Properties and Degredation of Au-GaAs Contacts

P. H. Holloway, Lu-Min Yeh and Y.-J. Xie*

University of Florida, Dept. of Materials Science and Engineering, Gainesville, Florida 32611

ABSTRACT

The effects of ion bombardment upon electrical properties and reactions at Au-GaAs interfaces have been studied. Electrical data (I-V, C-V) showed that bombardment of (100)GaAs with 0.5 to 3keV Ar^+ prior to Au deposition resulted in lower surface carrier concentrations and increased depletion distances irrespective of dopant concentration (~10^{17} to 10^{19} cm^{-3}) or type (n-Si or Te- or p-Zn). These effects are consistent with Ar^+ creation of deep level bandgap states. Ion bombardment cleaning of GaAs resulted in accelerated reaction rates between Au and the substrate when atomic disorder remained, but annealing of bombardment damage resulted in an atomically clean, atomically ordered interface which was more stable during heat treatment. The presence of interfacial oxygen accelerated the reaction between Au and GaAs.

INTRODUCTION

Electrical contacts to GaAs are becoming more important because of increasing use of this compound semiconductor for optoelectronic and high speed devices. For these applications, both rectifying (Schottky) and ohmic contacts are necessary. Contrary to silicon-based devices, it has not been possible to vary the Schottky barrier height or induce ohmic contacts by varying the work function of the metal used to contact GaAs. This is because the Fermi energy of GaAs pins near midgap during creation of contacts, and there is very little variation in the pinned position as the metal is varied. Ohmic contacts have been made by increasing the surface doping density and switching the transport mechanism from thermionic emission to tunneling.[1,2]

In addition to pinned Fermi energy levels, contact metals are commonly deposited on GaAs by sputtering, which can cause surface damage by energetic ion or neutral bombardment prior to metal coverage. Reactive ion etching is often used for pattern delineation, and again energetic surface bombardment damage may result. Finally contaminants (organics, hydrocarbons, oxides and hydroxides) are often left at the metal/GaAs interface unless extraordinary measures are used, such as in situ ion bombardment cleaning of the surface. As a result, it is of interest to understand the effects of ion bombardment upon electrical behavior of gold contacts to GaAs. This subject has been studied before,[3-10] however the type of dopant (n or p- type) and dopant concentration range has been limited. Thus one objective of the present study was to investigate the effects of varying dopant concentration and type.

The second objective of this study was to characterize the effect of the interface composition and structure upon the reaction between Au and GaAs. It is well established that Au will react with GaAs at temperatures as low as ~350°C.[1,2,11] In fact, ohmic contacts of Au to GaAs are created by a "sintering" treatment in which deposited thin films of Au-Ge-Ni are reacted at ~430°C[1] for ~2 minutes under forming gas.[1] The reaction products are generally not uniform layers. The condition of the Au-GaAs interface was varied in this study to determine whether interfacial contaminants would affect this reaction.

EXPERIMENTAL

The effects of ion bombardment was studied on (100)GaAs wafers doped with

* Visiting Scientist from Changchun Institute of Physics, Changchun, People's Republic of China.

$1x10^{17}cm^{-3}$ or $2x10^{18}cm^{-3}$ Si or $1x10^{18}cm^{-3}$ Te (n-type), or $1x10^{18}cm^{-3}$ or $1x10^{19}cm^{-3}$ Zn (p-type). Alloyed indium ohmic contacts were made on the back surface prior to depositing Au in an ultra-high vacuum (UHV) chamber. The samples were cleaned with concentrated HCl just before inserting into the UHV system, then sputter with 0.5, 1 or 3keV Ar^+ striking the surface at ~35°. The beam shape was Gaussian at 3keV (4mm FWHM) with a total current of 5μA, but at 0.5keV the ~1μA beam was nearly uniform over a 5x5mm area. Auger electron spectroscopy (AES) was used to monitor the surface composition before and after sputtering using a 3keV, 25μA primary beam and collecting derivative data with 5eVpp modulation voltage. Sputtering was generally continued until all contaminants (C,O and N) were removed and the Ga and As peak to peak heights (PPH's) were constant with time. It is clear that As is depleted from the surface by ion sputtering[3,12] but angle resolved electron spectroscopy shows that As may be near the stoichometric value in the first atom layer of a sputtered surface.[12,13]

Immediately after ion sputtering, Au thin films (~1000Å) were deposited in situ then analyzed ex situ by I-V and C-V techniques. For comparison, Au was also deposited on surfaces prepared by etching in concentrated HF, rinsing in D.I. water and drying in N_2.

To study the effects of interfacial condition on the Au-GaAs reaction, samples of Au were deposited on surfaces etched with HCl+HF (chemically cleaned), ion sputter cleaned (3keV Ar^+), sputter cleaned plus annealed in $1x10^{-8}$ Torr vacuum at 570°C for one hour, or surfaces etched in H_2O/H_2O_2 mixtures to remove organics and hydrocarbons then heated to 570°C to thermally desorb the oxides and hydroxides from the surface.[2,3,14] Thin films of Au were deposited on these surfaces in UHV. Reaction of Au with GaAs was induced by heating to temperatures between 350°C and 500°C for times ranging from 3 to 60 minutes. The extent of reaction was characterized by stripping the gold film with a cyanide etch and measuring the density and size of reaction pits left on the GaAs surface.[11]

RESULTS

Effects of the Ion Bombardment

Depending on the dopant type and concentration, Au contacts on chemically etched GaAs were Schottky, nearly ohmic, or ohmic. After sputtering, the I-V behavior was distinctly different from contacts on chemically cleaned surface. The data on n-GaAs will be discussed first, followed by data from GaAs.

Typical forward I-V curves of Au contacts to Si doped GaAs are shown in Figure 1. For $10^{17}cm^{-3}$ Si, Log I_f versus V_f data from chemically cleaned samples were linear indicating Schottky behavior, but sputter cleaning resulted in soft diode I-V characteristics. The current was highest after bombardment with 0.5keV Ar^+, and it decreased monotonically as the ion energy increased. For $2x10^{18}cm^{-3}$ Si doping, Au contacts on the chemically cleaned GaAs acted nearly ohmic (as demonstrated in reverse bias with high current), but contacts on sputter cleaned surface were rectifying with dramatically reduced current. For a given ion energy, the current increased a factor of 100 as the doping concentration increased by a factor of 10. The I-V curves for sputter cleaned n-GaAs were independent of whether the dopant was Si or Te, although the current levels for Si-doped samples were about 50% lower than for Te-doping.

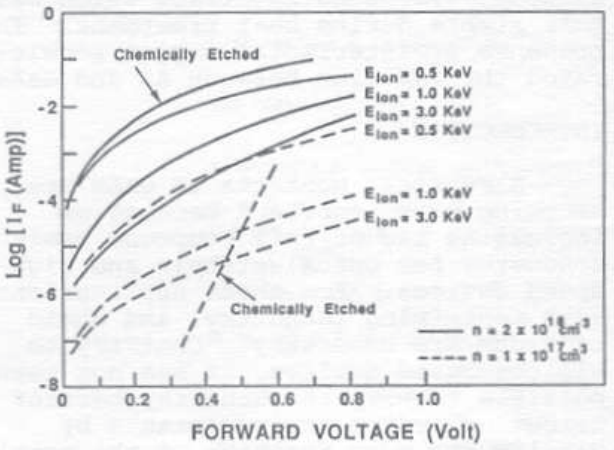


Fig. 1. Forward current versus voltage for contacts of Au on chemically cleaned or sputtered n-type GaAs doped by $1x10^{17}cm^{-3}$ or $2x10^{18}cm^{-3}$ Si.

Plots of log I_f vs. log V_f were linear for $2x10^{18}cm^{-3}$ Si or Te doped GaAs sputtered with 500eV Ar^+ which indicates that $I = I_o V^m$, where I_o and m are constants. Forward I-V data above 0.1V was described by $I = 0.08\ V^{2.1}$ for Si-doped and $I=0.6V^{2.7}$ for Te-doped GaAs

(I in amps and V in volts). For contacts on n-type GaAs with a lower Si-doping or higher energy Ar^+ sputtering, only part of the I-V curves ($0.1V < V < 0.5V$) can be fitted by $I = I_o V^m$.

For contacts to p-GaAs, the I-V behavior had both similarities and differences as compared to those on n-GaAs. Contacts on chemically cleaned GaAs doped with 10^{19} cm^{-3} Zn were ohmic, while those on 1×10^{18} cm^{-3} Zn-doped GaAs were nearly ohmic (Figure 2). All contacts to sputtered surfaces exhibited soft rectification with dramatically reduced current. Similar to n-typed samples, the current increased by 30 as the doping concentration increased by ± 10. In contrast to n-type materials, Ar^+ energy did not have a large effect on the current level in p-GaAs and the current was lower for p than for n-GaAs. In addition, there were intersections between the I-V curves for p-GaAs of the same doping density but different Ar^+ energy.

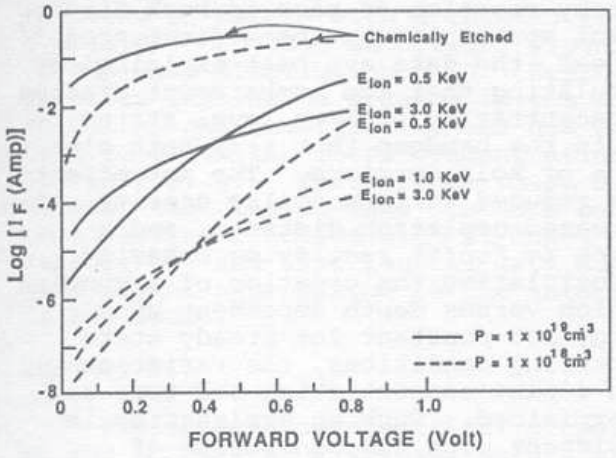


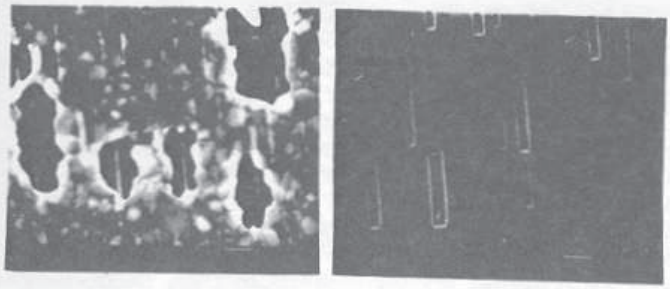
Fig. 2. Forward current versus voltage for Au contacts on chemically cleaned or sputtered Zn doped p-GaAs.

Measurements of C-V data could not be performed on ohmic or near-ohmic contacts, so contacts to chemically cleaned surfaces could not be measured on every substrate. However, all the contacts on sputtered GaAs were rectifying and in general capacitance were decreased by sputtering with larger decreases at higher energies.

Assuming changes in the GaAs dielectric constant are negligible, the depletion depth is equal to the contact area times the dielectric constant divided by capacitance. Depletion depths were calculated by assuming uniform carrier concentration and a Au contact barrier height of 0.9eV or 0.42eV on n- and p-type GaAs, respectively[15]. Depletion depths on both n and p-GaAs were increased by Ar^+ sputtering, and larger depths resulted from higher Ar^+ energies. The increases in depletion depth was larger for p-GaAs than for n-GaAs (comparing similar doping concentration). For contacts to sputtered GaAs of the same doping concentration, slightly larger depletion depths were found on Si-doped than on Te-doped samples. Increased capacitance with increased reverse bias was observed on some samples. Effective carrier concentration profiles were calculated from C-V data[15] and the data show changes in the ratio of effective carrier concentration with depth. For samples with depletion depths greater than 1000A, the calculated concentrations were the same as the manufacturer's specified values. For shallow depletion depths, the calculated concentrations were lower than the value specified by the manufacturer. Because the effective carrier concentration is less and the depletion depth is increased, Ar^+ sputtering apparently results in removal of carriers.

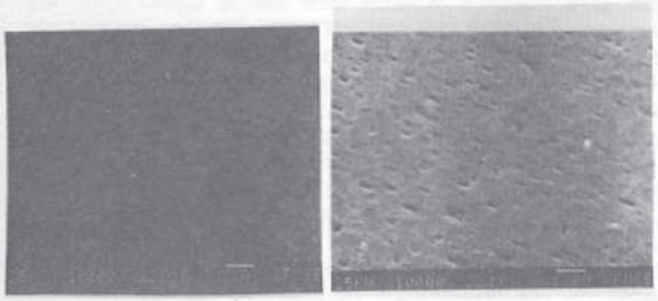
Effect of Surface Preparation

Uniform Au films were obtained on all as-deposited samples irrespective of the GaAs surface condition. Significant morphological changes occurred for Au films on chemically etched GaAs after annealing 3 min. at 380°C in UHV. As shown in Figure 3, after annealing the Au film was not uniform and the underlying GaAs (identified by point analysis with scanning AES) was partially exposed in the reacted areas. After stripping the top Au layer with a cyanide Au etchant, rectangular pyramidal reacted pits were revealed on the GaAs surfaces. The maximum pit length (L_{max}) was 3.5μm, the typical ratio of pit length to pit width (L/W) was about 9, the average Ga concentration in GaAs ($[Ga]_{Au}$) estimated from the amount of dissociated GaAs was about 5 at%, and the total density (D_T) of pits with $L \geq 0.1\mu m$ was about $1\mu m^{-2}$.



(a) (b)

Fig. 3. 1000A Au on chemically etched GaAs, after heating to 380°C for 3 minutes in UHV.
(a) surface morphology of the Au film,
(b) after stripping of the Au layer.



(a) (b)

Fig. 4. 1000A Au on thermally deoxidized GaAs, after heating to 380°C for 3 minutes in UHV.
(a) surface morphology of the Au film,
(b) after stripping the Au layer.

After a 3 min, 380°C anneal the Au film on thermally deoxidized GaAs was still uniform; no openings in the Au, symptomatic of extensive reaction, were observed. However small reacted pits were revealed after stripping the Au layer, as shown in Fig. 4. The L_{max} was about 0.5μm with a small L/W ratio of 3, and the DT was about $2\mu m^{-2}$. A similar morphology was observed for Au films on sputtered plus annealed GaAs after 3 min at 380°C (L_{max} about 0.4μm, L/W about 6). Both clean, annealed interfaces indicate a finite, but much smaller extent of reaction between Au and GaAs without oxides as compared to the reaction observed with thin oxides on chemically etched GaAs.

The morphology changes upon annealing of Au film on sputtered GaAs surfaces was considerably different from the others. The Au layer was discontinuous after heating to 380°C for 3 min and a high density of small square particles was observed. The ion beam used to sputter clean the surface had a Gaussian shape with a FWHM of 4mm, therefore different surface morphologies of reaction pits were obvious at different distances from the center of the sputter beam after annealing. Away from the sputter center, the extent of Au coalesce increased and the shape of the reaction pits changed from square to rectangular. Far away (7mm) from the center of sputtering, the reacted morphology was similar to that of chemically etched GaAs.

DISCUSSION

Effects of Ion Bombardment

While there are a number of possible explanations for the effects of ion bombardment on the transport of charge carriers across the Au-GaAs interface, dopant type conversion and thereby creation of back-to-back diodes by ion sputtering has been discounted.[15] Instead, the data are best explained by postulating that ion bombardment creates a concentration of deep level states within the bandgap that trap both electrons or hole carriers. The net effects is a reduced surface doping density and increased depletion distance, and a switch to "soft" rectifying behavior. By postulating the creation of a concentration versus depth dependent upon energy but constant for steady state sputtering conditions, the variation with dopant concentration and type can be explained. Such an explanation is consistent with the conclusion of previous studies.[3,6-9,15,16]

Earlier the reduced surface doping density has been suggested to result from site rearrangement for Si dopant during ion bombardment.[12] Silicon is an amphoteric dopant in GaAs and while it prefers to occupy the Ga sites and serve as an n-type dopant, at high concentrations it appears to compensate itself by occupying both Ga and As sites acting as both an n and p-type dopant. The dopant Te is not amphoteric in GaAs, and its behavior after ion bombardment was very similar, though slightly less modified by ion bombardment, therefore while some self compensation may occur during ion bombardment, the effect is a secondary one.

Effect of GaAs Surface Preparation

The condition of the GaAs surface obviously significantly affects the behavior of the two materials during heat treatment. The observation of more extensive reaction at the interface when oxides and hydroxides were present suggests that oxygen somehow accelerates the decomposition of GaAs. This is consistent with reports by Liliental-Weber, et al[17] that oxygen at the interface considerably modifies the reaction between Au and GaAs. The mechanism is unknown and largely undiscussed, however a reduction of the eutectic temperature in a quaternary (O-Au-Ga-As) system as compared to the ternary (Au-Ga-As) system is one possibility.

It is well established that the decomposition of GaAs in the presence of Au causes the Ga content of the overlying film to increase.[11,18,19] It is generally reported that As is not incorporated in the Au-Ga solid solution, but instead is released by sublimation to the ambient. However recent data show that GaAs regrows during continued heat treating of wafers with a thin Au film overlayer[20] through an Ostwald ripening of the GaAs dissolution pits. Regrowth requires that As be present in the solid solution, and quantitative AES has been used to establish these concentrations (~1 to 2 at.%). Furthermore these data suggest that the Au-GaAs contacts became ohmic during reaction with Si-doped substrates, and experimental data suggest that dopant segregation to the interface is the cause.[20]

SUMMARY

The effects on electrical properties of ion bombarding (100)GaAs wafers with Ar^+ at energies between 0.5 and 3.0keV has been studied as a function of dopant concentration (~10^{17} to 10^{19} cm^{-3}) and type (n or p). In addition the effects of atomic order and composition upon the interfacial reaction of Au and GaAs has also been studied. Ion bombardment resulted in a reduced surface carrier concentration and longer depletion depths in all instances, which suggests that Ar^+ creates deep level bandgap states which trap both hole and electron carriers. The result is a switch from near-ohmic behavior for highly doped n- or p-type GaAs to a "soft" rectifying contact for Au on ion bombarded GaAs. The condition of the GaAs surfaces strongly affected the reaction with Au thin films. Chemical cleaning, which leaves oxygen at the interface, accelerated decomposition of GaAs and formation of Au-Ga-As solid solutions. Similarly atomic disorder caused by ion bombardment also accelerated the reaction. Contrary to initial expectations, atomically clean and ordered surfaces resulted in less decomposition of GaAs and reaction with Au.

Acknowledgement: This research was supported by the US Army Research Office by Grant No. DAAG-29-84-K-0003.

REFERENCES

1. B. L. Sharma in Semiconductors and Semi-metals (Academic Press, NY, 1981) Vol. 15, Chap. 1.
2. L. J. Brillson, Surf. Sci. Repts. 2 (1982) 123.
3. Y. -X. Wang and P. H. Holloway, J. Vac. Sci. Technol. B2 (1984) 613.
4. A. Amith and P. Mark, J. Vac. Sci. Technol. 15 (1978) 1344.
5. S. Sinharoy and R. A. Hoffman, IEEE Trans. Elec. Dev. ED-3 (1984) 1090.
6. Y. A. Bitzurin, S. V. Gaponov, E. B. Klymenkov, and M. D. Strikovsky, Solid St. Commu. 45 (1983) 997.
7. J. M. Borrego, R. J. Gutman and S. Ashok, IEEE Trans. Nucl. Sci. NS-23 (1976) 1671.
8. P. D. Taylor and D. V. Morgan, Solid St. Elec. 19 (1976) 473.
9. M. E. Edweeb, E. J. Charlson, and E. M. Charlson, Appl. Phys. Lett. 43 (1983) 563.
10. W. J. Devlin, C. E. C. Wood, R. Stall and L. F. Eastman, Solid St. Elec. 23 (1980) 823.
11. G. H. Olsen, M. S. Abraham and T. J. Zamerowski, J. Electrochem. Soc. 114 (1974) 1650.
12. P. H. Holloway, Y.-X. Wang, Y.-J. Xie and T. D. Bussing in Thin Films: The Relationship of Structure to Properties, C. Aita and K. S. Sreeharsha, Eds. (North Holland, NY, 1985) 235.
13. T. D. Bussing, P. H. Holloway, J. Hammond and J. Moulder, J. Vac. Sci. Technol., in press.
14. A. D. Buonaquisti, Y.-X. Wang and P. H. Holloway, J. Vac. Sci. Technol. A1 (1983) 776.
15. L.-M. Yeh, Y.-J. Xie and P. H. Holloway, Submitted - J. Appl. Phys.
16. F. H. Mullins and A. Brunschweiler, Solid. St. Elec. 19 (1976) 47.
17. Z. Liliental-Weber, R. Gronsky, J. Washburn, N. Newman, W. E. Spicer and E. R. Weber, J. Vac. Sci. Technol. B4 (1986) 912.
18. T. Yoshiie, C. L. Bauer and A. G. Milnes, Thin Solid Films 111 (1984) 149.
19. C. L. Bauer, Surf. Sci. 168 (1986) 395.
20. L.-M. Yeh and P. H. Holloway, To be published.