HIGH ENERGY HEAVY ION BEAM ENHANCED ADHESION OF GOLD FILMS TO GaAs

Senior thesis by

Scott Paine

California Institute of Technology

Pasadena, California

May 25, 1984

ACKNOWLEDGEMENTS

I would like to thank my senior thesis advisor, Dr. Tom Tombrello, not only for sponsorship of this project, but also for much help and advice given over the last three years.

I would also like to thank Dr. Marcus Mendenhall for suggesting the initial experiments for the project, for help in the lab, and for providing the GaAs materials used. Many thanks are due to Dr. Rogerio Livi, who provided many hours running the accelerator used to irradiate the samples, and who gave very helpful advice concerning many aspects of the project. C. R. Wie also provided much help, particulararily with the scratch test. Finally, I wish to thank Dr. Thad Vreeland and Dr. David Rutledge, who each provided the use of their lab facilities for the preparation and testing of samples.

ABSTRACT

Improvement of the adhesion of gold films to GaAs substrates by irradiation with a beam of high energy heavy ions was studied by Scotch Tape, scrub, and scratch test methods. Simple measurements of the effect of irradiation on the electrical contact properties of the Au/GaAs interface were also made. Substrate materials were taken from four differently doped GaAs wafers, thus providing a selection of substrate electronic properties.

The results indicate dependence of the ion dose threshold for improved adhesion on the bulk electronic properties of the substrate.

TABLE OF CONTENTS

Introduction

The adhesion of thin metal films to a wide variety of substrates can be significantly improved by irradiating the metal/substrate interface with a beam of high energy heavy ions. Work done at Caltech has demonstrated ion beam enhanced adhesion for gold and silver films on metal, semiconductor, and dielectric substrates, using bombarding ions with energies on the order of 1 MeV/amu.[1,2] Recently, similar results have also been reported by investigators at other institutions using similar beam energies.[3] At these energies, the beam suffers negligible energy loss from passing through the metal film, and the beam particles do not stop until they have penetrated many atomic layers of the substrate. Thus the improved adhesion is not caused by the presence of the implanted ions, but is instead related to some mechanism or mechanisms initiated by the passage of the ions through the material near the interface.

Of the various mechanisms that have been proposed, none has been clearly established as the primary mechanism responsible. Most involve energy transfer from the ion beam to the material, for example through electron scattering or through nuclear scattering, resulting in the rearrangement of electronic states or the formation of a mixed layer.

It is possible that the primary mechanism varies depending on the combination of materials involved. For example, in dielectric materials, it has been suggested that the dielectric damage track formation mechanism could cause localized mixing of the film and substrate, effectively "spot welding" the film to the substrate.[4,5]

In metals, the electronic relaxation time is too short for damage tracks to form, so at least in metals some other mechanism must operate to produce the improved adhesion.[6]

One possibility is that the passage of the ion causes electron excitation or ionization, followed by a redistribution of electronic states. The resultant altered configurations could be directly or indirectly responsible for the improved adhesion. Mitchell et al. have observed that low energy electron beam irradiation produces an improvement in the adhesion of gold films to silicon similar to that observed for fast ion beams.[7] The electron energies used were well below the level required to displace nuclei, so the adhesion improvement in this case was evidently due to electronic processes. Such processed could operate in the case of fast ion irradiation as well.

Using semiconductors as substrates, it is possible to change some of the electronic properties through doping without significantly affecting the chemical and mechanical properties. This project is an experimental study of ion beam enhanced adhesion of gold films to gallium arsenide substrates doped with different impurity types and concentrations. The substrates are essentially identical chemically and crystallographically. They differ in electronic properties, notably carrier type and density, mobility, and bulk resistivity.

Because the electrical contact properties of the Au/GaAs interface are relevant to the adhesion properties for reasons that will be given, some rough measurements of the interface I-V characteristics before and after irradiation were made. Enhanced adhesion was qualitatively studied using the Scotch Tape test and the scrub test. Finally, a scratch test method was used to study the adhesion versus ion dose behavior. An attempt to explain the behavior of the different samples may help clarify the fast ion adhesion improvement mechanism.

Sample Preparation

A summary of all samples tested is given in table 1. Substrates for all samples were obtained from the four GaAs wafers described in table 2. They were cleaned by the following procedure:

1. Preclean in detergent and warm tap water.
2. Rinse in warm tap water. (4 times)
3. Rinse in methanol. (2 times)
4. Etch in a solution of 3-5 drops bromine in 100ml methanol. (approx. 10 minutes)
4. Rinse in methanol. (2 times)

The substrates were then glued to glass slides for convenience in handling. No effort was made to prevent surface oxidation of the GaAs, although samples were processed quickly to minimize exposure to airborne contaminants. Gold films were vapor deposited at approximately 5×10^{-6} Torr. The average deposition rate was about 100 Å/minute.

Samples were irradiated on the CIT-ONR tandem Van de Graaff accelerator. The beam current during irradiation ranged from 4 nA to 30 nA. The collimated beam diameter was 2.4mm. To minimize surface hydrocarbon contamination from the vacuum system, the last four samples used for the scratch test were surrounded by an aluminum shield cooled by liquid nitrogen during irradiation. Preliminary scratch testing had indicated that surface contaminants could affect the test results. One sample showed different behavior before and after the gold film had been rinsed in methanol.

After irradiation, these last four samples were cleaned in an oxygen plasma in a Plasmon benchtop plasma etch system running at half the maximum rated RF power for 10 minutes.[8] This system does not provide a calibrated measurement of plasma power density. The oxygen plasma should have been effective in removing organic contaminants. There was some concern that the dissociated oxygen might diffuse through the gold film to the film/substrate interface during cleaning, so a previously Scotch Tape tested sample was cleaned before the scratch test samples. Subsequent testing of this sample showed no reduction in adhesion, indicating that the plasma cleaning was a safe procedure.

The only visible effect of the plasma cleaning was to make the beam spots less discernible. Prior to cleaning, the locations of the higher dose spots on each sample could be found by breathing on the sample. The condensed moisture had a different appearance on these spots than on unirradiated areas. The positions of the visible spots were marked on the edge of each sample. After plasma cleaning, some of the previously visible spots could no longer be seen this way.

Electrical Contact Properties

To facilitate interpretation of the adhesion experiment results, measurements of the electrical properties of the Au/GaAs interface were made on unirradiated and irradiated samples. Very good diode-like behavior would imply the existance of a depletion region near the interface under no bias. Since the experiment depends on the ablity to vary the resistivity of the substrate near the interface, a depletion region would not be desirable.

An additional complication caused by the presence of a depletion region is the possibility of an electrostatic adhesion effect. For an idealized metal film/semiconductor interface, the force on the metal film may be estimated as follows. The electrostatic potential in the depletion region is approximately[9]

$$\varphi = -2\pi N e x^2/\varepsilon,$$

where N is the donor density, ε is the dielectric constant of the semiconductor, and x is distance measured from the bottom of the depletion region. The thickness of the depletion region is

$$x_0 = (\varepsilon|\varphi_0|/2\pi N e)^{\frac{1}{2}},$$

where φ_0 is the semiconductor work function. The electric field near the interface is then

$$E(x_0) = -\frac{\partial\varphi}{\partial x}\bigg|_{x=x_0} = (8\pi N e|\varphi_0|/\varepsilon)^{\frac{1}{2}}.$$

The surface charge density in the metal film is

$$\sigma = N e x_0 = (N e \varepsilon|\varphi_0|/2\pi)^{\frac{1}{2}}.$$

The force per unit area on the film is thus

$$F = \sigma E(x_0) = 2Ne|\varphi_0|$$

For $\varphi_0 e = 1 eV = 1.6x10^{-12}$ erg, and for $N=10^{18}$ cm^{-3}, this gives $F=3x10^6$ $dyn/cm^2=30$ N/cm^2. This simplified analysis suggests that electrostatic forces could have a significant effect on adhesion measurements.

Since any attempt to produce an ohmic back contact for test purposes through heat or pressure might alter or damage the sample being tested, "back to back" measurements of the I-V characteristics of the interface were made using the arrangement shown in figure 1. This arrangement only allows accurate measurement of the reverse breakdown behavior, since the two junctions in series are always under opposite bias. An effort was made to see some of the forward-biased behavior by evaporating a large gold contact onto the substrate, but even the large contact had sufficiently high reverse breakdown voltage to prevent measurement of the forward-biased I-V characteristics of the small contact. In the future, it would be useful to prepare samples with ohmic contacts prior to irradiation.

Reverse I-V curves for the Te, Si, and Zn doped substrates are shown in figure 2. The Cr compensation doped substrate could not be tested because of its very high resistivity. The Te and Si doped substrates show a decrease in reverse breakdown voltage after irradiation accompanied by an apparant increase in contact resistance. Contact to the unirradiated Zn doped substrate was ohmic before irradiation. The only effect of irradiation appears to have been an increase in contact resistance.

An increase in the resistivity of all three substrates could be due to an increase in the density of crystal defects produced by the slowed beam particles. A layer of high resistivity probably forms in the substrate below the beam spot at the nuclear stopping depth, causing an increase in contact resistance. In fact, damage to the crystal structure may occur much closer to the interface. X-ray scattering analysis by Mendenhall has shown that high energy heavy ions can produce lattice damage in GaAs.[10] The mechanism by which this damage occurs is unknown. In the Zn doped p-type sample, substrate resistivity might also be increased by the compensating effect of implanted Cl ions, which should act as electron donors. The most important result from the point of view of these experiments is that the poor reverse breakdown characteristics of the n-type samples indicate the presence of free carriers near the Au/GaAs interface.

Scotch Tape and Scrub Tests

The Scotch Tape test and the scrub test were used in an attempt to determine the approximate dose threshold for the onset of enhanced adhesion.[11] For the Scotch Tape test, a strip of adhesive tape is pressed onto the sample, then quickly peeled off. Unless the film/substrate adhesion exceeds the tape/film adhesion, the film will be pulled off the substrate. The tape test thus provides a threshold adhesion test. In practice, the test has been found to be very repeatable, and only slightly dependent on the rapidity with which the tape is peeled.

The tape test results for the GaAs samples are summarized in table 3. For the most part, the test did not provide much quantitative information. The only result that correlates well with later scratch test results is the threshold of 9×10^{13} ions/cm^2 observed for the first Te doped sample.

One interesting result of the tape test concerns the behavior of the unirradiated film areas. On Zn and Cr doped p-type samples that had been irradiated in some areas, the unirradiated film did not peel at all except for one instance when it peeled partially. However, on completely unirradiated control samples, the film peeled off easily. It may be that irradiation of part of the sample can affect adhesion elsewhere. This could be related to electrostatic effects similar to those described above, but that is by no means clear. In later scratch testing, no similar effect on adhesion of unirradiated film could be observed.

The scrub test was used primarily to verify an improvement in adhesion on samples where the tape test could not remove any film at all. To perform this test, the film is simply rubbed with a cotton Q-tip swab under moderate pressure until film ceases to be removed. In all cases, the unirradiated film was rubbed off, leaving behind well-defined beam spots. The results of the test are summarized in table 4. Although threshold values are given, they should not be taken too seriously, since this test is much less repeatable than the tape test.

Scratch Test

Samples were tested using the scratch test described by Benjamin and Weaver.[12-14] A smooth, loaded spherical tip is drawn across the film. Deformation of the substrate under the tip gives rise to a shear force between the film and substrate. If this force is sufficiently high, the film will be displaced and debonded. Benjamin and Weaver analyzed the forces between film and substrate using an idealized plastic deformation model. In practice, experimental conditions limit the applicability of this analysis. Possible improvements for future experiments are described below.

The tests were performed with a Leitz "Miniload" microhardness tester fitted with a 0.5mm radius chrome plated steel tip. Surface roughness of the tip was specified by the manufacturer as 2 microinches (0.05 micron) maximum. The hardness of the tip was measured by diamond indentation and verified to be greater than that of the GaAs substrates. The load on the tip was selectable using fixed weights ranging from 5g (4.9×10^{-2} N) to 500g (4.9 N). Samples were mounted on a motor driven translation stage. The translation rate was 4 mm/minute.

On each sample, a series of parallel scratches was made under various loads and examined with an optical microscope. Figure 3 shows the results for the Cr compensation doped GaAs substrate over a region irradiated with 4×10^{13} ions/cm^2 of 18 MeV Cl^{4+}. Below 300g, the film is scratched, but not removed from the substrate. This fine scratching is probably caused by small dust particles or irregularities of the scratch tip. Consistent partial stripping of the gold film begins at a 300g load. At 500g, the film is almost completely removed. This beam spot is a particularily good demonstration of the scratch test. Most spots on this sample and the others did not show both the onset of film removal and total film removal within the 5g to 500g range of the microhardness tester. More often, a sample would already show partial removal at 5g, or would show partial removal or only fine scratching at 500g.

Results and Discussion

In unirradiated areas the film was always totally removed at all tip loads on every sample. For loads from 10g to 500g, the scratch width scales with the load. For unknown reasons, the scratch width at 5g was often significantly greater than the scratch width at 10g, raising some doubt as to the reliability of this test arrangement at loads below 10g. Figure 4 shows a series of scratches in the unirradiated area between the two highest-dose spots on the Te doped GaAs sample. The circular boundaries of the beam spots are clearly visible. The residue at the edge of the left beam spot in each scratch line is the gold removed from the unirradiated region as the tip moved from right to left. Buildup of stripped film only begins to occur when the film is being totally removed from the substrate, so it should not cause large errors at tip loads near the film removal threshold.

The loads required to strip the gold film from the substrate are plotted against ion dose for each sample tested in figure 5. The bottom of each bar indicates the load at which partial stripping occurs as indicated in figure 3. The top of each bar indicates the load at which the film was almost completely removed. A bar running beyond the boundary of the plot indicates loads outside the 5g to 500g range.

The Si doped and Te doped n-type samples both exhibited a jump in adhesion at a dose near $5x10^{13}$ ions/cm^2. The two p-type samples also showed less definite jumps at slightly lower doses. Figure 6 illustrates the abrupt increase in adhesion with dose between two adjacent beam spots on the Te doped sample.

The Cr compensation doped sample was the only one to show high adhesion improvement at doses below $5x10^{13}$ ions/cm^2. It was also the only substrate that was a good insulator, meaning that the electronic relaxation time in this substrate is considerably longer than in the others. Electrons scattered by the fast ions will remain inhomogeneously distributed for a relatively longer time, allowing more energy to be transferred to the GaAs lattice through Coulomb forces.

These results suggest that a "slower" or "higher lattice energy" process that can only operate in the insulating substrate may be responsible for the adhesion improvement at low doses. A "fast" electronic process with a higher threshold might then produce the improvement at higher doses. This simple conjecture would not explain why the Zn doped p-type conducting substrate failed to show adhesion improvement comparable to the two n-type samples.

A more definite conclusion that can be drawn from the scratch test data is that the presence of a thin oxide layer is not the sole contributing factor in fast ion improved adhesion on conducting substrates. It has been suggested that the presence of a thin, insulating natural oxide layer is the cause of the enhanced adhesion on conducting substrates.[15] However, the very dissimilar adhesion versus dose behavior of each of the four GaAs substrates tested indicates that this behavior is determined by the bulk properties of the GaAs, and not by surface oxide. All of the samples had the same crystallographic orientation, and they were all prepared together, so they should have had very similar surface oxide.

Improvements

The scratch test described could be extended and refined in a number of ways. One of the difficult problems with this test is correct visual interpretation of the scratch. Measurements of the cross-sectional profile of the scratch with a sensitive profilimeter might provide additional useful information. It would also be valuable to determine the uniformity of the film thickness by surface profilimetry. It is reasonable to expect the scratch test results to improve with film uniformity. If necessary, films could be made thicker than the 650 Å films used for the above tests.

Another problem that came up during testing was the presence of dust particles and removed film residue in the path of the scratch tip. The dust problem could be solved simply by performing the tests in a cleaner environment. The residue problem might be reduced by using smaller tip radii, since the removed film might be more easily pushed aside by a smaller tip.

Conclusions

It has been shown that by controlling the electronic properties of semiconductor substrates through doping, it is possible to observe the effect of these properties on ion beam enhanced adhesion. Based on the behavior of the small number of gold on GaAs samples tested, it appears that the bulk electronic properties of the substrate material have a controlling effect on fast ion enhanced adhesion that is independent of other substrate properties. In particular, it appears that surface oxide alone does not control enhanced adhesion on conducting substrates.

References

1. J. E. Griffith et al., "Ion Beam Enhanced Adhesion in the Electronic Stopping Region," Nuclear Instruments and Methods, 198, 607 (1982).
2. M. Mendenhall, "High Energy Heavy Ion Induced Enhanced Adhesion," Ph.D. Thesis, Caltech, 1983.
3. S. Jacobson, B. Jonsson, and B. Sondqvist, "On the Use of Fast, Heavy Ions for Improving Thin Film Adhesion," unpublished.
4. Griffith, op. cit., p. 609.
5. R. L. Fleisher et al., <u>Nuclear Tracks in Solids</u>, University of California Press, Berkeley, 1975.
6. Mendenhall, op. cit., Sec. 5.2.
7. I. V. Mitchell et al., "Thin Film Adhesion Changes Induced by Electron Irradiation," Applied Physics Letters, 44(2), 15 January 1984.
8. Plasma cleaning of the gold films was suggested by Dr. Nicolet.
9. C. Kittel, <u>Introduction to Solid State Physics</u>, 5th ed., Wiley, NY, 1976.
10. Mendenhall, op. cit., Sec. 6.4.
11. Mendenhall, op. cit., Sec. 3.1.
12. P. Benjamin and C. Weaver, "Measurement of adhesion of thin films," Proceedings of the Royal Society of London, A254:163, 1960.
13. P. Benjamin and C. Weaver, "The adhesion of metals to crystal faces," Proceedings of the Royal Society of London, A274:267, 1963.
14. K. L. Chopra, <u>Thin Film Phenomena</u>, McGraw-Hill, NY, 1969, pp. 314-322.

15. Jacobson et al., op. cit.

16. S. M. Sze, Physics of Semiconductor Devices, 2nd ed., Wiley, NY, 1981, p. 21.

Table 1

Summary of Samples Tested

Sample	Dopant	Film	Beam	Dose Range	Tests
1	Zn	500Å Au	18MeV Cl^{5+}	2.25×10^{13} to	Scotch Tape
*2	Si			7.2×10^{14}	Scrub Test
3	Te				Plasma clean check
4	Cr				
*broken before irradiation					
5	Te	500Å Au	unirradiated		Control samples for
7	Cr				reverse breakdown
9	Si				tests and Scotch Tape
11	Zn				tests
6	Te	500Å Au	18MeV Cl^{4+}	4×10^{13} to	Scotch Tape
8	Cr			2.2×10^{14}	Scrub Test
10	Si		12MeV F^{3+}	1.6×10^{14} to	Reverse breakdown
12	Zn			8.8×10^{14}	Preliminary scratch
					testing
13	Cr	625Å Au	18MeV Cl^{4+}	8.3×10^{11} to	Scratch test
14	Zn			9.7×10^{14}	
15	Si				
16	Te				

Dose is measured in ions/cm^2

Table 2

Substrate Material Characteristics

Dopant	Carrier concentration (cm^{-3})	Mobility (cm^2/v-s)	Resistivity ohm-cm	Cut
Si (n)	3.5×10^{18}	10^{-3}	1350	⟨100⟩
Cr (p)	compensation doped			⟨100⟩+1°
Te (n)	5×10^{17}	2100	3×10^{-3}	⟨100⟩
Zn (p)	7×10^{17}	1000	9.6×10^{-3}	⟨100⟩

Ionization Energies (eV) in GaAs.[16]

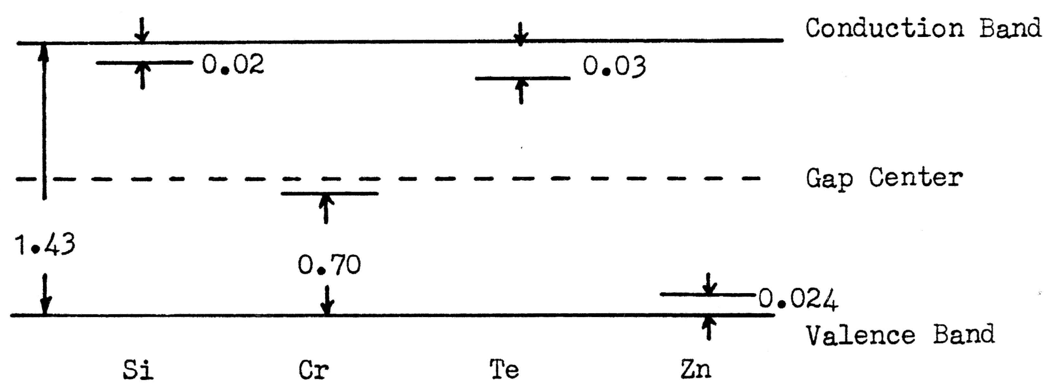


Table 3

Summary of Scotch Tape Test Results

Substrate	Sample	Results
Si doped	9	Unirradiated sample peeled easily
	10	Highest-dose Cl and F beam spots peeled, others did not. Unirradiated film peeled.
Cr doped	4	Partial peel of unirradiated film only.
	7	Unirradiated sample peeled easily.
	8	No peel anywhere, including unirradiated film.
Te doped	3	Threshold at $9\times10^{13}cm^{-2}$ for 18MeV Cl^{5+}.
	5	Unirradiated sample peeled easily.
	6	Partial peel of unirradiated film- no threshold visible.
Zn doped	1	No peel anywhere, including unirradiated film.
	11	Unirradiated sample peeled easily.
	12	No peel anywhere, including unirradiated film.

Table 4

Summary of Scrub Test Results

Substrate	Sample	Results
Cr doped	4	Threshold $\sim 9\times10^{13}$ cm^{-2} 18MeV Cl^{5+}
	8	Only unirradiated film removed.
Te doped	3	Threshold $\sim 1.8\times10^{13}$ cm^{-2} 18MeV Cl^{5+}
	6	Only unirradiated film removed.
Zn doped	1	Threshold $\sim 9\times10^{13}$ cm^{-2} 18MeV Cl^{5+}
	12	Only unirradiated film removed.

Figure Captions

Fig. 1 Electrical test configuration. The film on the unirradiated part of the sample was removed by tape or scrub test. A new large gold contact was then evaporated over half of the GaAs substrate. Fine (30 ga.) wires leading to the curve tracer were brought into light contact with the sample as shown. All of the exposed beam spots on each sample were tested. There was no visible difference in the I-V curves for all of the spots on a given sample.

Fig. 2 Reverse breakdown curves for the Te, Si, and Zn doped samples. Note the different scale for the Zn doped sample.

Fig. 3 Photo showing a series of scratches on Cr compensation doped sample #13 over a region irradiated with 4.0×10^{13} ions/cm^2 of 18 MeV Cl^{4+}. Tip loads are indicated at the right of the photo. Partial stripping of the film begins at a 300g load. Total stripping occurs at 500g.

Fig. 4 Photo showing a series of scratches over the region between the two highest-dose spots on Te doped sample #16. Tip loads are indicated at the right of the photo. Note the accumulation of stripped film left by the tip at the edge of the left beam spot as it moved from right to left.

Fig. 5 Plots of tip loads required to cause film stripping versus ion dose in ions/cm^2. The bottom of each bar indicates the tip load at which partial stripping of the film begins to occur. The top of each bar indicates the tip load at which total stripping occurs.

Fig. 6 Photos illustrating the sharp threshold in adhesion versus ion dose on Te doped sample #16. The photo on the left shows three scratches at the loads indicated over a region irradiated with 4.0×10^{13} ions/cm^2 of 18 MeV Cl^{4+}. The photo on the right shows the same scratches over a region irradiated with 9.2×10^{13} ions/cm^2.

Figure 1

Electrical Test Configuration

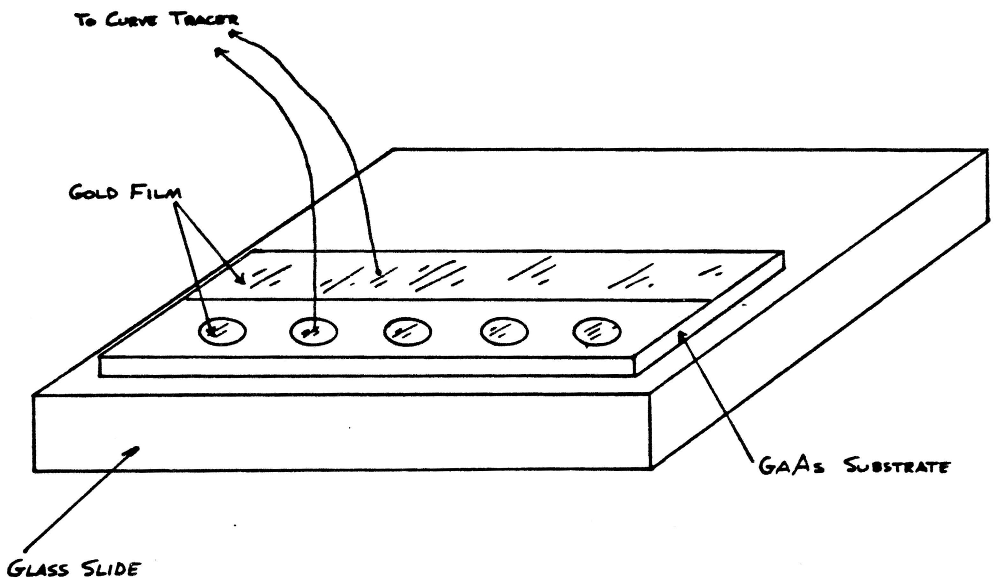
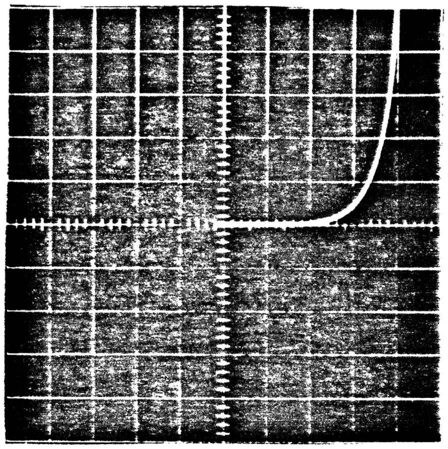


Figure 2

Reverse Breakdown Curves

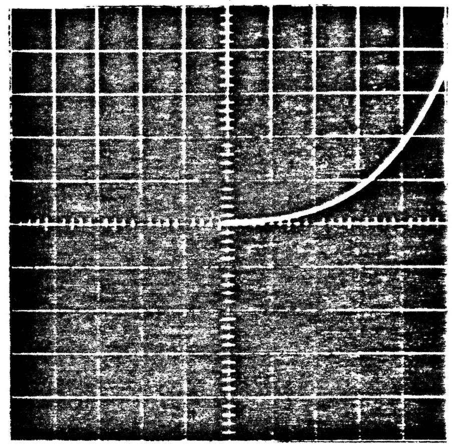
0.5mA/div.



1V/div.

Te doped unirradiated

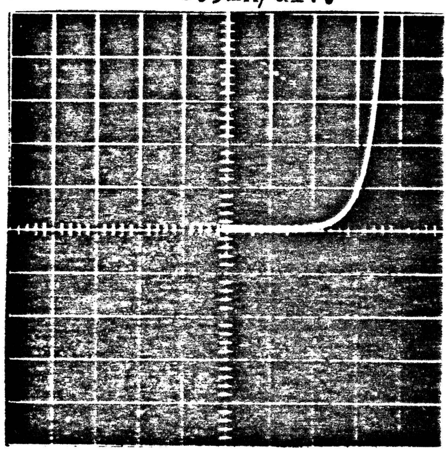
0.5mA/div.



1V/div.

Te doped 10^{14}ions/cm^2

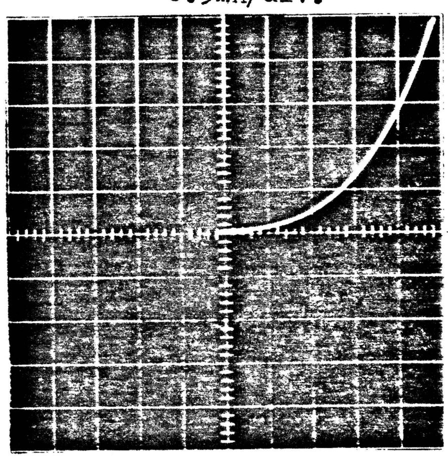
0.5mA/div.



1V/div.

Si doped unirradiated

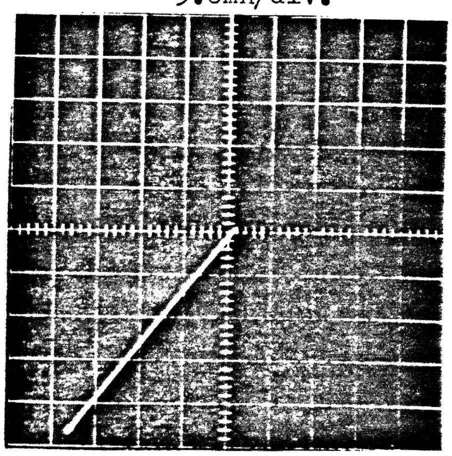
0.5mA/div.



1V/div.

Si doped 10^{14}ions/cm^2

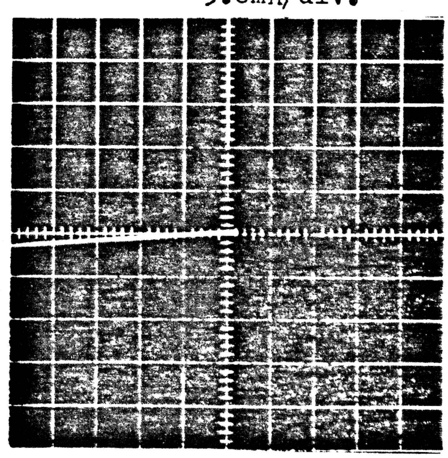
5.0mA/div.



0.01V/div.

Zn doped unirradiated

5.0mA/div.



0.01V/div.

Zn doped 10^{14}ions/cm^2

Figure 3

500g (total stripping)

385g

300g (partial stripping)

200g

125g

100g

Cr doped GaAs substrate

4.0×10^{13} ions/cm^2

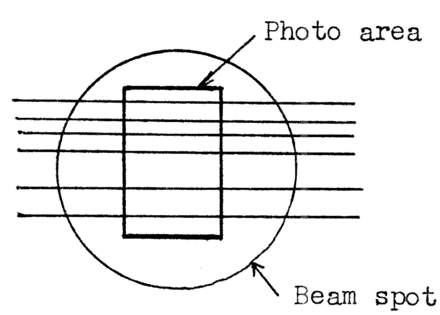
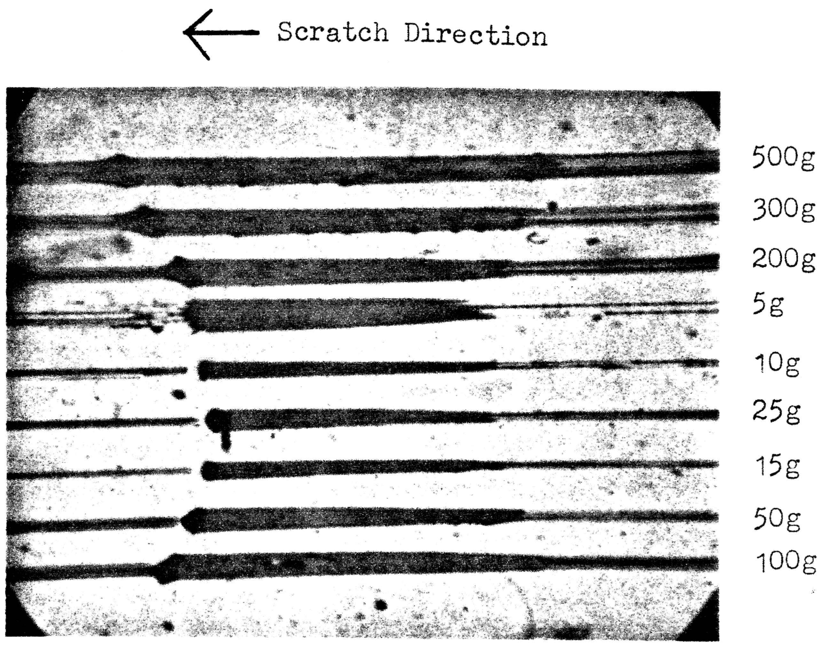


Figure 4



Te doped GaAs substrate

Left side- 9.7×10^{14} ions/cm^2

Center- unirradiated

Right side- 4.4×10^{14} ions/cm^2

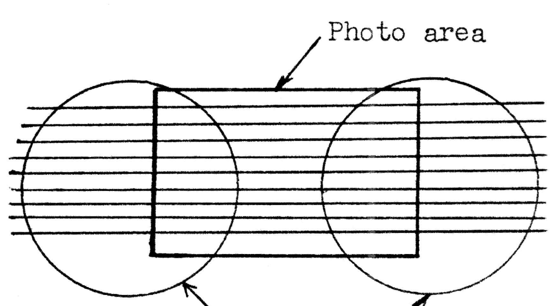
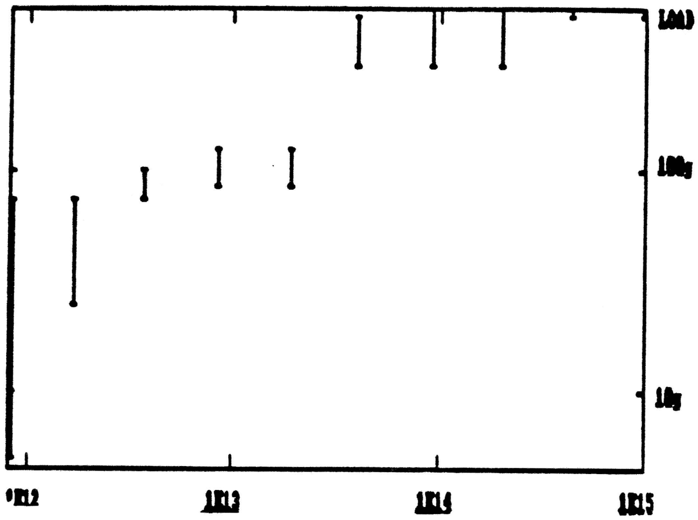
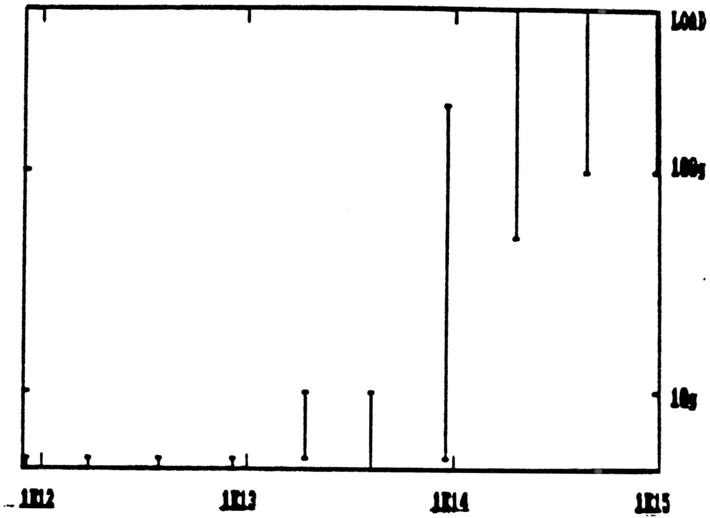


Figure 5

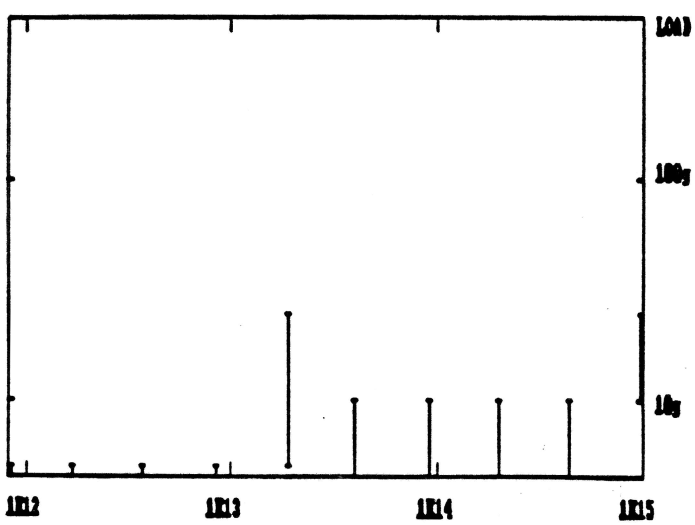
Plots of Scratch Test Data



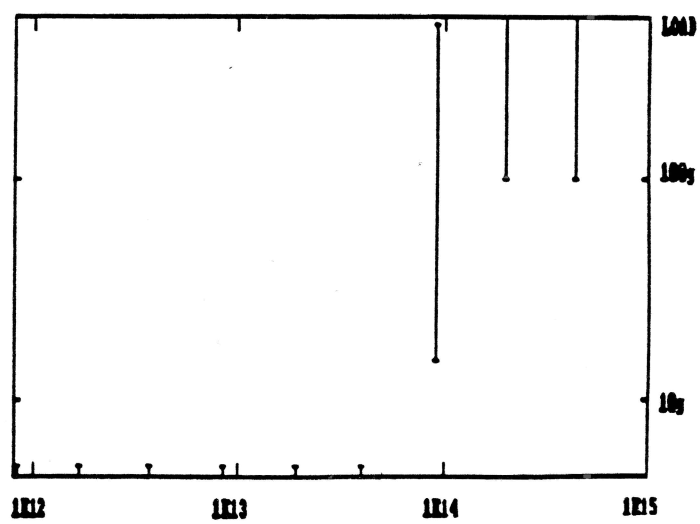
#13 Cr doped p-type
compensation doped



#15 Si doped n-type
1350 ohm cm



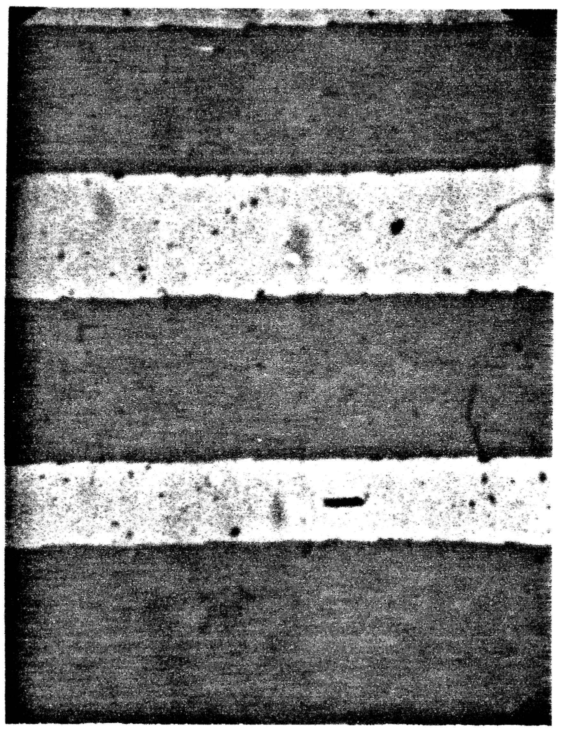
#14 Zn doped p-type
$9.6x10^{-3}$ ohm cm



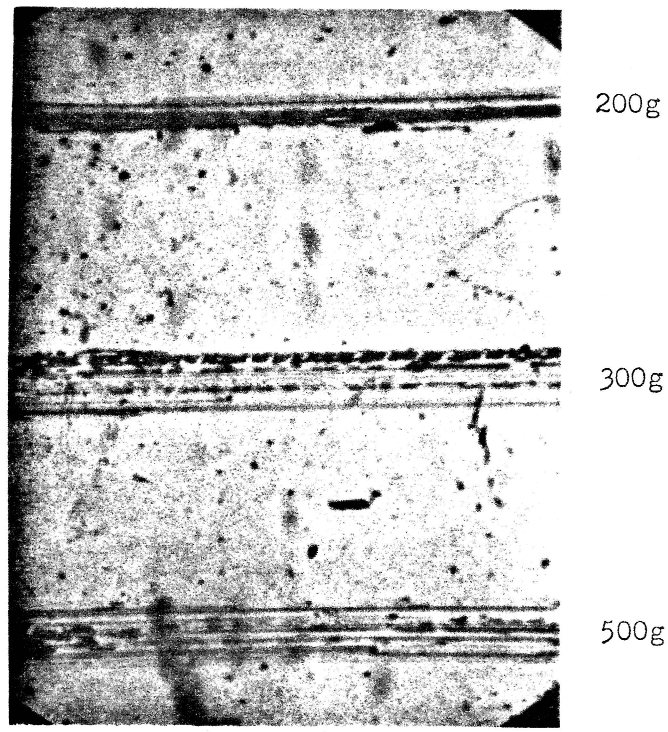
#16 Te doped n-type
$3x10^{-3}$ ohm cm

Horizontal scale is ions/cm^2 of 18 MeV Cl^{4+}.

Figure 6



$4.0x10^{13}$ ions/cm^2



$9.2x10^{13}$ ions/cm^2

Te doped GaAs substrate