math.h>
#include <stdlib.h>
#include <conio.h>
#include <string.h>
#include <strstream.h>
```

```
int main() {
```

```
clrscr();
char InputFileName[100], OutputFileName[100];
cout<<"Please enter your input file name (specify path): ";
cin>>setw(sizeof(InputFileName))>>InputFileName;

ostrstream(OutputFileName,sizeof(OutputFileName))<<InputFileName<<ends;
int I=0;
while (OutputFileName[I] && OutputFileName[I]!='.') I++;
if (OutputFileName[I]=='.') OutputFileName[I]='\0';
ostrstream(OutputFileName,sizeof(OutputFileName),ios::app)<<".SM"<<ends;

cout<<endl<<"Output file is "<<OutputFileName<<endl<<endl;
```

```
ifstream InputFile(InputFileName);
ofstream OutputFile(OutputFileName);
if (!InputFile) {
    cout<<"Error: opening file";
}
```

```
int repeat;
cout<<endl<<"How many times would you like to do the smoothing? ";
cin>>repeat;
```

```
int N;
float EnergyInc, E0;
```

```

double constant;
InputFile>>N>>EnergyInc>>E0>>constant;

double k[1000], Fit[1000], Chik[1000];
for (int p=0; p<1000; p++) {
    k[p] = 0.0;
    Fit[p] = 0.0;
    Chik[p] = 0.0;
}

for (int j=1; j<=N; j++) {
    InputFile>>k[j]>>Fit[j]>>Chik[j];
}

int counter=0;
do {
    for (int m=3; m<=N-2; m++) {
        Chik[m] = (-3*Chik[m-2] + 12*Chik[m-1] + 17*Chik[m] + 12*Chik[m+1] - 3*Chik[m+2])/35;
    }
    counter++;
} while (counter<repeat);

OutputFile<<N<<endl<<EnergyInc<<endl<<E0<<endl<<constant<<endl;
for (int q=1; q<=N; q++) {
    OutputFile<<k[q]<<"      "<<Fit[q]<<"      "<<Chik[q]<<endl;
}

InputFile.close();
OutputFile.close();

cout<<endl<<"All done!"<<endl;

return 0;
}

```