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Final Technical Report

"Ohmic Contacts, Irradiation Effects, and Thin Film Growth of GaAs and $Al_{1-x}Ga_xAs$"

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Summary

A study of the effects of interfacial chemistry upon the electrical properties of metal contacts to GaAs and $Al_{1-x}Ga_xAs$ has been performed. The literature, experimental approach, results, and conclusions from several phases of this work are reported in the attached papers.

The initial step in the investigation was to study the effects of chemical cleaning, thermal desorption, and ion sputtering on the surface chemistry of GaAs and $Al_{1-x}Ga_xAs$. The results, reported in J. Vac. Sci. Technol. Al (1983) 776, showed that chemically cleaning with HF to remove oxide and H_2O_2 to remove hydrocarbon and organic contaminants were the best approaches. Thermal desorption of As, µ gallium oxides, and chemisorbed oxygen was quantified. It was shown that hydrocarbons and organics did not thermally desorb. The oxide on $Al_{1-x}Ga_xAs$ decreased due to thermal desorption of gallium oxides, but Al_2O_3 remained on the surface to interfere with contact formation.

Using this information, the effects of sputtering on ohmic contact formation on heavily doped GaAs was studied. It was found (Appl. Phys. Lett., submitted) that Au contacts on Si-doped ($\sim 2 \times 10^{18} cm^{-3}$) GaAs was nearly an ohmic contact when the surface contamination (carbon and oxides) were reduced prior to deposition by chemical cleaning. However, when ion sputtering was used in situ to clean the surface, rectifying contact was produced whose barrier height varied with the energy of the sputtering ion. This was explained using deep-level-transient-spectroscopy data as resulting from ionization of deep level acceptor states. It was shown that annealing after sputtering could restore the contact to nearly an ohmic character.

Continuing to study the influence of sputtering on contacts properties, the use of magnetrons to sputter deposit contacts onto μ GaAs of varying doping densities were studied (Surface and Interface Analysis, submitted). Without reducing the surface concentration of carbon and oxide, the contacts were all found to be rectifying. Furthermore, evidence was found that energetic neutral particles reflected from the magnetron target were striking the GaAs and causing interfacial damage similar to that observed for ion sputtering.

The effects of ion sputtering on interfacial chemistry was also studied in more detail (J. Vac. Sci. Technol. article submitted and summary abstract in press). In this study, Auger and photoelectron spectroscopies were used to measure the extent of As depletion during Ar^+ sputtering of the GaAs surfaces. This As depletion was correlated with a general decrease in the barrier height of the rectifying Au contact deposited in situ. However, non-destructive angle-resolved XPS measurements showed As was depleted at the outer surface more by 1keV than 3keV Ar^+, and thus a combination model of sputter damage and effective work function is required to explain the results. These data are a first attempt to quantify the chemical changes resulting from energetic ion damage and their effect on electrical properties of contacts to GaAs.

In summary, significant progress was achieved through this grant in understanding the significance of interfacial chemistry upon the properties of electrical contacts to compound semiconductors. The data and conclusions have been well documented by reports to archival scientific journals with the proper acknowledgement for NASA support.

Interfacial chemistry of electrical contacts on GaAs and $Al_{0.3}Ga_{0.7}As$

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Thermal restructuring of oxides of GaAs and $Al_{0.3}Ga_{0.7}As$ substrates has been studied using Auger electron spectroscopy and both neutral and secondary ion mass spectrometry. The oxide underwent restructuring at $\gtrsim 250$ °C while gallium oxides desorbed at temperatures depending upon the type of oxide. Reoxidation at low oxygen pressures resulted in surface oxygen species different from those in native oxides. These species desorbed at ~ 520 °C while native oxides desorbed at 600 °C. Carbon-containing contaminants did not desorb. The implications of these results for electrical contacts are discussed.

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I. INTRODUCTION

The properties of metal contacts to GaAs and $Al_xGa_{1-x}As$ are currently the subject of investigation. Typical semiconductor processing includes a chemical etch to remove the bulk of the specimen's native oxide. These processes still leave surface chemical compounds (oxides, hydroxides, etc.) which becomes incorporated in the contact as an interfacial layer. Garner *et al.*[1] studied the electrical significance of such residues. The electrical character of the resulting contact varied as the arsenic content of the interfacial oxide layer increased. In an attempt to remove the layer completely, Sakaki *et al.*[2] used vacuum thermal annealing before contact deposition. They clearly demonstrated that such an annealing process significantly affected the Schottky barrier height of the contacts. Electron diffraction data were used to support the concept of oxide removal but chemical analysis of the surface was not performed.

In this publication we present data indicating the chemical changes in the oxides of GaAs and $Al_{0.3}Ga_{0.7}As$ induced by vacuum thermal annealing. The initial surface condition of the specimens is typical of that developed during contact fabrication. Thus we consider the desorption of native oxides and compare this behavior with oxides regrown *in situ* at low oxygen pressure. Our data are compared with previous work reported in the literature[3-5] for those cases where comparisons are valid. Chemical changes in the oxide before the major desorption process and differences between native and *in situ* oxide desorption are reported. For both GaAs and $Al_{0.3}Ga_{0.7}As$ the implications of our research on the electrical character of contacts are considered.

II. EXPERIMENTAL

The analysis was performed in a Perkin–Elmer ultrahigh vacuum chamber. A base pressure of 2×10^{-10} Torr was achieved after baking using titanium sublimation, sorption, and ion pumps. The Auger data were taken using a Physical Electronics model 545 scanning system with a single pass cylindrical mirror analyzer. Desorbed ions and neutrals were analyzed using a modified UTI quadrupole mass spectrometer (model 300C) controlled by electronics for a 3M Company model 310C secondary ion mass spectrometer.

The GaAs specimen was held in a tantalum envelope which was spot welded to 0.025 cm diam tungsten wires. The wires were Joule heated, causing GaAs to be uniformly heated to $T \lesssim 700$ °C. The specimens were step heated with temperature increments of ~ 50 °C. Each setting was held for ~ 3 min. This corresponds to an equivalent temperature ramp of ~ 20 °C/min. On occasions longer durations were allowed at some settings with a consequent slow rate of temperature rise. Temperature was measured with a W-3% Re, W-26% Re thermocouple spot welded to the tantalum envelope. Good thermal contact between the substrate and the Ta was normally achieved as verified by comparing temperatures for thermal desporption of gallium oxide with and without indium solder between the Ta and GaAs. The desorption temperature with and without solder were within 20 °C of one another.

The specimen chamber was backfilled with oxygen by using an auxiliary chamber equipped with a thermocouple gauge. The ratio of volumes between the main and auxiliary chambers was measured to be 100:1. This system allowed the specimen to be exposed to unexcited oxygen for durations sufficient to provide significant oxygen coverages ([illegible] mTorr for several to hundreds of minutes). After exposing the GaAs, the system was always rough pumped then ion pumped to residual vacuums of $\sim 1\times10^{-7}$ Torr before Auger analysis. This avoided problems with "activated oxygen" causing rapid reoxidation. The substrates were boat growth *n*-type GaAs (100) doped with 3×10^{17} cm^{-3} Si. $Al_{0.3}Ga_{0.7}As$ specimens were prepared by molecular beam epitaxy at a doping density of 2×10^{18} cm^{-3}. Both sets of specimens had been exposed to ambient conditions for several months before chemical processing. Substrates $\sim 0.5\times1\times0.1$ cm were degreased and etched on 0.1% H_2O_2 before being placed in the vacuum system. Depth profiles were performed using 3 keV Ar^+ sputtering. The main chamber was backfilled to a pressure of 5×10^{-5} Torr and the ion incidence angle was ~ 60° from the sample normal.

III. RESULTS

A. GaAs

The thermal desorption of native oxide is shown in
The major desorption process can be seen to commence

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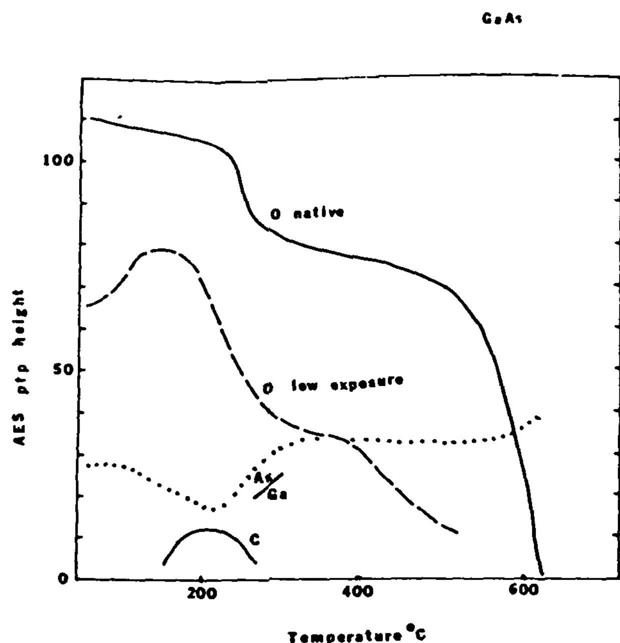

FIG. 1. AES and QMA data for thermal restructuring of GaAs. Both native oxide and low oxygen exposure are shown.

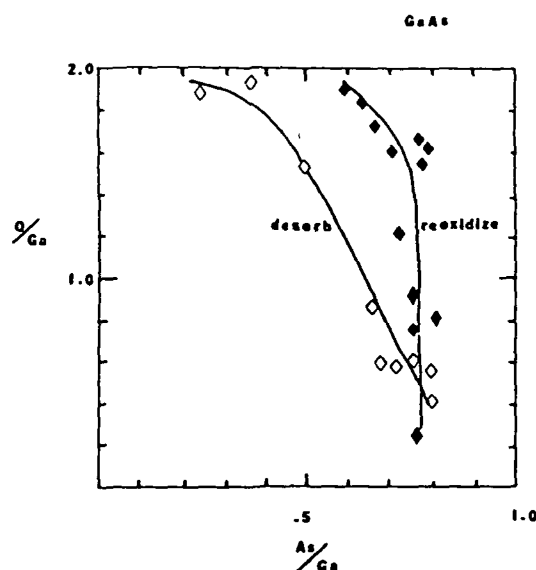

FIG. 2. AES data of relationship between O/Ga ratio and As/Ga ratio for GaAs. Indicates different patterns of behavior for desorption of native oxide and reoxidation.

~540 °C but the oxygen Auger signal did not fall to the detection limit until the specimen had been heated to 625 °C. A significant decrease in the oxygen signal (25%–35%) is noted at ~250 °C. This is coincident with a change in the As/Ga Auger peak ratio. There is a temporary increase in the carbon Auger signal in this temperature range. When carbon was high on the surface at room temperature, it did not desorb even at temperatures up to ~700 °C.

A complex pattern of neutral and ion desorption can be associated with annealing in the temperature range of 250–650 °C. The initial decrease in the oxygen Auger signal is accompanied by desorption of As and As_2 ($m/e = 75,150$). At about 350 °C Ga^+ and Ga (69 and 71) and GaO (85 and 87) become increasingly evident. Between 525 and 625 °C the desorbed spectrum is comprised of As, As_2, Ga^+, and Ga_2O (152, 154, and 156). Above 600 °C Ga^+ and As^+ desorption increases significantly. Sputter-cleaned, air-reoxidized surfaces showed similar behavior.

Figure 1 also shows the oxygen Auger signal for the desorption from a specimen exposed (typically 1×10^7L) to a low pressure (1×10^{-3} Torr) of unexcited oxygen (after heat cleaning). The thermal desorption from the reoxidized surface was distinct from that of the native oxide. As before the initial decrease in oxygen Auger signal was at ~250 °C but the final fall to the detection limit of our system occurred at temperatures of ~520 °C.

The differences between the behavior of the native oxide and the low exposure reoxidized surfaces were studied further. Figure 2 presents Auger peak ratio plots of O/Ga vs As/Ga. Data relating to the desorption of a native oxide is contrasted with the pattern for subsequent reoxidation. The two processes obviously do not cause the same ratios to be observed.

B. $Al_{0.3}Ga_{0.7}As$

The changes in surface composition with thermal processing of an $Al_{0.3}Ga_{0.7}As$ sample with a native oxide layer are shown in Fig. 3. The O Auger signal decreased at ~625 °C, but did not decrease to the detection limits as observed with GaAs. At ~300 °C some surface restructuring appears to occur as evidenced by increased O and C Auger signals, but the effect isn't as dramatic as for GaAs. The Auger peaks

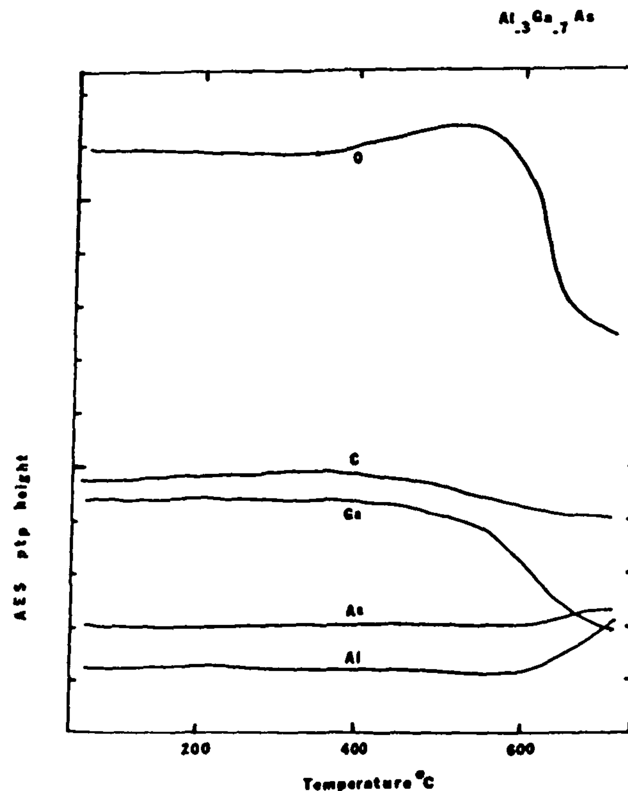

FIG. 3. AES data indicating the thermal restructuring of $Al_{0.3}Ga_{0.7}As$.

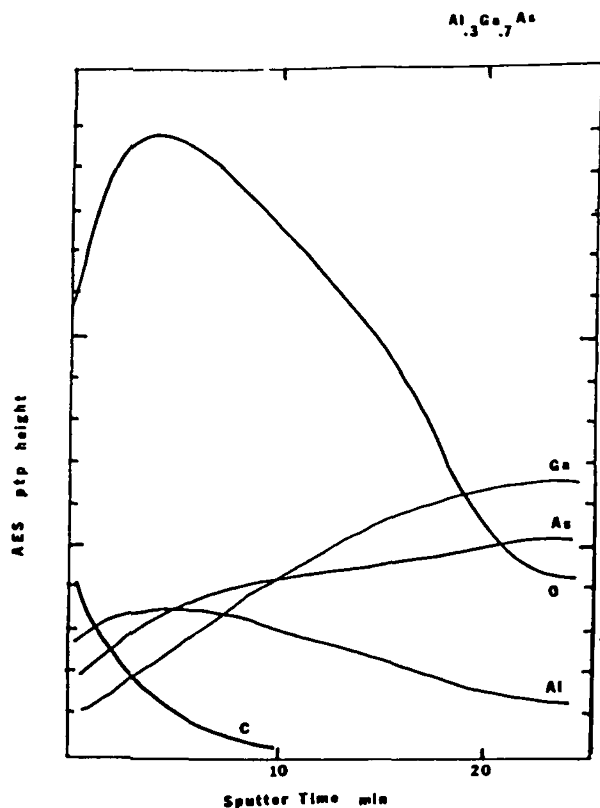

FIG. 4. AES sputter profile of restructured of $Al_{0.3}Ga_{0.7}As$.

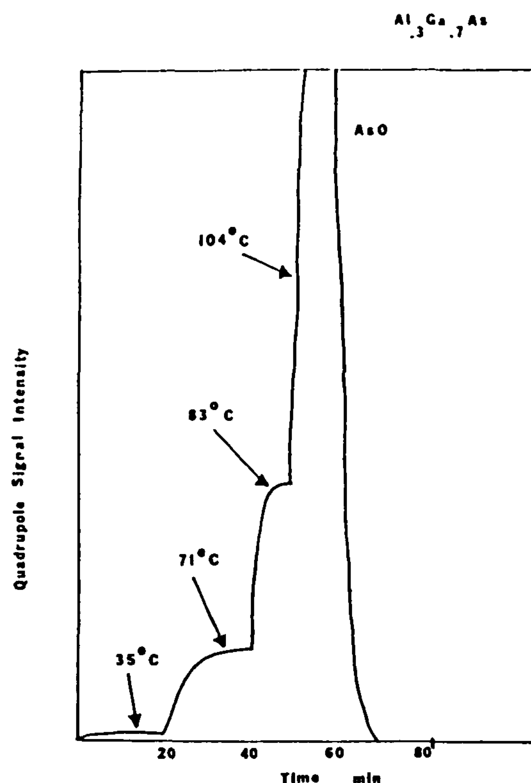

FIG. 5. Quadrupole mass analysis data indicating low temperature desorption of AsO.

after heating to 650 °C show that the surface is rich in aluminum and oxygen. This is substantiated by the sputter depth profile (Fig. 4) which shows that both Al and O are enriched at the surface. Both Ga and As are depleted relative to the bulk, but Ga is more depleted than As.

Analysis of desorbed neutral species showed a significant low temperature desorption of arsenic oxides (Fig. 5). The main constituents were AsO (91) and As_3O_4 (288). As shown, the sample was step heated to temperatures up to 104 °C and desorption measured as a function of time at these temperatures. At 104 °C, the mass spectrometer signal for AsO saturated between 50 and 60 min, but decreased to a low value at $\gtrsim 70$ min, apparently due to depletion of this surface species. The behavior for As_3O_4 vs T and time was the same as for AsO. However, minor amounts of species other than AsO and As_3O_4 were observed at these low temperatures, these included As, As_2O, AsO_2, and AsO_3. At higher temperatures (~ 600 °C), desorption of As (75) and Ga_3O (223) was observed. At lower temperatures, secondary ion species were also observed. For example, at ~ 425 °C GaO^+ and GaO_4^+ were detected, while Ga^+ and As_2^+ were detected at $\gtrsim 600$ °C.

Reoxidation of the $Al_{0.3}Ga_{0.7}As$ after Ar^+ sputter cleaning was measured as a function of time in 100 mTorr oxygen at room temperature. Auger data during thermal processing followed the same pattern as for native oxide except that there was no evidence of the low temperature evolution of arsenic oxide. After thermal processing the specimen was held at 670 °C for ~ 60 min. The Auger data from the surface were constant. After ~ 20 min a significant desorption of As was noted.

IV. DISCUSSION

A. Thermal processing

The temperatures at which chemical change took place in the oxide are an important aspect of this work. Thus, the accuracy of our temperature measurement was checked with specimens which were thermally coupled to the heater with indium solder. This showed our temperatures to be accurate to $\pm$ 10 °C. Further evidence that the measurement was accurate is apparent from the temperature at which elemental Ga^+ and As^+ desorbed from the GaAs substrate. Our data indicated a temperature of > 600 °C which compares with a figure of > 580 °C reported by Arthur.[3]

Data in Fig. 1 indicate that the desorption of native oxides is distinct from the desorption of oxides produced by low pressure, unexcited oxygen. The oxygen Auger signal fell to the limit of detection at ~ 520 °C for surfaces resulting from low oxygen exposures. This compares with a value of 527 °C reported by Arthur.[3] However, some differences still exist. Arthur[3] measured desorption of gallium oxide species (primarily Ga_2O) to determine when thermal desorption of the oxide was occurring. He did not report data directly indicating the surface composition, such as the Auger data in the present study. Our data did show though that Ga_2O desorption correlated well with the major oxide removal near 520 °C for low exposure oxide, and 600 °C for native oxide. Thus we expect our data to be comparable. However, Arthur's reported temperature of 527 °C results from a maximum desorption rate with a linear temperature ramp of ~ 300 °C/min. The temperature in our experiment which corresponds to that reported by Arthur[3] is where the derivative of oxygen Auger peak height versus temperature is a maximum. The

would occur near 470 °C and 590 °C for the low exposure and native oxide data shown in Fig. 1. Thus, neither comparable temperature agrees with Arthur's data. We still believe Arthur's data should be compared to our data for low exposure oxide because (1) Arthur's data were taken from oxide regrown *in situ* using activated[1] oxygen, and (2) our heating rates were lower and procedures were different from Arthur's and would result in the observation of a maximum desorption rate at a lower temperature.

Although there is reasonable agreement between Arthur's data and our data for regrown oxide, we suspect that there may be some differences between the oxide layers studied in the two experiments. Our use of unexcited oxygen at higher exposures might well produce a surface with a higher component of chemisorbed oxygen. This is in part supported by data in Fig. 2 which provides further evidence that there is a difference between native oxide and the oxides developed by low exposure reoxidation. The pattern of reoxidation has a stable As/Ga Auger peak ratio until the O/Ga Auger peak ratio is quite high. This is consistent with a chemisorbed oxygen layer as reported by Ranke.[5] The native oxide has a much lower As/Ga Auger peak ratio. This can be ascribed to the analysis of a layer containing a high proportion of gallium oxides.

The desorption of the native oxide is seen to progress in several stages. The initial decrease in the oxygen Auger signal is coincident with a rise in the carbon signal and desorption of arsenic. This may be associated with a restructuring of the oxide resulting in a surface suitable for carbon adsorption (via CO or CO_2). The desorption of the oxide begins at 350 °C with release of various species including GaO. The major fall in the oxygen signal does not occur until 540 °C with the desorption of Ga_2O. The process is not completed until 625 °C. This compares with Ranke's estimate of 597 °C for cleaning sufaces subjected to a "saturation exposure."[5] Bachrach reports that thermal cleaning process can require up to 650 °C for complete removal of oxide layers.[4]

The pattern of oxide desorption is significant since arsenic components are initially desorbed. The arsenic components of residual oxides produced by chemical etching has been determined to be a significant factor for electrical behavior.[1] A change of the abundance of this component by thermal annealing suggests consequences for the electrical character of the contact layer (even without complete removal of the oxide). This is the subject of the next section.

The data for $Al_{0.3}Ga_{0.7}As$ indicate (by desorbed species) a rearrangement at 104 °C. However, the Auger electron data are not sufficiently sensitive to show this restructuring. As with GaAs, gallium oxide is detected during the major desorption event at ~625 °C.

While $Al_{0.3}Ga_{0.7}As$ shows desorption of arsenic oxides at low temperature and gallium oxides at high temperatures, a surface layer rich in aluminum oxide (presumably Al_2O_3) certainly exists at the surface after thermal processing. The morphology of this surface layer is uncertain, and it is not known, for example, whether the aluminum oxide is continuous or "patchy." There was a 20 min delay before As was observed to desorb from the surface at ~650 °C. This suggests that the Al_2O_3 is continuous since a delay would be expected for diffusion of As through the layer. However, more data is required on this subject.

V. IMPLICATIONS FOR CONTACT FABRICATION PROCESSES

The use of thermal processing to desorb native oxides from GaAs is not new. Nevertheless, it is significant that the desorption process follows several stages. Processing at lower temperatures results in the evolution of some arsenic components while gallium oxides desorb at higher temperatures. Thus, it is possible to create oxides with different compositions. This is significant because Sakaki *et al.*[2] used thermal processing to change the Schottky barrier height of Al contacts on GaAs diodes. They showed that the barrier height could be reduced on specimens processed at temperatures in the range 550–580 °C (0.83–0.76 eV). These values approached but did not reach the height for an MBE-processed specimen (0.67 eV). Electron diffraction was used to postulate that the oxide layer was being removed by thermal processing. A temperture of 580 °C was considered sufficient to completely remove the native oxide. Nevertheless, obvious differences remained between the electron diffraction patterns and barrier heights of the MBE-processed specimen and that thermally desorbed at 580 °C. The present data indicate that slightly higher temperatures are required to remove the oxide completely. There is therefore, strong evidence to suggest that the process of desorption was not fully achieved. Nevertheless, it is clear that thermal processing significantly modified the electrical properties of the diodes. Such effects may result simply from the reduction in oxide thickness. This concept is supported by the work of Pruniaux and Adams[6] who found a linear relationship between Schottky barrier height and oxide thickness for the gold contacts on GaAs where the native oxide was thickened due to heating in air.

Along these same lines, Garner *et al.*[1] studied the electrical character of oxides on GaAs and $Al_{1-x}Ga_xAs$ resulting from different etch processes. Their data indicated that different etch processes produced oxides with different compositions. In particular, the arsenic oxide component was a dominant factor influencing electrical characteristics of the contacts. From the present study it is evident that thermal processing between 350 and 550° C could specifically influence the arsenic component of the oxide layer. Thus, it is possible that thermal processing in this temperature range can produce oxides of specific composition and electrical character without involving changes due to reduction of oxide thickness. Indeed, the work of Sakaki *et al.*[5] does indicate some variation in Schottky barrier height in this temperature range. Furthermore, the lack of arsenic oxide on samples reoxidized *in situ* suggest that better diodes may result from samples first cleaned and then reoxidized in the vacuum system. Investigation of these facts plus characterization of the properties of clean interfaces are currently being conducted.

The thermal processing of oxides on $Al_{0.3}Ga_{0.7}As$ was also seen to have several stages and to exhibit desorption of arsenic oxides at low temperatures. Thus, we might expect modification of the contact properties. Of perhaps more sig-

nificance is the near-surface thermal redistribution for $Al_{1-x}Ga_xAs$ resulting in a surface rich in Al and O. For photovoltaic application, the main use of $Al_{1-x}Ga_xAs$ surface layers is the reduction of surface recombination by the graded band gap associated with the ternary material. The band structure of such a thermally modified surface layer may well affect the ability to reduce this recombination.

The observation that thermal desorption of carbon contaminants was very difficult suggests that it is critical to remove these species by the chemical processing prior to contact deposition. The effects of these carbon-containing contaminants upon electrical properties are also being studied.

VI. SUMMARY

The thermal processing of oxidized $Al_{0.3}Ga_{0.7}As$ has been studied using Auger electron spectroscopy and both neutral and secondary ion mass spectrometry. Oxides were thermally desorbed from both materials in at least two stages. At lower temperatures, arsenic components desorbed, while at temperatures near 600 °C, gallium oxides were desorbed. An aluminum oxide layer remained on the $Al_{0.3}Ga_{0.7}As$ surface following heating. Reoxidation in the ultrahigh vacuum system produced an oxide layer with a thermal desorption behavior different from the native oxide. When carbon contaminants were concentrated on the initial surface, they could not be thermally desorbed from the surface at temperatures up to 700 °C. The implications of these results for electrical contact properties were discussed.

ACKNOWLEDGMENTS

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Ohmic versus Rectifying Contacts of Au to n-GaAs by Ion Sputtering

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Introduction

The effects of ion sputtering on Au Schottky contacts to n-GaAs ($\leq 2 \times 10^{17}$ cm^{-3} Si) has recently been studied.[1,2] It was found, as previously reported,[3] that charge carrier transport accross a Au/low doping density n-GaAs contact was controlled by thermionic emission when the interfacial native oxide was removed prior to Au deposition. When a thick (∿30Å) native oxide was present at the interface, oxide defect states were postulated to cause an interfacial charge and result in transport by tunneling. Sputtering caused the oxide layer to be removed, but the surface layer was damaged creating shallow donor defects. The density of these defects was sufficient to also create a surface charge which again modified the barrier (lowered the height) and probably resulted in field assisted thermionic transport.[3] The donor-like damage layer was correlated with Auger and photoelectron measurement of sputter depletion of As ("preferential sputtering") at the surface.[1] It was concluded that As vacancies caused the donor-like damage layer and resulting lower barrier height. In this short note, data showing an opposite result from argon ion sputtering of heavily doped n-GaAs will be reported.

In contrast to Schottky behavior between Au contacts and n-GaAs doped to $<2 \times 10^{17}$ cm^{-3}, Au contacts to heavily doped n-GaAs ($>3 \times 10^{18}$ cm^{-3}) may exhibit nearly ohmic behavior. This is demonstrated in Figure 1 where I-V data are shown for a 1000Å thick Au dot (o.5mm diameter, 2mm spacing on dot center) deposited through a shadow mask in an ultra-high vacuum system.[1] Three interfacial conditions are shown--surface chemically cleaned with 50% H_2O--50% HF prior to Au deposition, surface chemically cleaned then exposed to laboratory air for at least three days to form a native oxide at the interface, and surface sputtered to remove the

native oxide and carbon interfacial contaminants.[1] Argon ion sputtering was performed as described in reference 1. The I-V characteristics are shown in Table 1; the chemically cleaned sample exhibited nearly ohmic behavior while the native oxide and sputtered samples exhibited rectifying behavior with barrier heights ranging from 0.74 to 0.55 eV. The largest barrier is with native oxide at the interface, while the lowest barrier is for the lowest energy argon ion (1keV). When native oxide is present, the barrier height is largely controlled by oxide defect states.[4] Chemical cleaning can produce a minimum of interfacial oxide because re-oxidation of GaAs at atmospheric pressures, is dependent on time but is not linearly dependent upon oxygen pressure.[5,6]

Degradation of ohmic contacts on GaAs by radiation damage has been reported previously by Blundell, et al.[7] They showed that implantation of 0.46 to 1.4 MeV protons or alpha particles would change ohmic Ag/Sn contacts to rectifying contacts with barrier heights of 0.48 to 0.68eV. It has now been demonstrated that similar effects will occur for much less energetic particles when the damage occurs prior to deposition of the contact. In fact, these effects will be expected to be observed due to damage during dry processing (reactive ion etching) of GaAs.

Blundell, et al.[7] did not investigate why radiation damage caused the change in electrical contact behavior, but this has been studied in more detail in the present investigation. Our data show that both the shallow donor defects and deeper level defects are created by sputtering. For low doping density substrates, the shallow donor level was dominant. However, the deeper acceptor levels appear to be more important in the present instance. DLTS data, summarized in Table 2, showed deep levels at 0.31 and 0.60 eV below the bottom of the conduction band. The level at 0.31 eV has previously been assigned to Ga vacancies,[8] while

the origin of the 0.60 eV level is unknown. The Ga vacancy has been reported to have an acceptor character associated with it.[8]

Since sputtering caused heavily doped GaAs to develop a barrier, contrary to lightly doped GaAs where sputtering lowered the barrier, the shallow donor-like defects important in the latter instance aren't so important for the junction to GaAs doped to >3 x $10^{18}cm^{-3}$. The difference probably results from the level of the Fermi energy in light versus heavily doped GaAs. For example, calculations show that at 3 x $10^{18}cm^{-3}$ of Si in GaAs, the Fermi energy is only 0.05 eV below the conduction band. Even though the energy of the shallow donors couldn't be measured in the present study, it is postulated that they lie sufficiently below the Fermi level such that little ionization occurs. Under these circumstances, the 0.31 eV and 0.60eV acceptor levels will be populated resulting in an interface charge which would create the observed barrier. Note that this postulate is consistent with electrical and DLTS data in Tables 1 and 2, respectively, which show that both the barrier height and the density of the deep level defects increased as the ion energy increased. Blundell, et al[7] point out that damage near the contact may influence carrier transport by modifying both tunneling currents and recombination rates near the junction.

The effects of annealing the GaAs to 400°C for 20 min. in the ultra-high vacuum (<2 x 10^{-9} Torr) after sputtering was studied. As reported previously,[1] this time and temperature are sufficient to restore the sputtered surface to stoichiometric GaAs. The data shown in Fig. 1 establishes that this anneal restored the contact behavior to that of nearly ohmic. No barrier could be calculated from the I-V data.

In summary, ion sputtering of GaAs doped to >3 x $10^{18}cm^{-3}$ may be used to change ohmic contact to rectifying contacts. The barrier

height of the contact can be changed by changing the ion energy. The behavior results from sputter-creation of deep level acceptor states at the GaAs surface.

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Table 1 Schottky barrier height, ϕ_{Bn}, ideality factor, n, and reverse bias current at 300mV for heavily doped GaAs.

Interface Condition		ϕ_{Bn}(eV)	n	I_r(A)
Chemical Etched		near ohmic contact		
1keV	sputtered	0.55	4.82	1×10^{-4}
3 keV	sputtered	0.57	1.75	5.5×10^{-5}
5 keV	sputtered	0.59	3.29	3.0×10^{-5}
Native oxide		0.74	3.57	5.5×10^{-8}
After annealing		near ohmic contact		

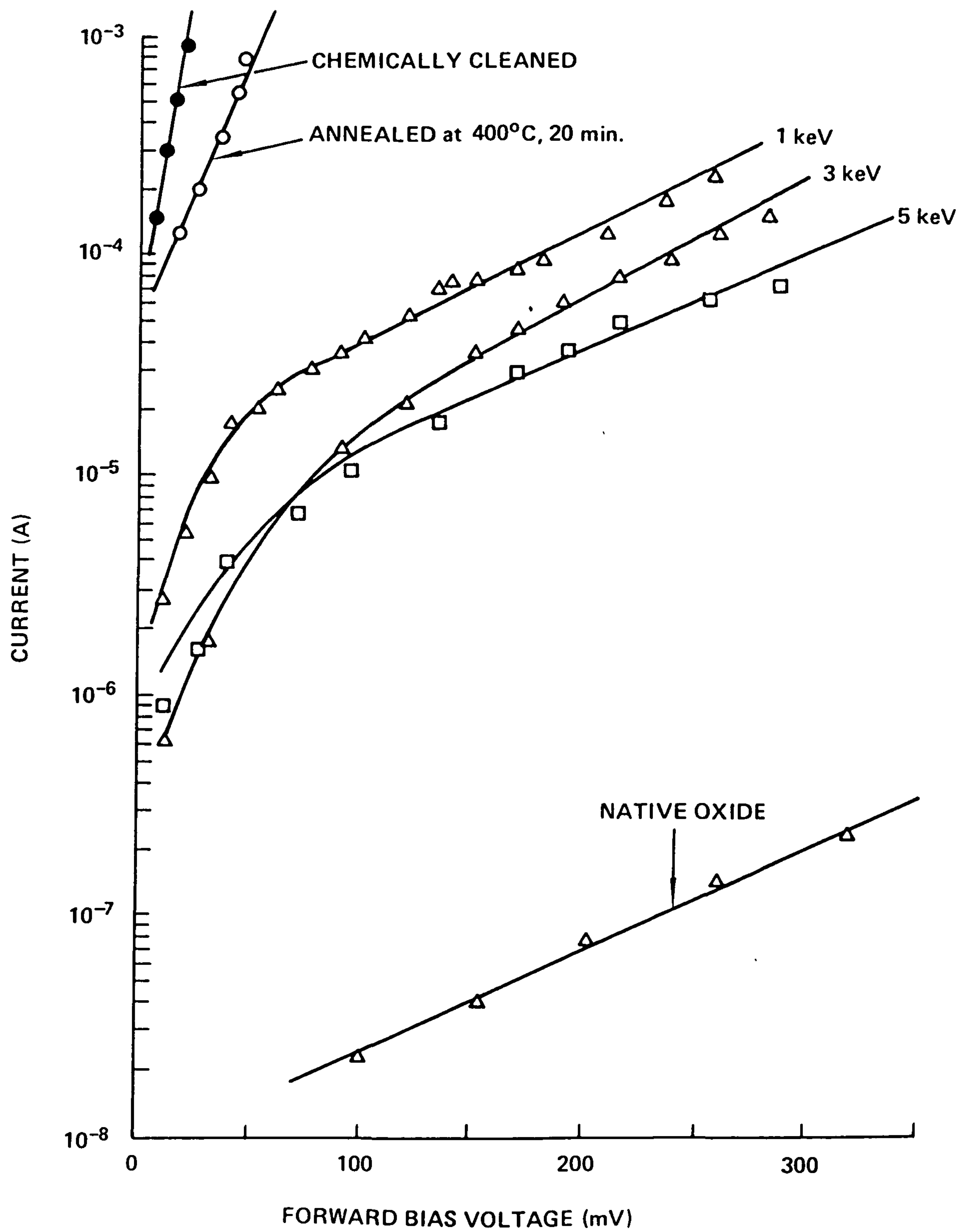
Table 2 Carrier density, N_D, and defect density at 0.31 or 0.6eV below the conduction band as calculated from DLTS data.

E_{ion}	N_D (cm^{-3})	E_1 = 0.31 ev (cm^{-3})	E_2 = 0.60 ev (cm^{-3})	E_3 = 0.91 ev (cm^{-3})
1keV*	5.2×10^{16}	4.6×10^{15}	-----	8.4×10^{15}
3keV	4.3×10^{17}	6.5×10^{15}	2.4×10^{15}	-----
5keV	1.2×10^{17}	8.1×10^{15}	7.3×10^{15}	-----

*The specimen was not cleaned completely by sputtering. The 0.91eV state is believed to result from contamination by oxygen at the contact interface.

Figure Captions

Fig. 1 Current versus voltage for gold contacts on heavily doped GaAs. Prior to deposition of the gold contact, the GaAs surface either had a native oxide film, was chemically cleaned, was sputter cleaned, or was sputter cleaned and vacuum annealed (400°C, 20 min.).



CHEMICALLY CLEANED
ANNEALED at 400°C, 20 min.
1 keV
3 keV
5 keV
NATIVE OXIDE
CURRENT (A)
FORWARD BIAS VOLTAGE (mV)
10^-3
10^-4
10^-5
10^-6
10^-7
10^-8
0
100
200
300

MAGNETRON SPUTTERED GOLD CONTACTS ON n-GaAs

by

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Introduction

DC planar magnetron sputtering[1] has been used to deposit gold Schottky barrier electrical contacts on n-type GaAs. The electrical character of the contact was determined from current-voltage (I-V) and electron-beam-induced voltage (EBIV) data.[2] These data showed that the Schottky barrier height of magnetron sputter-deposited contacts was lower than for vapor deposited contacts. The barrier height was a function of the deposition rate for electrically isolated substrates, was dependent upon the surface treatment prior to contact deposition, and was dependent upon doping density and post-deposition heat treatment. These effects are discussed in terms of particle irradiation of the surface during contact deposition.

Experimental

Specimens of n-type GaAs were selected from wafers with Te doping concentrations of $1x10^{18}$ and $3x10^{17}$ cm^{-3}. These were degreased in trichloroethylene vapor with subsequent immersion in acetone, water, and methanol baths. Dry nitrogen was used to blow-dry the samples. They were then chemically etched in a process consisting of a 40 second treatment in a 6:1:1 mixture of H_2SO_4 (95%), H_2O_2 (30%), and H_2O. Some specimens were subsequently subjected to a 60 second etch in HF.[3] Surfaces were examined by optical microscopy to detect any development of etch pits. Ohmic contacts were produced on the back side using indium solder or a Au-Ge eutectic preform processed at 350°C for 15 minutes in forming gas.

The Au contacts were deposited in a Univac thin film coating system. A planar dc magnetron sputter gun (US Gun) was used as the Au source. The system base pressure of $<10^{-7}$ Torr was achieved using an ion/cyrogenic pumping combination in combination with a Balzer turbomolecular pump. A Sloan thin film monitor was used to measure the rate of metal deposition

and automatically stop the sputtering at the required contact thickness (2000 Å). Specimens were positioned over a stainless steel shadow mask; the contact diameter was 600μm. The mask and specimen were placed on an electrically isolated substrate support during contact deposition. Contacts were deposited at an argon pressure of $1x10^{-3}$ Torr. Deposition rates were selected in the range 0.5 to 7 Å/sec. This corresponded to open circuit voltages of 800 to 1400 V and deposition working voltages of 400 to 600 V with current values of 5-20 mA. Chromel-alumel thermocouple measurements indicated that the shadow mask temperature was <50°C for all deposition procedures.

The electrical characterization of the device was performed using forward bias I-V measurements and electron-beam-induced-voltage (EBIV). The bulk of our data was collected using the electron beam technique. This has the advantage of providing spatially resolved data for different regions of each contact. The electron beam data were acquired using a modified JEOL JSM 35C scanning electron microscope.

The technique of EBIV has only recently been developed. Parameters such as Schottky barrier height and ideality factor can be determined from these data.[2] The technique is based on the concept that electron-beam-induced electron hole pairs separate under the influence of the Schottky barrier depletion layer. Under open circuit conditions a voltage develops at the devices' contacts. This is a result of both the electron-beam-induced carriers and the thermally generated carriers produced at room temperatures. The flux of thermally generated carriers are dependent upon factors including the device contact area. The electron beam generated component is dependent upon the generation factor which is the number of electron hole pairs produced per incident electron. By taking these

factors into account, the analysis of Huang et al.[2] can be used to calculate Schottky barrier height and ideality factors from plots of beam current versus open circuit voltage. For this study, the value of Richardson's constant was taken as 8 A cm^{-2} k^{-2}.[4]

Results

The effects of contact deposition rate are shown in Figure 1. There is a trend toward lower Schottky barrier heights, ϕ_B, with increasing deposition rate. These specimens were processed at constant argon gas pressure. Under these conditions the deposition rate corresponds to the magnetron gun working voltage and current. By way of comparison, Figure 1 shows an electrical characteristic for a diode fabricated by thermal evaporation. As can be seen, the Schottky barrier height is significantly higher than for any of the magnetron sputtered devices.

The effects of different specimen preparation conditions upon the EBIV data are displayed in Figure 2. The 6:1:1 etch resulted in specimens with electrical character similar to those which were only degreased. Higher Schottky barriers were developed when the 6:1:1 etch procedure was followed by an HF etch.

The effects of thermal annealing at 315°C in forming gas are shown in Figure 3. An initial increase in barrier height is followed, after one minute, by a steady decrease. With the present device geometry, range of beam current, and typical values of the carrier generation factor, the EBIV technique was calculated to have a limit of detection at ϕ_B = 0.47 eV. The processing of specimens doped with $1\text{x}10^{18}$ cm^{-3} for seven minutes produced diodes with barrier heights below this limit. When specimens with doping densities of $3\text{x}10^{17}$ ions cm^{-2} were subjected to similar processing as deposited diodes had higher barrier heights (0.7 eV), the initial rise in

barrier height was more pronounced, and processing of the device for seven minutes produced a barrier of .52 eV.

Discussion

The change in device Schottky barrier height with different rates of contact deposition can be ascribed to process-induced radiation damage. Process-induced damage effects have been observed with a number of systems including Al-Si diodes,[5] dc magnetron sputtered MOS devices,[6] and Ti W/Au GaAs diodes.[7] For the devices studied here, damage may result from the impingement onto the substrate of neutrals reflected out of the source. These would be argon and residual gas neutrals together with gold from the rarget. Typically, after ionization of sputtered species in the magnetron discharge, many ions can be neutralized and reflected from the target surface as atoms. Reflected factors can be as high as 0.4 with particles retaining substantial amounts of their original energies.[8] Thus, during deposition the substrate surface is subjected to a flux of energetic particles. The energies of the particles would be dependent on the working voltage of the source. As even the slowest deposition rates required working voltages of ~ 400 V, it is clear that process-induced damage effects cannot readily be avoided.

The electrical character of devices was also sensitive to the chemical etch procedures applied to the substrate. In this experiment, two processes must be considered: 1) the intrinsic effect of chemical etch processes on diode electrical properties, and 2) the effect of magnetron induced damage on residual layers. Our results would seem to be consistent with effects due to different chemical etch processes on diode electrical character. Aydinli et al.[9] made use of the 6:1:1 (H_2SO_4,H_2O_2,H_2O) etch to create residual layers with excess arsenic. The excess of this

element at the interface was thought to be responsible for reducing ϕ_B. A similar trend can be detected in our data. The work of Shiota[10] indicates that a subsequent HF etch significantly reduces the residual oxide thickness and results in better quality diodes. Our data indicate that this process produced diodes with higher Schottky barrier height.

The change in electrical character may also be due to the effect of process-induced damage on residual layers. If the oxide layer is particularly sensitive to low energy particle damage, thinning of this layer would reduce the suscsptibility of a device to the magnetron processing effect. Thus, one would expect to see relatively little difference between the degreased and 6:1:1 etched diodes as these would have similar oxide coverages. Nevertheless, the HF etched specimen would have higher Schottky barrier heights because of the removal of the damage sensitive layer. This speculation is consistent with the data.

The effect of thermal processing may be considered as having two stages. Initially there was a recovery of barrier height due to thermal repair of process-induced damage. This was observed before thermally stimulated metal semiconductor interdiffusion produced significant changes in electrical character. With the onset of metal semiconductor interaction the barrier height fell in a manner similar to that reported by Robinson[11] for thermally deposited Au-GaAs devices.

Conclusions

From the study it can be concluded that:

1) Magnetron sputtering induces electrically significant process-induced damage.

2) The effect is dependent upon the rate of contact deposition.

3) For even the slowest deposition rates, the effect is significant.

4) Substrate etch processes have significance due to changes induced in the interfacial oxide composition and/or thinning of the damage-sensitive oxide layer.

5) Annealing devices at 315°C in forming gas is sufficient to initiate repair of the process-induced damage.

Acknowledgements

We are indebted to G. Blakeslee for the use of furnace facilities and to K. Jones for preparation of the evaporated layers. We are also indebted to John Thornton for useful discussion of the magnetron sputtering process. We would like to acknowledge the support of NASA under contract no. NAG-1-154.

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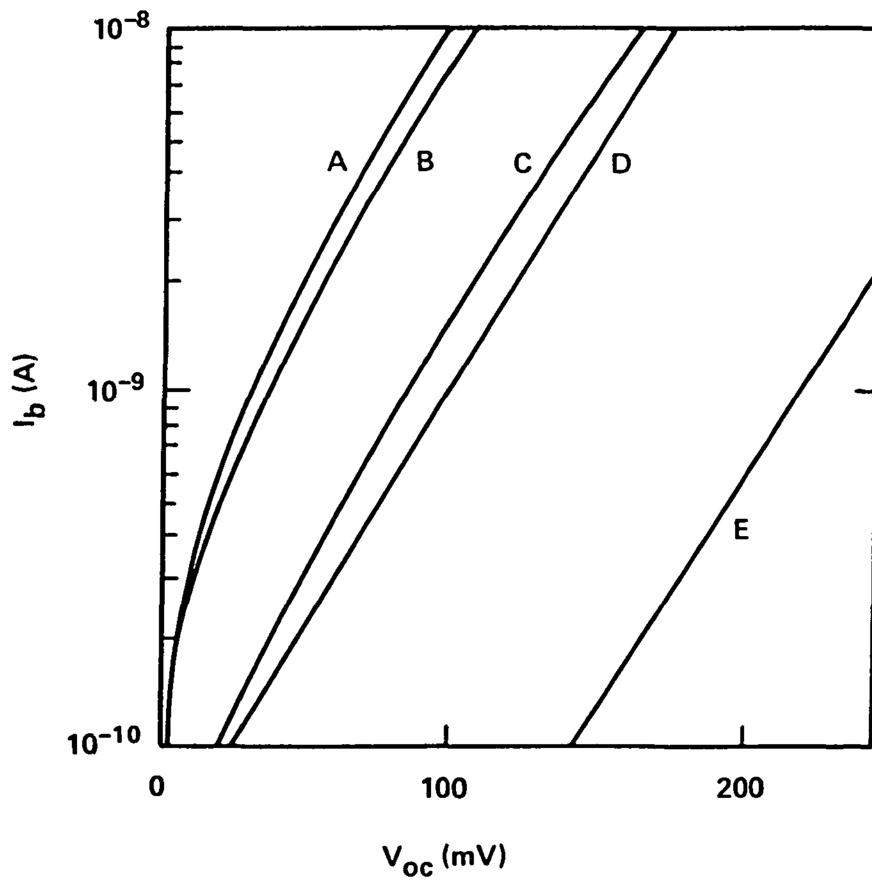
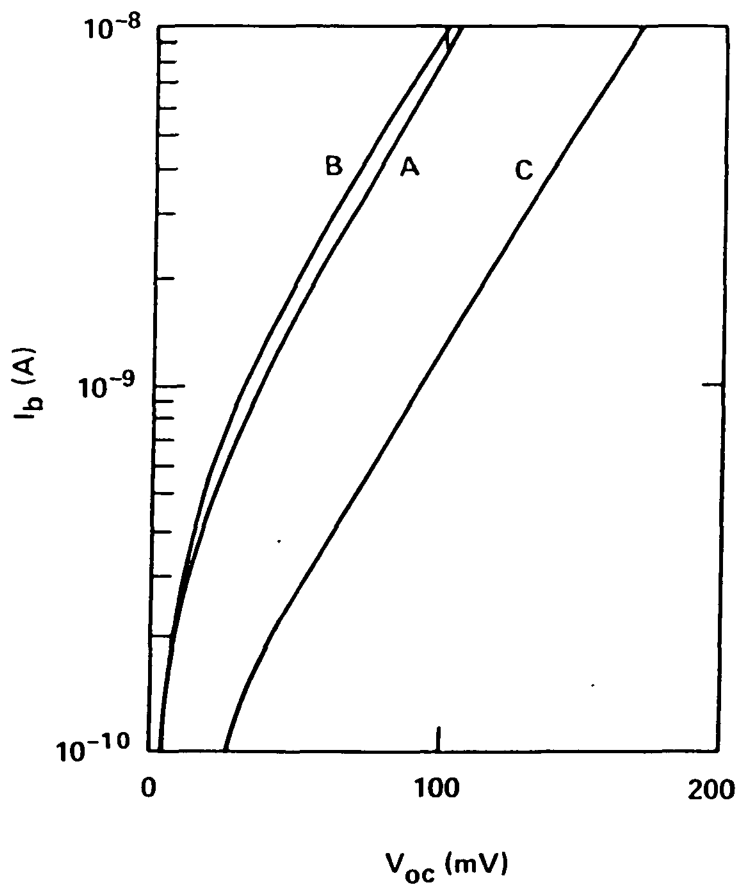


10^{-8}
10^{-9}
10^{-10}
I_b (A)
A
B
C
D
E
0
100
200
V_{oc} (mV)



10^{-8}
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I_b (A)
B
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0
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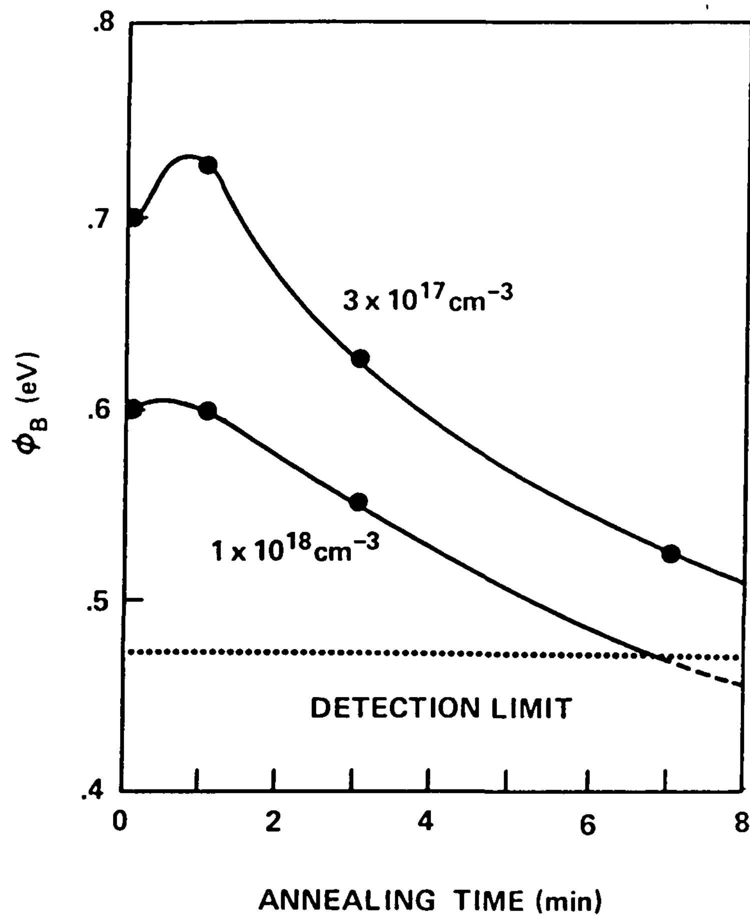
V_{oc} (mV)



.8
.7
.6
.5
.4
Φ_B (eV)
$3 \times 10^{17} cm^{-3}$
$1 \times 10^{18} cm^{-3}$
DETECTION LIMIT
0
2
4
6
8
ANNEALING TIME (min)

List of Figure Captions

Figure	Caption
1	Open circuit voltage versus beam current for Au contacts prepared by magnetron sputter deposition or evaporation. The deposition rate and Schottky barrier heights are: A: 5Å/s, 0.57eV; B: 7Å/s, 0.58eV; C: 2Å/s, 0.62eV; D: 0.5Å/s, 0.63eV; E: Evaporated contact, 0.72eV. In all cases, the substrates dopant was 1 x10^{18} cm^{-3} of Si and the ideality factor was $\sim$1.2.
2	Open circuit voltage versus beam current for Au contacts prepared by magnetron sputter deposition. The substrate preparation procedure and Schottky barrer heights are: A: degrease in TCE and acetone, rinse in H_2O and methanol, 0.58eV; B: as in A plus 40 sec. etch in 6:1:1 solution of H_2SO_4:H_2O_2:H_2O, 0.57eV; C: as in B plus 60 sec. in HF, 0.63eV. In all cases the dopant was 1 x 10^{+18} cm^{-3} of Si and the ideality factor was $\sim$1.2.
3	Schottky barrier height versus time of anneal at 315°C in forming gas. The effects on substrates doped with Si to 3 x 10^{17} cm^{-3} and 1 x 10^{18} cm^{-3} are shown.

Effect of Ion Sputtering on the Interface Chemistry and Electrical Properties of Au/n-GaAs (100) Schottky Contacts*

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Extended Abstract

With the use of sputter deposition and reactive ion etching in the electronics industry, the effects of sputtering upon metal semiconductors contacts is becoming very important. It has been found that both magnetron sputtering and reactive ion etching causes interface damage which leads to lower Schottky barrier heights for n-type semiconductors (either Si[1,2] or GaAs[3,4]). In the present case, interface sputter damage effects have been measured for Sn-doped ($<2 \times 10^{17}$ cm^{-3}) (100) oriented GaAs. The sputtered surfaces were characterized with Auger and x-ray photoelectron spectroscopies, then Au contacts were deposited in situ on these characterized surfaces. Subsequent electrical tests included I-V and C-V measurements.

The electrical data showed that the sputtered Schottky junction exhibited soft I-V characteristics, i.e., lower Schottky barrier heights and larger ideality factor. (See Table 1). The barrier heights measured by C-V were also lower after sputtering, but were larger than those measured by the I-V techniques. The effect of sputtering upon the electrical behavior was a function of ion energy. For contacts on chemically etched GaAs, the barrier height was $\sim$ 0.9eV. For 1 keV, 3keV and 5keV ions, the barrier heights were 0.60eV, 0.69eV, and 0.65eV, respectively. Thus the barrier height did not monotonically decrease as ion energy increased, but exhibited a small maximum near 3keV ion energy. (See Figure 1.)

After sputtering, AES data showed that the surface layer sampled by the Auger electrons (mean free path of $\sim$12Å) of GaAs was deficient in As, but the deficiency was a function of the ion energy. (See Fig. 2). Similar results have been reported by Singer, et.al[5]. By rotating the sample, non-destructive depth profiling was measured with XPS. These data demonstrate that for 1.5keV ions the outermost $\sim$3Å of GaAs was rich in Ga, consistent with the AES data. In contrast, ion sputtering at 3 and 5keV caused the outermost $\sim$3Å of GaAs to be rich in As, even though over the Auger sampling depth the surface was depleted in As.

In order to explain the "soft" I-V characteristics of ion sputtered Si, Mullins et.al.[6] proposed a tunnelling model. They proposed that the ion sputtered surface layer was donor-like. Thus it contained a

positive charge which enhanced tunneling transport. Subsequent studies of sputtered surfaces using deep level transcient spectroscopy (DLTS) support this model.[7] Yamasaki, et.al.[4] have shown that ion sputtering will degrade the Schottky contact between Au-Ti and GaAs and they explained the results based upon the model of Mullins, et.al. Similarly, the general lowering of the barrier height by sputtering in our study can be explained by the creation of a donor-like layer which may coincide with the As depletion. Vacancies of As have been reported to have a donor-character.[8]

However, in addition to a general lowering, the barrier was higher for 3keV than for 1 or 5keV ion sputtering. This is contrary to Si where the barrier decreased monotonically as the ion energy was increased. The different behavior for Au/GaAs is attributed to variations in the outermost surface composition with ion energy. Using the data by Woodall and Freeouf,[9] the barrier height for a surface rich in As (ratio of As to Ga of 1.22) corresponds to a barrier height of about 0.8eV. However, they also report that the barrier height for a Ga contact to GaAs is very low ($\sim$ 0.3eV). Since the outermost surface layer is Ga-rich after 1.5keV Ar^+ sputtering, the barrier height for surfaces sputtered at 1.0keV should be low. At 3keV, the outermost layer is nearly stoichiometric, thus the barrier height should be higher as observed. The increase from 1.0keV to 3keV energies is not as large as expected from the composition change because the donor layer effect is larger at 3keV (as compared to 1.0keV) and results in a smaller rise in the barrier. Since in going from 3keV to 5keV Ar^+, the outermost layer becomes enriched in As, an increased barrier height might be expected. However, a reduced barrier is observed experimentally, and this is attributed to the fact that the donor layer increases significantly for 5keV sputtering; this results in a net reduction in the barrier height. Note that the barrier height after 5keV sputtering (0.65eV) is higher than after 1keV sputtering (0.6eV).

*This work supported in part by NASA Grant NAG-1-154

Table I Electric Measurement Results

Specimen	$\phi_{\beta n}^{IV(1)}$ (eV)	$n^{(1)}$	$\phi_n^{CV(2)}$
Native Oxide	0.78	1.97	1.40
Chemical Etched	0.89	1.04	0.90
1keV SPT	0.60	1.96	0.80
3keV SPT	0.69	1.54	---
5keV SPT	0.65	3.92	---

1. From F-V data.

2. From C-V data.

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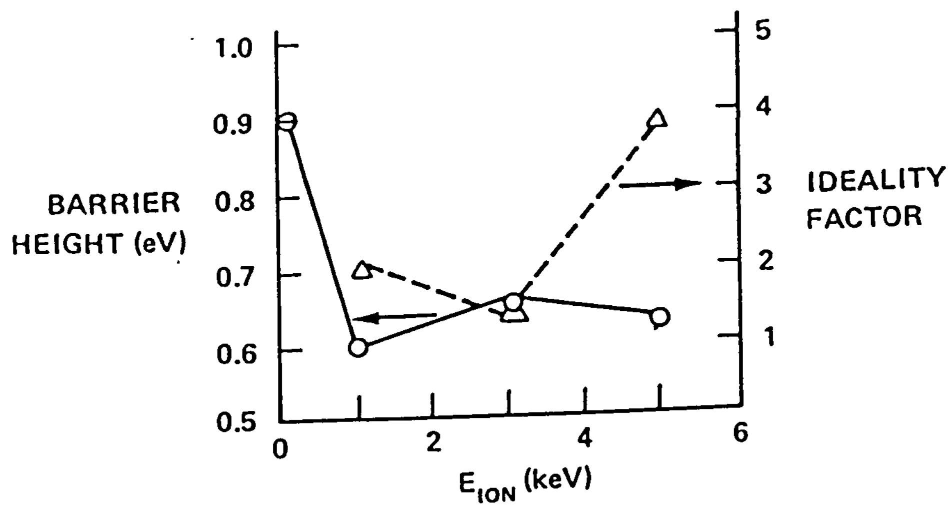

Fig. 1 - Schottky barrier height and ideality factor (from I-V data) versus argon ion energy.

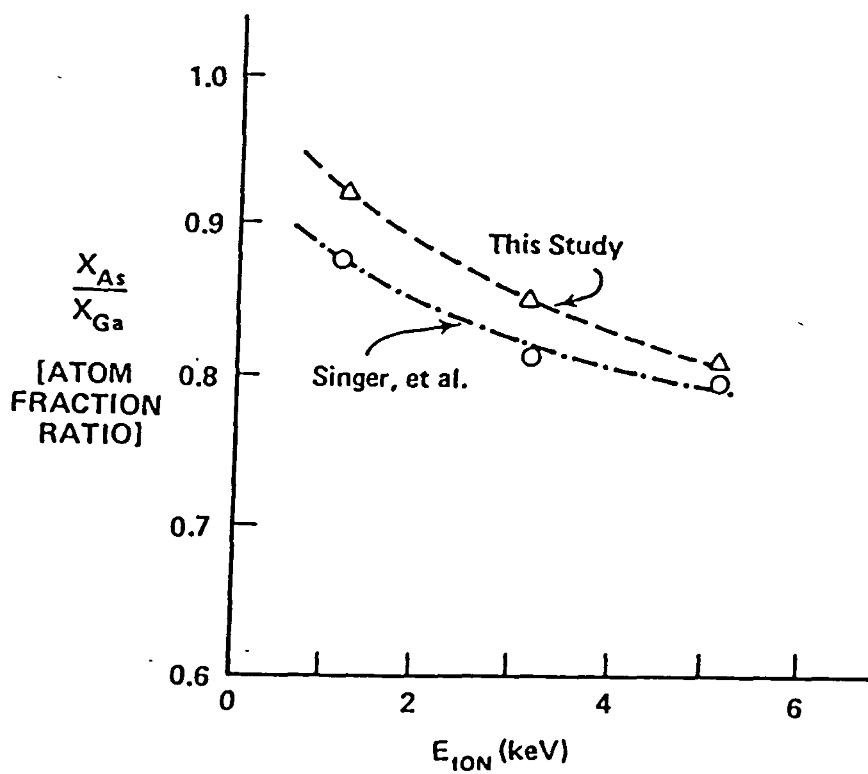

Fig. 2 - Atom fraction ratio of AS to Ga (AES) versus argon ion energy. Data from this study and ref. 5 are shown.

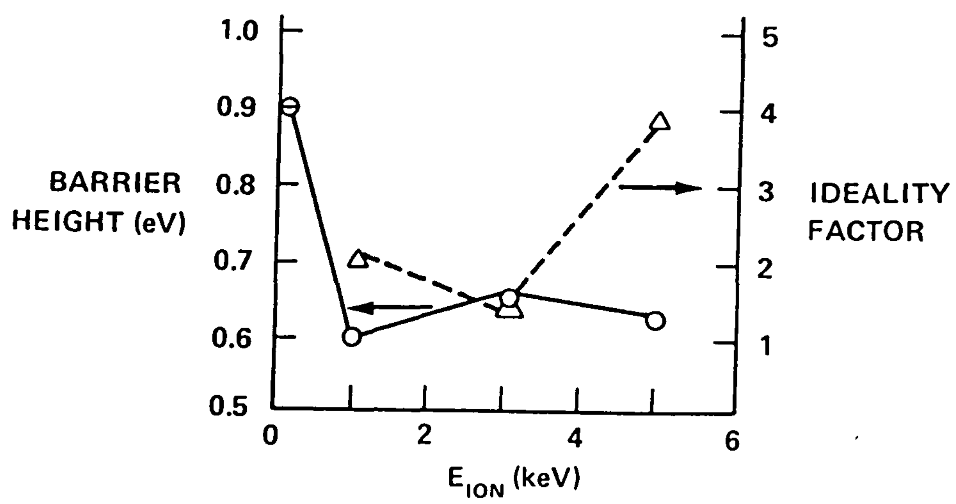

Fig. 1

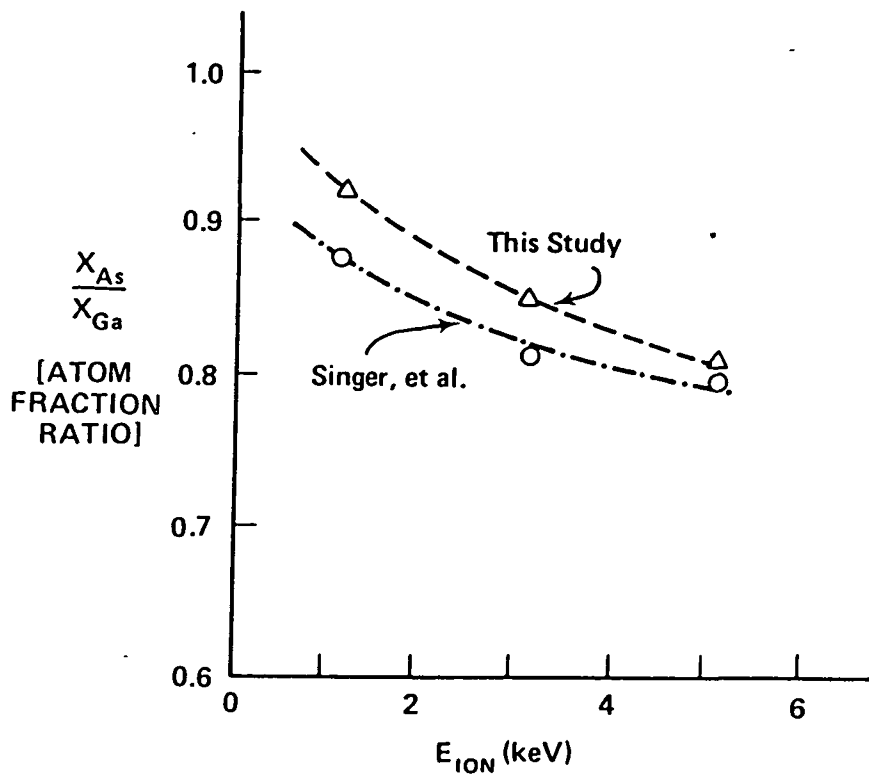

Fig. 2

Effect of Ion Sputtering on Interface Chemistry and Electrical Properties of an GaAs (100) Schottky Contacts

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Abstract

The effects of sputtering n-type GaAs with 1 keV to 5keV argon ions has been studied in ultra-high vacuum. Auger electron and x-ray photoelectron spectroscopies have been used to characterize the surface before and after sputtering. Gold Schottky contacts were prepared in situ to avoid contamination at the metal/semiconductor interface. The data show that sputtering depletes the surface in As, and the extent of depletion increased as the ion energy was increased. However angular-resolved photoelectron data showed As was enriched on the outer atom layer by 5keV but depleted by 1 keV Ar^+ sputtering. Current and capacitance versus voltage data showed that sputtering always lowered the Schottky barrier height and generally increased the ideality factor. However the barrier height after 3 keV sputtering was higher than after 1 keV sputtering. Those effects are explained based on a combined effective work function model and creation of a donor-like surface damage layer. The donor layer was correlated with As depletion by sputtering. Deep level trap formation and annealing of sputtering effects were studied.

Introduction

Because of the use of sputter deposition and reactive ion etching, the effects of sputtering upon metal/semiconductors contacts is becoming very important. It has been found that both magnetron sputtering and reactive ion etching lead to lower Schottky barrier heights for n-type semiconductors (either Si[1,2] or GaAs[3,4]). Ion sputter effects for Schottky contacts on silicon have been studied by E. Grusel, et al [(2)] and Mullins and Brunnschweiler[5] (referred to hereafter as MB). MB[5] proposed a model in which ion sputtering created a donor-like damage layer; these defects resulted in increased tunneling current. Their calculation of diode characteristics based on the sputter-damage model agreed quite well with the experimental results.

Yamasaki, et al [(4)] observed "soft" current voltage (I-V) characteristics and a lower Schottky barrier height (ϕ_{Bn}) on magnetron deposited Au/Ti contacts to n-GaAs (100). They also attribute the lower ϕ_{Bn} to creation by energetic particles of a donor-like damage layer at the contact interface. More recently, Kwan et al [(6)] have studied the effects of ion sputtering on Al contacts to n-GaAs. They measured the I-V characteristics as a function of the ion energy (up to 1 keV) and found sputtering increased the diode current and the ideality factor (i.e. caused "soft" diode characteristics).

In this study, we will report on the effects of ion bombardment on Au-nGaAs contacts. Defects at the interface were introduced deliberately by ion sputtering in an ultra-high vacuum (UHV) system. The sputter surfaces were either annealed or not annealed in the UHV system. But in every case the gold contact was formed by in situ UHV deposition of Au. Conventional I-V and C-V

(capacitance-voltage) measurements were used to measure the contact characteristics, while Auger electron (AES) and X-Ray photoelectron spectroscopies (XPS) were used to measure the surface composition and damage layer.

Experimental

The (100) oriented GaAs used in this study was n-type material with a Si doping density of $< 2 \times 10^{17}$ cm^{-3}. All the specimens were cleaned by boiling in trichlorethylene, acetone, methanol, rinsing in D.I. water, dipping in 4:1:1 solution of $H_2SO_4:H_2O_2:H_2O$, rinsing in de-ionized water, then drying with N_2 gases. A Au-Ge (88 at % Au) alloy was evaporated onto the back of GaAs wafer and H_2 annealed at 415°C for 3 minutes to produce an ohmic contact. Once an ohmic contact was formed, the samples were placed in the UHV system ($< 2 \times 10^{-9}$ Torr) and the surface contamination was measured using AES with a Physical Electronics Model 545 system. Typical operating conditions were a 3keV, 1.5μA primary electron beam, 3eVpp modulation voltage, a cylindrical mirror analyzer (CMA), a sweep rate of < 10eV/sec., and a lock-in amplifier time constant of < 0.1 sec. The samples were, when appropriate, sputtered with Ar^+ (PHI ion gun Model 04-191) until the surface was void of oxygen and carbon as measured by AES. The primary ion energy was between 1 and 5 keV, the beam was incident at ~ 15° from the surface plane; 10 to 20 min. was sufficiently long to clean the surface and produce stable values for the As and Ga Auger peak heights. The ion beam had a Gussian shape with a maximum current density of $100mA/cm^2$ and $300mA/cm^2$ in the AES and XPS experiment, respectively. The beam was scanned over 4mm x 4mm and 7mm x 7mm

areas respectively for the AES and XPS experiments. In the XPS experiments, a Kratos XSAM 800 system using MgKα X-ray excitation was used. Variable photoelectron take-off angles were used in order to determine the depth profiling without sputtering (see below). For those samples where the contact interface had a native oxide film, the samples were kept at room temperature at least 3 days after the last chemical cleaning. For chemically etched samples, the surface was swabbed with 50% HF, 50% H_2O then rinsed in DI H_2O and dried immediately prior to placement in the UHV system for Au contact deposition.

To avoid contamination from atmosphereic gases on sputtered surfaces, Au Schottky contacts were deposited in situ in the UHV system. A stainless steel shadow mask which defined the Au contact on the GaAs substrate had circular holes of 500 μm diameter separated by about 2mm. Generally, the specimen was moved behind the shadow mask after sputtering. In early experiments, the shadow mask was placed on the specimen during sputtering, but AES showed that the GaAs was then contaminated with Fe at the interface (and probably Ni and Cr). After sputtering, Au was deposited using the in situ evaporator shown in Fig. 1. The Au source was a tungstun wire with a 0.20" gold wire wound on the middle. The Au contact was 500 to 1000Å thick, and could be deposited within 2 to 3 min. at ~50 watts.

Following deposition of the Au Schottky contact, the samples were removed from the UHV system and I-V and C-V measurements were made. Current voltage measurements were made in the dark using an Al-shielded box. A Hewlett/Packard STB 6112A constant DC voltage source was used with a Kiethley 173A digital multimeter. The resulting data were assumed to be described by[7]:

$$J = A^{**} T^2 \exp(-q\phi_n/kT) \exp(q[\Delta\phi + V]/kT) \qquad (1)$$

and using the slope and intercept at V=0, then

$$n = \frac{q}{kT} \frac{\partial V}{\partial(\ell n J)} \quad (2)$$

and

$$\phi_{Bn} = \frac{q}{kT} \ell n \ (A^{**}T^2/J_s) \quad (3)$$

where A** is the effective Richardson constant (8.6 for GaAs), $\Delta\Phi$ is the Schottky barrier lowering, n is the ideality factor, ϕ_{Bn} is the Schottky barrier height, and J_s is the current at V=0.

For C-V measurements, the differential capacitance was measured using a synchronous $1MH_z$ bridge which impressed a 15 mV AC signal on a ramped DC bias voltage (Princeton Applied Research Model 410 C-V plotter). The Schottky barrier height was estimated using[7]:

$$C^{-2} = \frac{2}{N_o q \epsilon_o \epsilon_s A^2} (V_D - V_r) \quad (4)$$

and

$$\phi_{Bn} = V_D + \frac{kT}{q} + V_F - \Delta\phi \quad (5)$$

where V_D is the diffusion potential, V_r is the reverse bias voltage, V_F is the depth of the Fermi level below the bottom of the conduction band, and $\Delta\phi$ is a correction for image force lowering of the barrier. For GaAs

$$\frac{kT}{q} + V_F - A \ll V_D \qquad (6)$$

thus

$$\phi_{Bn} \simeq V_D \qquad (7)$$

where V_D is defined by equation (4).

The procedure for DLTS measurements were the same as reported by Lang[8]. The parameters for recording the data were 17MH$_z$ RF, a reverse bias of -2V, a time constant of 1 sec., and the temperature was varied from 170 to 400K.

RESULTS

Surface Analysis

Auger electron spectra from GaAs substrates chemically cleaned, with a native oxide film, or sputter cleaned are shown in Fig. 2. Note that the relative intensity of the major Ga and As peaks at 1070eV and 1228eV are charged by the sputtering process. This partly results from the fact that the native oxide is largely gallium oxide[9] and also from the fact that ion sputtering depletes the surface of As (enriches it in Ga).[9,10,11] Using sensitivity factors from the literature,[10,12] the Auger peak-to-peak heights may be converted to atom fractions and these values are plotted in Fig. 3. As is obvious, the As is depleted from the surface for all Ar^+ energies, but the depletion becomes more severe at higher ion energies. This is consistent with the data by Singer, et al.[10]

To provide more detail on the surface compositions resulting from sputtering, the depth profile was measured using XPS angle-resolved measurments. The 3d photoelectron peaks from Ga and As (E_B ~ 20eV and 40eV, respectively) were used to determine the atom fraction ratio of As to Ga. The chemical state of the As and Ga was also investigated using the energy of XPS peaks. To study the depth distribution of As, the angle between the sample normal and the lens axis of the electron energy analyzer was varied. Thus when the two axes were parallel, the XPS technique sampled over several mean-free-path lengths ($\lambda \approx 15Å$ for 1430eV electrons).[13] However when these two axes were far apart (~ 80°) the sampling depth was only ~ 2.6Å. Consistent with AES in Fig. 3, the XPS data in Table 1 show depletion of As when the electrons detected were emitted parallel to the surface normal. In addition, the As depletion increased as the ion energy increased. However when the measured electrons were emitted 10° away from the surface (yielding an escape depth normal to the surface of ~ 2.6Å), the As/Ga ratio was different. At 1.5keV Ar^+, the As was depleted near the surface and deeper in the sample. But for 3 and 5keV Ar^+, the As had a higher concentration near the surface than the average depletion measured for 90° photoelectron take-off angles. In fact, for 5keV Ar^+ the As appeared to be enriched at the surface.

To attempt to learn how the As or Ga depletion was accomodated, the energy difference between the As and Ga 3d photoelectron peaks was measured. This was compared to energy differences reported in the literature.[14] As shown in Table 2, the energy difference measured in this study is consistent with the presence of elemental Ga or As with the counter element being combined as GaAs. It is clear though that the data are not consistent with

both Ga and As being in the elemental state, nor as Ga and As being exclusively combined together in stoichiometric GaAs. Thus the sputter depletion is at least partially accomodated by formation of elemental Ga or As.

It was possible to eliminate the As surface depletion by annealing after sputtering. Typical data (see Fig. 4) show that stoichiometric GaAs is restored by heating to ~ 350°C to 400°C for 20 min. The damage created by lower energy sputtering tended to anneal slightly more rapidly than for 5keV damage. Heating to temperatures above 400°C resulted in a surface enriched in As. The data shown were recorded after sputtering the surface until it was clean and the Ga and As peak intensities were independent of time. Then the sample was step-heated to progressively higher temperatures; the sample was held at each temperature for 20 min. The time dependence of the surface composition change is shown in the inset in Fig. 4.

Electrical Properties

Typical log I versus V (forward bias) and C versus V data are shown in Figs. 5 and 6, respectively, for various surface preparations. Note that the zero voltage intercept for the I-V data is larger (lower ϕ_{Bn}) and the slope is lower (larger ideality factor, n) for the sputtered versus chemically etched surface. This was generally true as shown in Table 3 where the barrier height calculated from either I-V or C-V data are shown. Ideality factors and reverse bias currents (at 300mV) from I-V data, and excess carrier concentrations from C-V data are also shown. The C-V data are reported for only the 1keV Ar^+ sputtered surface; for the higher ion energies the interface

damage distorted the C-V data so much that the data reduction scheme was not valid. Note that the barrier height from I-V or C-V data are similar for the chemically etched surface, but the C-V barrier height is larger for the native oxide or 1keV Ar^+ sputtered surfaces. Finally, note that ϕ_{Bn} did not decrease monotonically with increasing ion energy (and therefore As depletion). Rather ϕ_{Bn} for 3keV Ar^+ sputtering was higher than for 1, 4 or 5keV Ar^+ sputtering.

Data from reverse bias DLTS studies showed deep trap centers in the sputtered GaAs samples. The defect energies and concentrations calculated from these data are listed in Table 4. Defects levels were found at 0.31eV and 0.60eV below the bottom of the conduction band. Typical defect densities were $5 \times 10^{+15}$ cm^{-3}, with higher densities of the 0.31eV state. The defect density was also higher for 5keV Ar^+ than for 3keV Ar^+ bombardment.

Discussion

It is well known that thermionic emission is the dominant conduction mechanism for Schottky contacts to low doping density GaAs.[5,7] The present data for chemically etched surfaces are consistent with this conclusion in that the high barrier value (ϕ_{Bn} = 0.9eV) and near unity ideality factor (n = 1.04) were measured for a chemically cleaned surface (see Table 3). The Auger spectrum of a chemically etched surface (Fig. 2) shows that very little oxide reforms on the etched surface, and that the surface is rich in As($X_{As}/X_{Ga} \sim 1.2$). Similar observations have been reported by other investigators.[15,16] The oxide is thin because reoxidation of GaAs is time-dependent rather than linearly dependent upon both time and pressure.[17] Since the oxide is so thin, it does not significantly interfere with the thermionic

transport mechanism. In fact, Freeouf and Woodall[17] developed a model to explain the high Schottky barrier value when excess As was present at the interface (termed the Effective Work Function-EWF-Model).

When the thicker native oxide (~ 30Å[20]) was present at the metal/semiconductor interface, ϕ_{Bn} was lower and n was higher (Table 3). Robinson[19] has concluded that the lower barrier and larger ideality factor resulting from interfacial oxides results from creation of interface states coincident with the formation of the native oxide. These interface states result in an interface charge which increases the probability of conduction by tunneling (as opposed to thermionic emission). This both lowers the effective barrier height and increases the apparent ideality factor.

When the native oxide was removed by ion sputtering, the effective barrier height was reduced further. The ideality factor varied with ion energy, and was lower for 3keV Ar^+, about the same (~ 1.9) for 1 and 4keV Ar^+, and higher for 5keV Ar^+ (see Table 3). These variations in ϕ_{Bn} and n are consistent with trends reported by Mullins and Brunnschweiler[5], Yamasaki, et al[4] and Kwan, et al[6]. Sputtering not only removed the native oxide layer and any carbonacious contamination, but it also created a damage layer at surface with a small residual amount (~ 10^{13} cm^{-2}) of C, O , and implanted Ar (see Fig. 2). MB[5] proposed that sputtering created donor-like damage near the metal/semiconductor interface. This donor-like damage layer would also result in a higher tunneling probability (thermionic-field emission[19]) and therefore ϕ_{Bn} would be lowered, n would be > 1, a large reverse current would be expected, and the interface capacitance would be larger. These effects were all observed (Table 3 and Fig. 4). Since the the ideality factor deviates

from a value of two, the soft diode characteristics appear not to result from an increased recombination mechanism.[6,7]

While previous investigators have postulated the existence of a donor-like damage layer, none have studied the interface chemistry to determine its origin. In this study, it has been shown that sputtering depletes As from the surface region, but not in a uniform manner. At low energy (~ 1keV) As is depleted all the way to the outer layer, while at higher energies (3 and 5keV), As appears to be stoichiometric or in excess at the outer layer but depleted deeper in the substrate. The depth of depletion appears to correlate with the range of the ion[10], therefore it becomes greater at larger ion energies. Singer, et al[10], have reported ranges of 20Å, 60Å, and > 120Å for Ar^+ or 1, 3 and > 4keV, respectively. In the present experiment, an incidence angle 15° away from the mean surface plane was used resulting in effective ranges normal to the surface of 5Å, 15Å, and > 30Å, respectively. Over this depth, the GaAs is expected to be amorphous[21] and the XPS data show that excess concentrations of Ga or As appear to be accomodated by elemental bonding states. This implies that when As is depleted, that As vacancies will exist in the damage layer. Chiang and Pearson[22] have reported that As vacancies have a donor character. Therefore the observation of As depletion by preferential sputtering is consistent with the earlier postulate based on electrial properties, of sputter-creation of a donor-like damage layer at the metal/semiconductor interface. Obviously, defects other than As vacancies will be created (e.g. Ga vacancies, As and Ga anti-sites, interstitials, and complexes). However, most of these other defects are deep in the forbidden band and may be acceptors in n-type GaAs. Since AES and XPS data suggest that

As depletion dominates the surface layer and since the electrical properties suggest a donor layer is formed, it is concluded that As vacancies dominate the damage layer.

In general therefore, the creation by sputtering of a donor-like damage can explain the lower ϕ_{Bn} and larger n. However, the above arguments suggest that ϕ_{Bn} should monotomically decrease as the ion energy is increased. In fact, ϕ_{Bn} is larger for 3keV Ar^+ sputtering than for 1 or 5keV Ar^+ sputtering. This fact may be explained by recalling that XPS data showed that the outer surface layer of GaAs was depleted in As at 1keV, but As-rich at 5keV sputtering. According to Freeouf and Woodall[18], excess As at the surface increases while excess Ga decreases the Schottky barrier height (EMF model). Thus, ϕ_{Bn} is expected to be lowered even more than normal by 1keV sputtering since this produces a donor layer and a Ga-rich surface. Normally, ϕ_{Bn} for 3keV sputtering would be expected to be lower than for 1keV sputtering since the ion range is greater causing a larger donor layer to be formed. However, XPS data showed that the outer layer of 3keV sputtered GaAs was nearly stoichiometric GaAs, resulting in a higher ϕ_{Bn} than for 1keV sputtering. Therefore to explain the data in Table 3, a combination of the MB and EWF models must be used.

Even recognizing that the MB model alone will not explain the present data, it is still interesting to estimate the density of donor-states present after sputtering. In the MB model, the donor states, N, were assumed to be distributed away from the surface according to:

$$N(X) = N_{ts} \exp(-X/L) \tag{8}$$

where N_{ts} is the surface trap density, L is the characteristic length, and X is the depth into the sample. In the work of Mullins and Brunnschweiler[5], the values of N_{ts} and L were both unknown but the ion range in our study is ~ 5Å for 1keV Ar^+. For reverse bias conditions, Mullins and Brunnschweiler[5] showed:

$$N_{ts} = \frac{(\phi_{B0} - \phi_{B1})\ \varepsilon\varepsilon_o}{qL^2} \tag{9}$$

where ϕ_{B0} and ϕ_{B1} are the barrier heights before and after ion sputtering and q is the charge on the carrier. From the C-V data for 1keV Ar^+, ϕ_{B0} = 0.9eV, ϕ_{B1} = 0.8eV and

$$N_{ts} = 2.9 \times 10^{20} cm^{-3} \tag{10}$$

as a surface density of donor states. The XPS data showed that the outer surface layer was ~ 35% As - 65% Ga, and the atomic density of As in GaAs is 2.2×10^{22} cm^{-3}. Assuming that one in ten of the depleted As was all accomodated by As vacancies, this yields a surface vacancy density of 3.4 x 10^{20} cm^{-3}. This number is nearly equal to that in eq. (10) lending credence to the proposed correlation.

The data from DLTS showed that sputtering created traps at 0.31eV and 0.6eV below the bottom of the conduction band. The measured densities were ~ $10^{15} cm^{-3}$. Their energy places them below the Fermi level, they may act as acceptors and their densities are much lower than that of the donor states. As a result they have only minor effects upon the observed electrical behavior.

Auger data showed that the depletion of As caused by ion sputtering could be eliminated by annealing at temperatures of ~ 400°C for ~ 10 min (Fig. 4). This observation correlates well with data reported by Yamasaki, et al[4]. They showed that ϕ_{Bn} for a sample sputtered at 200 W for 10 min. was reduced from 0.7eV to 0.4eV. However, when the sputtered sample was annealed for 1 hour in N_2 at 400°C, ϕ_{Bn} increased to ~ 0.6eV. Only a very slight increase was observed in 1 hour at 300°C. For samples sputtered for shorter times and/or at lower power settings, ϕ_{Bn} recovered to ~ 0.7eV (or higher) after annealing at 400°C. Thus, the annealing studies tend to confirm the correlation between As depletion and donor-layer formation at the metal/semiconductor interface.

Conclusions

The effect of ion sputtering upon Au Schottky contacts to low doping density ($\lesssim 2 \times 10^{17} cm^{-3}$ Si) n-type GaAs has been studied. Electrical property data (I-V and C-V) showed that argon ions with energies between 1keV and 5keV caused a lowering of the effective barrier height and a larger ideality factor. The barrier height from I-V data was always lower after sputtering, but, ϕ_{Bn} for 3keV Ar^+ was higher than for 1, 4, or 5keV Ar^+ sputtering. Auger electron (AES) and X-ray photoelectron spectroscopies (XPS) were used to show that sputtering removed surface oxides and carbon contaminants, but also generally depleted the surface in As. Angle-resolved XPS data showed that while As was generally depleted and the depletion increased with ion energy, that the As concentration was actually larger than Ga on the outer atomic layer of 5keV Ar^+ sputtered GaAs. The sputtering was argued to have created a surface layer rich in As vacancies which acted as a donor defect layer. This

layer caused enhanced tunneling transport across the metal/semiconductor interface, effectively lower the apparent barrier and increasing the ideality factor. However, the lower ϕ_{Bn} at 1keV (as compared to 3keV Ar^{+}) suggests that the Ga-rich outer atomic layer caused a further reduction in ϕ_{Bn}formation. Thus a combination of work function effects and tunneling transport caused the observed electrical responses. The creation of deep traps (measured by DLTS) and annealing of the surface damage layers were discussed.

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Table 1. X-Ray Photoelectron Data Versus Sample Orientation

Ion Energy	Electron take-off angle: Normal to sample surface	Electron take-off angle: 10° from surface plane
1.5keV	$\frac{X_{As}}{X_{Ga}} = 0.71$	0.54
3keV	0.69	0.75
5keV	0.67	>1.2

Table 2. Energy difference, ΔE, between the As and Ga 3d photoelectron peaks for various bonding states of the elements and for sputtered surfaces

Condition	ΔE
Literature Data	
GaAs	21.2eV
Elemental Ga and Elemental As	23.1eV
Elemental Ga and As in GaAs	22.2eV
Elemental As and Ga in GaAs	22.1eV
Present Study	
1.5keV sputtered	22.3eV
3.0keV sputtered	22.1eV
5.0keV sputtered	22.2eV

Table 3. Schottky barrier height, ϕ_{Bn}, ideality factor, n, current at 300mV reverse bias, and excess carrier concentration calculated from either I-V or C-V data

	I-V			C-V	
	ϕ_{Bn}	n	I_r	ϕ_{Bn}	N_O-N_A
Native oxide	0.78	1.97	$<10^{-8}$	1.40	1.43×10^{17}
Chemical etched	0.81	1.04	$<10^{-8}$	0.90	1.67×10^{17}
1 KV SPT	0.60	1.96	6.0×10^{-6}	0.80	3.30×10^{17}
3 KV SPT	0.69	1.54	3.0×10^{-7}	--	--
4 KV SPT	0.67	1.90	7.0×10^{-7}	--	--
5 KV SPT	0.65	3.92	1.5×10^{-6}	--	--

Table 4. Carrier density, N_D, and density of deep level traps after ion sputtering

Ion Energy (keV)	Carrier Density (cm^{-3})	$E_1 = 0.31eV$ (cm^{-3})	$E_2 = 0.60eV$ (cm^{-3})
3	4.3×10^{17}	6.5×10^{15}	2.4×10^{15}
5	1.2×10^{17}	8.1×10^{15}	7.3×10^{15}

FIGURE CAPTIONS

1. Schematic of evaporator for in situ preparation of Au Schottky contacts.

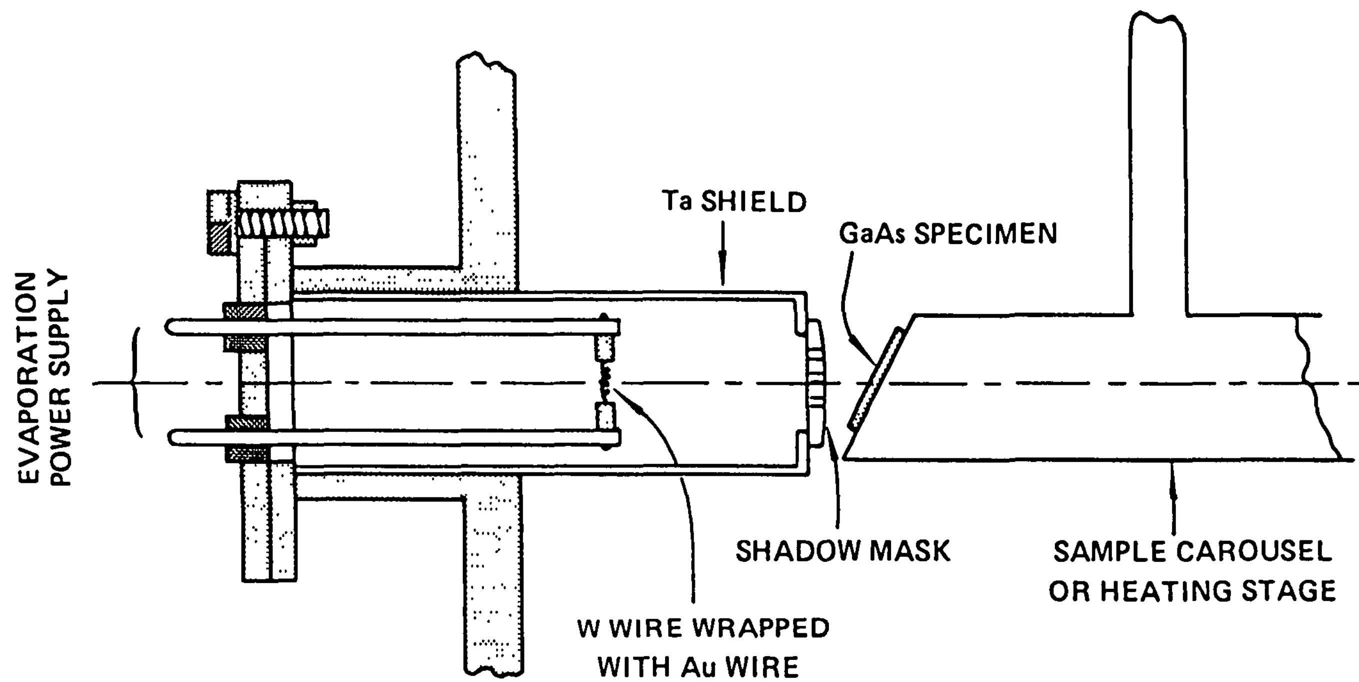
2. Auger electron spectra from GaAs with native oxide, ion sputter cleaned, and chemically cleaned.

3. Atom fraction ratio of As to Ga (measured by AES) versus Ar ion energy. The data from Singer, et al, were taken from ref. 10.

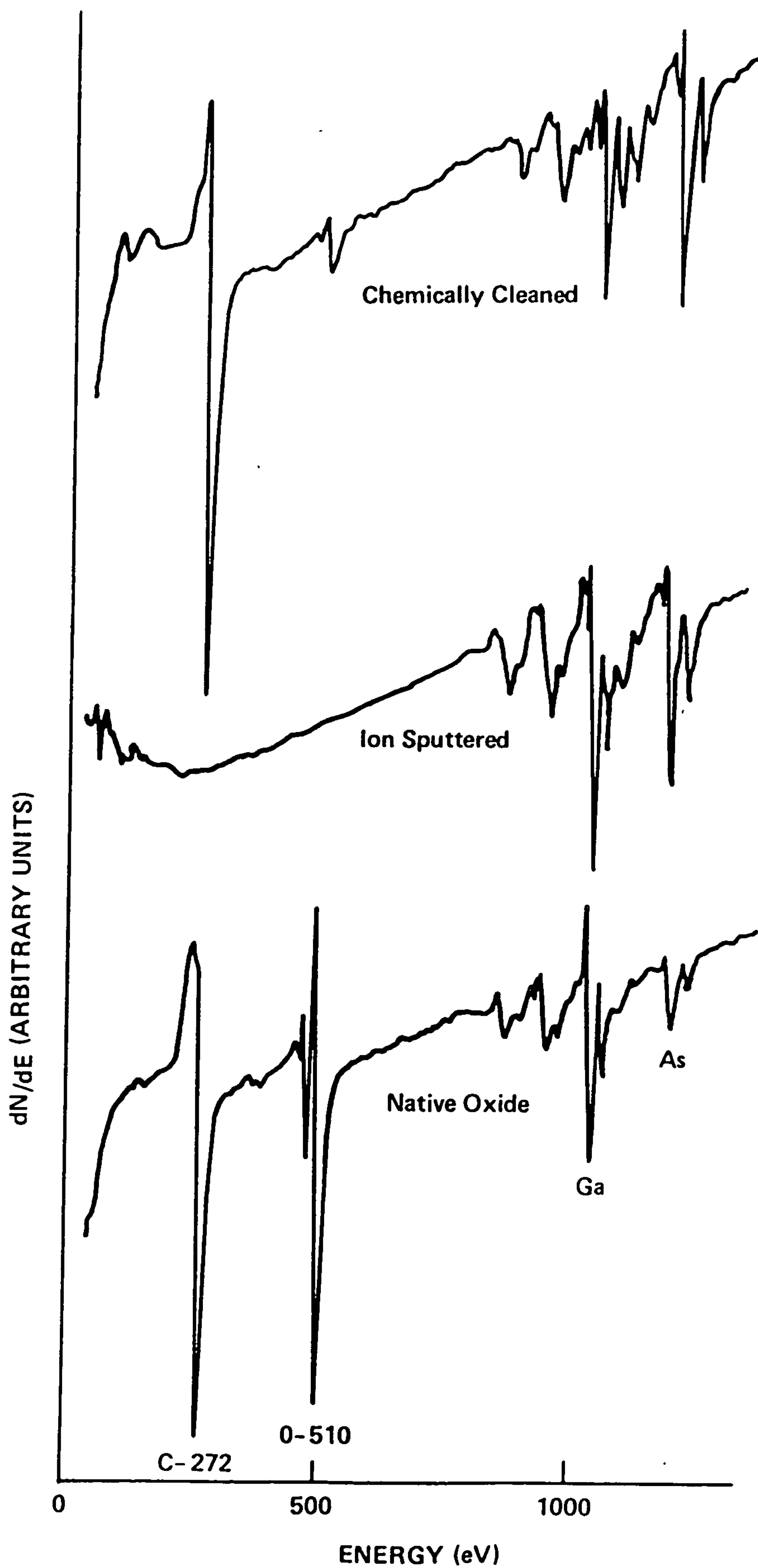
4. Atom fraction ratio of As to Ga (measured by AES) versus temperature of annealing. Data at each temperature taken after twenty minutes at temperature of anneal. Inset: Time dependence of ratio at T=400°C.

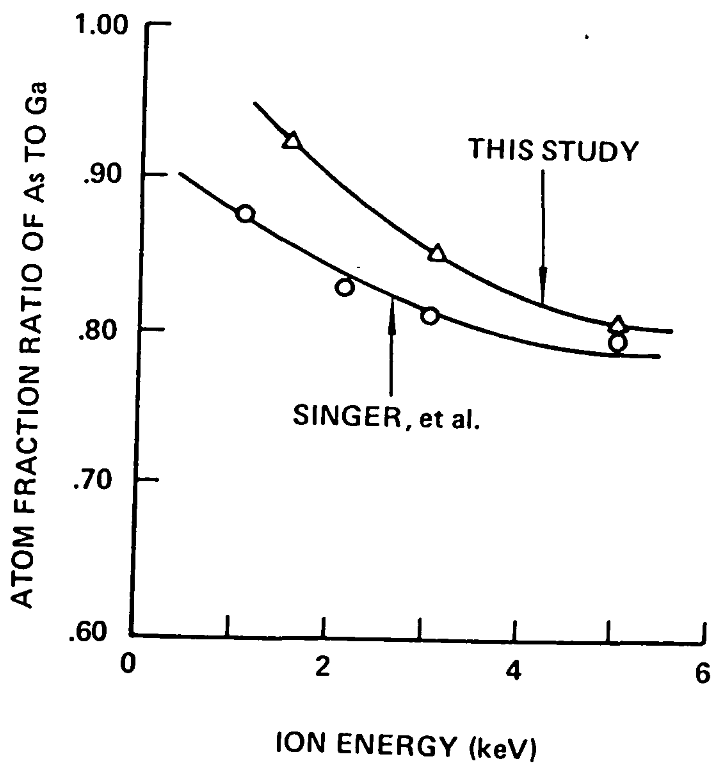
5. Current versus voltage data for a chemically cleaned (forward bias) and a 3keV sputtered sample (forward and reverse current shown).

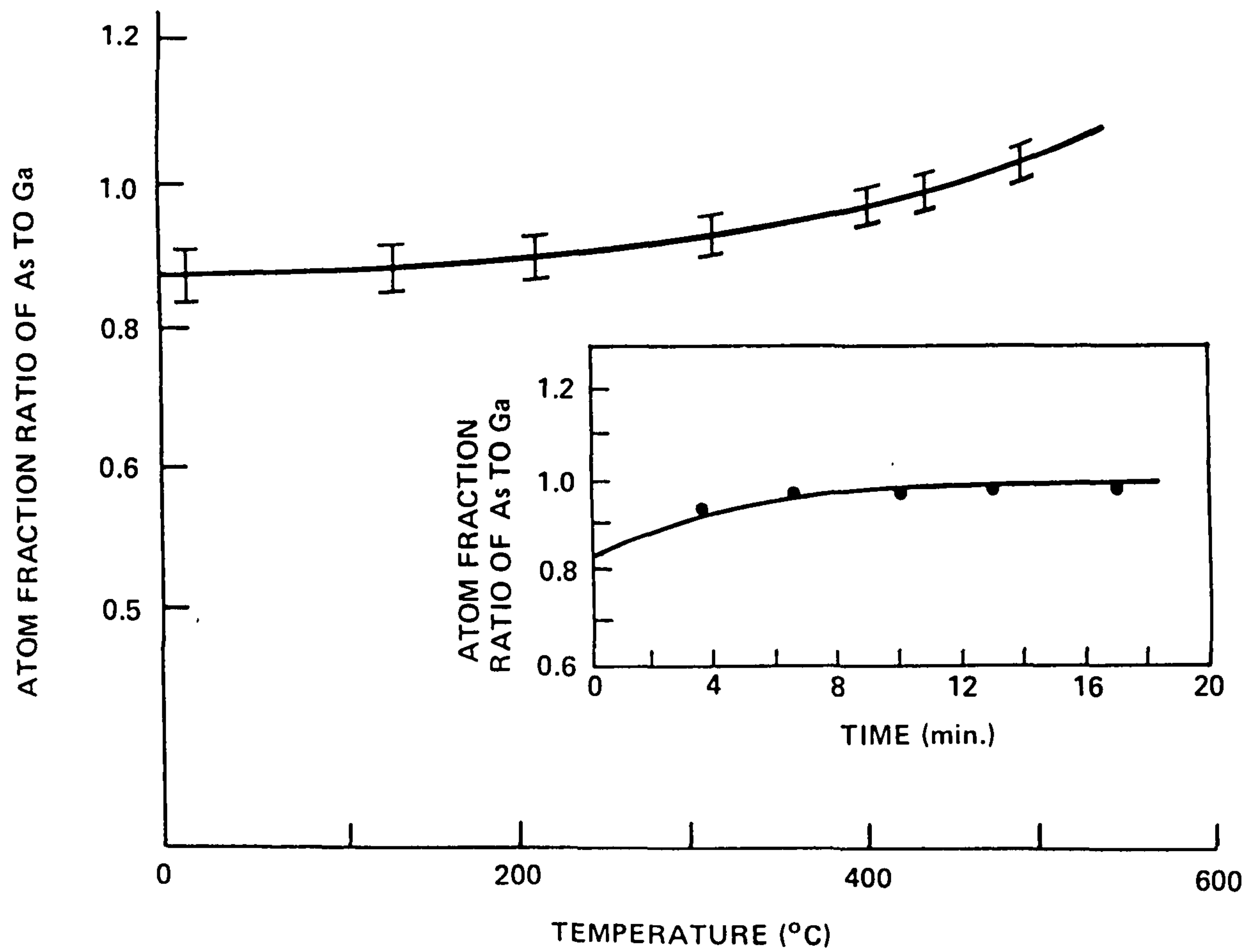
6. Capacitance versus voltage data for samples chemically cleaned, with a native oxide, or ion sputtered (5keV).



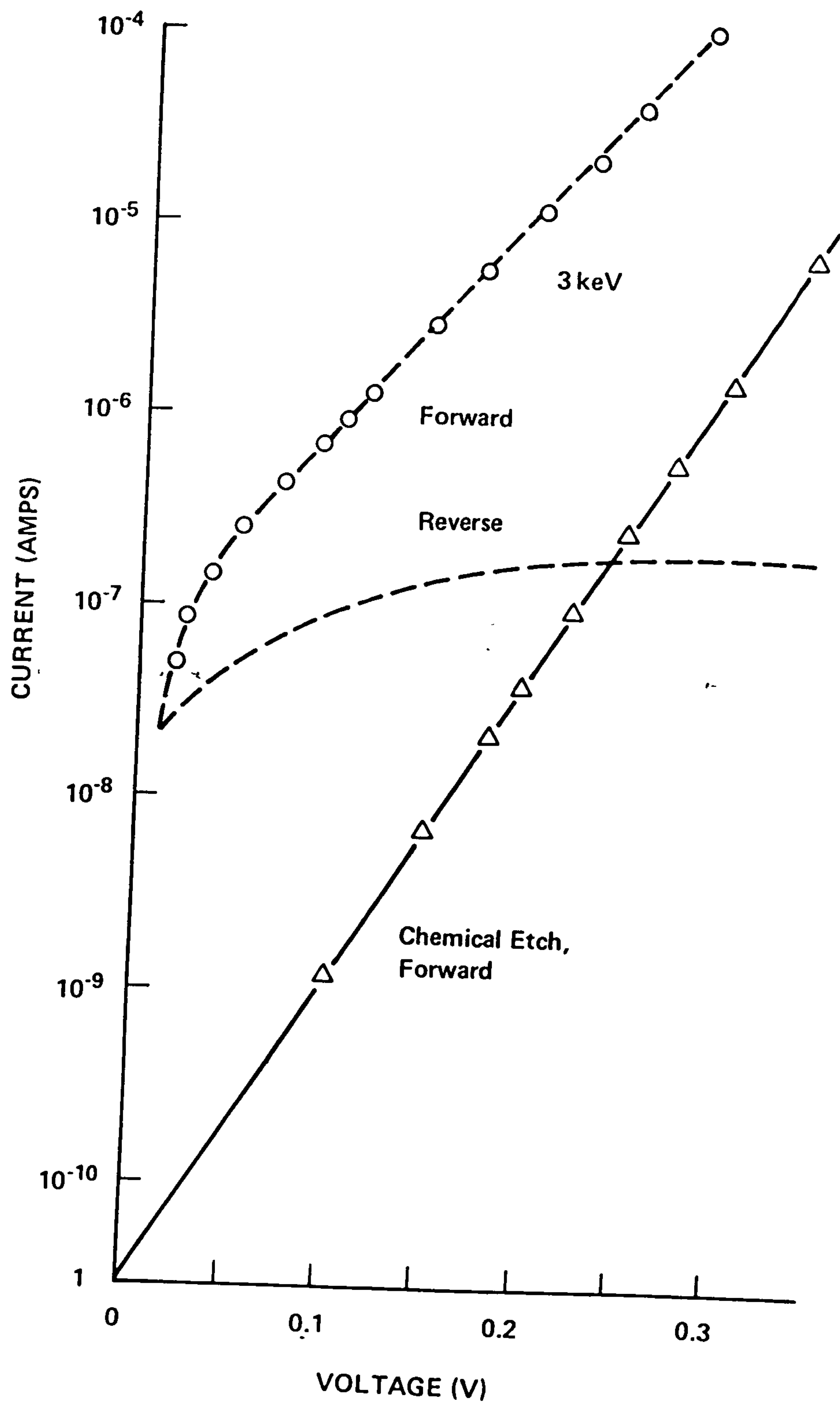
EVAPORATION
POWER SUPPLY
Ta SHIELD
GaAs SPECIMEN
SHADOW MASK
SAMPLE CAROUSEL
OR HEATING STAGE
W WIRE WRAPPED
WITH Au WIRE

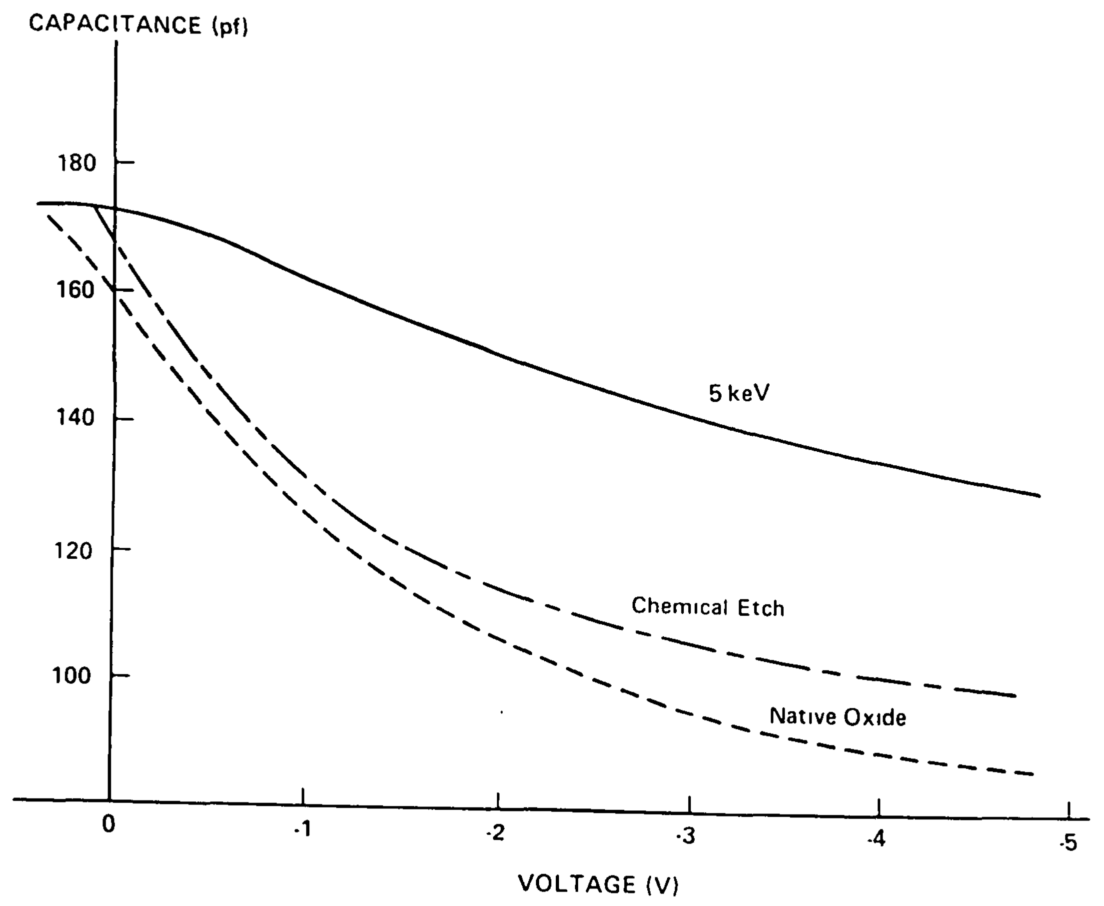

Chemically Cleaned
Ion Sputtered
Native Oxide
As
Ga
C- 272
0-510
0
500
1000
ENERGY (eV)
dN/dE (ARBITRARY UNITS)


1.00
.90
.80
.70
.60
ATOM FRACTION RATIO OF As TO Ga
THIS STUDY
SINGER, et al.
0
2
4
6
ION ENERGY (keV)



ATOM FRACTION RATIO OF As TO Ga
1.2
1.0
0.8
0.6
0.5
0
200
400
600
TEMPERATURE (°C)
ATOM FRACTION RATIO OF As TO Ga
1.2
1.0
0.8
0.6
0
4
8
12
16
20
TIME (min.)


10-4
10-5
3 keV
10-6
Forward
Reverse
10-7
CURRENT (AMPS)
10-8
Chemical Etch,
Forward
10-9
10-10
1
0
0.1
0.2
0.3
VOLTAGE (V)



CAPACITANCE (pf)
180
160
140
120
100
5 keV
Chemical Etch
Native Oxide
0
-1
-2
-3
-4
-5
VOLTAGE (V)