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Materials & Molecular Research Division

Presented at the Materials Research Society
Fall Meeting, Boston, MA, December 2-7, 1985

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November 1985

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THE STRUCTURE AND ELECTRICAL PROPERTIES OF AU CONTACTS TO GaAs

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ABSTRACT

The structure and electrical properties of Au contacts to GaAs have been studied by analytical and high-resolution transmission electron Microscopy (TEM) combined with electrical characterization and photoemission spectroscopy (PES). The contacts were prepared by in-situ deposition of Au onto ultra-high vacuum cleaved n-GaAs (110) surfaces. The effects of annealing on the electrical, morphological and chemical properties of the Au:GaAs contacts were studied. It was shown that the formation of Schottky contacts is correlated with the change in stoichiometry of the GaAs substrate near the Au/GaAs interface. The change to Ohmic behavior for the samples annealed above Au-Ga eutectic was explained by leakage currents at the periphery of the devices. TEM micrographs of the structures revealed the existence of elongated Au crystallites on the GaAs surface at the periphery of the contacts. These leakage currents were eliminated by removing the current path at the periphery using a mesa-etch.

INTRODUCTION

Metal-semiconductor contacts, both Ohmic and Schottky, are crucial to semiconductor devices, but the physical mechanisms involved in their formation are not well understood. The simplest Schottky explanation [1] was that the barrier height is the difference between the metal work function and the electron affinity (for n-type semiconductors), and therefore the Schottky barrier height should be proportional to the metal work function. This is not the case for GaAs and many other semiconductors [2]. Observations show that the pinning position of the Fermi level for many metals as well as for oxygen falls within a narrow range of $\sim 0.95 \pm 0.1$ eV below the conduction-band minimum (CBM) for p-type GaAs and $\sim 0.7 \pm 0.1$ eV below the CBM for n-type GaAs [3-5]. Many models have been developed to explain these metal-independent midgap pinning levels. There were many attempts to explain the measured barrier heights in terms of semiconductor surface states, metal-induced gap states, anion clusters, or other defects near the interface.

One model, called the "effective work function," involves metallurgical effects, due either to clustering of adsorbed metal atoms or to disruption of the semiconductor lattice induced by metal deposition [6]. This model suggests that the Fermi level at the surface is not fixed by interface states but rather is related to the work functions of microclusters of the interface phases resulting from oxygen contamination or metal-semiconductor reactions that occur during metallization. For most compounds metallization or oxidation results in the formation of cation alloys along with anion compounds and in some cases free excess anions. The difference between the

This work was supported by Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and partly by the ONR and DARPA Contract No. N00014-83-K-0073.

work function of the free access anions which are released from the substrate during metalization and the semiconductor electron affinity is found to be in good agreement with the major barrier height of Au on many III-V and some II-VI compounds [6].

The results of photoemission spectroscopy (PES) studies on unannealed thin metal film/semiconductor systems (sub- to several monolayer coverages), led to the development of a microscopic model - the unified-defect model [3]. This model suggests that, for metal/III-V semiconductors, the localized states responsible for pinning the interface Fermi level are associated with native point defects, at or near the semiconductor surface, induced by the deposition of foreign atoms. Spicer et al [3-5] suggested that two defects are responsible for these two levels: an acceptor and a donor level. However Grant et al. [7] attributed these two levels to only one defect. Weber et al. [8] found experimentally that bulk As_{Ga} double donors have two energy levels identical with interface Fermi-level pinning positions. Thus an experiment is needed to test if such anion antisite defects are involved in the Fermi-level pinning at metal/GaAs interfaces.

PES studies indicate that the pinning position of the Fermi level at the unannealed Au:n-type GaAs interface is 0.9 ± 0.1 eV below the CBM. This is distinctly different from the pinning position of 0.7 ± 0.1 eV below the CBM for other metals on n-type GaAs [4]. Spicer et al. [5] suggested that the pinning position of the Fermi level of Au on n-type GaAs is at the donor level of the unified-defect model, due to the formation of an atomic dipole at the interface. The driving force for this dipole was attributed to strong tendency to attract electrons at the interface due to its large electronegativity. This depletes electrons from the 0.95 eV donors, thus pinning the Fermi level at that point even for n-type GaAs.

Interesting observations were made for thick metal film Au:n-GaAs devices annealed above the Au-Ga eutectic temperature (360°C). Leakage currents were found to dominate the I-V characteristics for annealed devices. This is believed to be caused by the Ohmic-like contacts that were found to occur at the periphery of the device [9-11]. Because Au has a high work function and is not known to form a shallow donor level in GaAs, the physical mechanism responsible for this "Ohmic" behavior is unclear at this time. These structures are of particular interest, as they allow one to study barrier-type behavior as well as Ohmic behavior in the same Au-GaAs system. Therefore, in this study electron microscopy and microscopic analytical methods were applied to as-deposited, annealed and mesa-etched Au contacts deposited on UHV-cleaved GaAs.

SAMPLE PREPARATION

Au diodes were prepared by in situ deposition of Au on n-GaAs (110) surfaces cleaved in ultrahigh vacuum (UHV) [9,11]. The intimate diodes were fabricated in the vacuum chamber, which was baked out to obtain UHV conditions, $\sim 2 \times 10^{-10}$ torr (base pressure). During the metalization the typical pressure was $< 4 \times 10^{-10}$ torr. Evaporation of the metal was performed using a resistance-type evaporator. Approximately 100 nm of gold was deposited in roughly 27 steps: 9 intervals each of 0.1 nm, 1 nm, and 10 nm evaporation. Each evaporation interval lasted 30-120 seconds. The samples were then allowed to cool for 30-120 seconds before the next evaporation interval. The metal thickness was determined by a quartz thickness monitor placed in close proximity of the GaAs sample. Two sizes of diodes, ~ 500 μm and 1000 μm in diameter, were defined by a shadow mask.

Annealing was performed for 10 min at 405°C in a N_2 atmosphere. Prior to annealing the samples were cleaned using TCE, then methanol, then DI water rinse (for ~ 2 min each).

EXPERIMENTAL METHODS

The study was carried out by transmission electron microscopy (TEM) methods: microdiffraction, bright-, dark-field, and high-resolution imaging, and a microanalytical method: energy-dispersive x-ray spectroscopy (EDXS). Plan-view and cross-section TEM specimens were observed in a JEOL JEM 200CX electron microscope with an ultrahigh-resolution pole piece operated at 200 KeV. EDXS was performed with a Kevex 7000 spectrometer on a Philips 400 electron microscope and with a Kevex 3400 ultrathin window detector and system 8000 spectrometer mounted on the JEOL 200CX TEM/STEM.

The same samples were used for both electron microscopy and I-V characteristic measurements. The structure of both the interface and the periphery of Au dots was examined both parallel and perpendicular to the interface plane. Cross-section specimens of $\{110\}$ and $\{100\}$ orientation were prepared by making sandwiches of GaAs/Au interface strips pressure-bonded with silver epoxy followed by annealing at 90°C for 30 min. Specimens were thinned to electron transparency by careful mechanical polishing to attain a mirror finish and a thickness less than $80\text{ }\mu\text{m}$. The samples were subsequently thinned by Ar ion-beam milling while being cooled with liquid nitrogen. For plan-sections only the gallium arsenide side was polished mechanically to $\sim 100\text{ }\mu\text{m}$ thick, followed by chemical thinning using chlorine gas in methanol. Only when a sample did not reach an electron transparency was it ion milled for a few minutes on one or both sides, depending on need.

EXPERIMENTAL OBSERVATIONS

1. As-deposited Samples

A general view of the distribution of Au-Schottky diodes on GaAs substrates is shown in Fig. 1. As can be seen, flat areas on the surface are separated by a number of cleavage steps which are clearly visible in the figure.

The as-deposited layer of Au was polycrystalline with a grain diameter in the 10-50 nm range (Fig. 2).

For bigger single grains the orientation relationships between the substrate and the Au layer are $\{011\}_{\text{GaAs}} \parallel \{211\}_{\text{Au}}$, with $(0\bar{2}2)_{\text{GaAs}} \parallel (0\bar{2}2)_{\text{Au}}$ and $(200)_{\text{GaAs}} \parallel (\bar{1}11)_{\text{Au}}$; and $\{110\}_{\text{GaAs}} \parallel \{110\}_{\text{Au}}$, with $\langle 111 \rangle_{\text{GaAs}} \parallel \langle 111 \rangle_{\text{Au}}$. TEM observations of cross-section samples show additional relationships:

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Fig. 1. General view of Au diodes on GaAs.

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Fig. 2. Polycrystalline layer of Au in an as-deposited sample.

$\{001\}_{\text{GaAs}} \parallel \{\bar{2}33\}_{\text{Au}}$ with $(2\bar{2}0)_{\text{GaAs}} \parallel (0\bar{2}2)_{\text{Au}}$ and $(220)_{\text{GaAs}} \parallel (311)_{\text{Au}}$. The unannealed interface is found to be atomically flat (Fig. 3); a confirmation of earlier work done on unannealed chemically prepared samples [12].

The periphery of the Au diodes (dots) repeats the shape of the mask through which the Au was evaporated. There is no evidence of Au migration outside the deposited dots (Fig. 4).

EDX spectra were taken in different areas of the cross-section samples, starting in the substrate far from the interface and approaching the interface at ~ 10 nm steps until the electron beam reached the top of the Au layer. The nanoprobe mode was used for the experiment with a beam diameter ~ 4 nm. The ratio $\text{AsK}\alpha/\text{GaK}\alpha$ remains constant in the substrate far from the interface. In the area within ~ 10 nm from the interface with Au, a slight increase in the intensity of As lines were observed in most cases, suggesting accumulation of the As near the interface. The $\text{AsK}\alpha/\text{GaK}\alpha$ ratio near the interface increased ~ 1.5 – 2% compared with the ratio on the substrate far from the interface. In the Au layer the diffusion of both Ga and As was observed, with clear Ga domination on the Au surface. The spectra from these particular areas are shown in Fig. 5(a–c).

2. Au Layer on GaAs Annealed at 405°C

The interface between the Au layer and the UHV-cleaved GaAs remains flat and abrupt after annealing for 10 min at 405°C in a N_2 atmosphere (Fig. 6a). This is in contradiction to the work of Yoshie [12], who observed protrusions growing on the interface after annealing at elevated temperatures. Our work shows that such protrusions were observed only when Au was deposited on air-exposed cleaved GaAs surfaces and subsequently annealed at 405°C (Fig. 6b). (The Au deposition and annealing treatment for the sample shown in Fig. 6b was performed in the same chamber and vacuum condition as was used for UHV-cleaved samples.)

So that the air exposed surfaces were not subjected to any unnecessary heat before metalization, a chamber bakeout was not performed. For the diodes produced on the air-exposed surfaces, the pressure during metal deposition was approximately 10^{-7} torr. This demonstrates that the formation of protrusions is not the result of annealing at elevated temperatures alone, and is clearly affected by the surface preparation technique. For UHV-cleaved surfaces the interface remains flat upon annealing except in areas where cleavage damage occurred. In such places voids were present on the interface, and the gold layer followed the shape of the cleavage damage (Fig. 7a,b).

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Fig. 3. The Au/GaAs interface in an as-deposited sample.

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Fig. 4. The periphery of the Au diodes in an unannealed sample.

Fig. 5. The EDX spectra taken: a) on the GaAs substrate far from the interface; b) on the GaAs about 10 nm from the interface; c) on the Au layer about 4 nm from the substrate.

Moire' fringes with a periodicity of 1.5 nm, which is typical for Au, are observed on the whole Au layer (Fig. 7b). The fringes suggest that after annealing new crystallographic phases are not formed.

Selected-area-diffraction patterns taken from the interface do not show any additional spots other than those characteristic of Au. The crystallographic relationship between the layer and the substrate in cross-section samples remains: $\{001\}_{\text{GaAs}} \parallel \{233\}_{\text{Au}}$ with $(220)_{\text{GaAs}} \parallel (022)_{\text{Au}}$ and $(220)_{\text{GaAs}} \parallel (311)_{\text{Au}}$. This shows that the two different $\langle 110 \rangle$ directions in GaAs are not equivalent with respect to epitaxial Au regrowth and that GaAs does not behave as a cubic crystal. This phenomenon was discussed by Kuan for Pd on GaAs regrowth [13].

Clusters of another phase were consistently observed within ~ 10 nm of the Au interface. EDX spectra show an increase in the $\text{AsK}_{\alpha}/\text{GaK}_{\alpha}$ ratio of ~ 5 –6% compared to the ratio on the substrate far from the interface. In

Fig. 6. The Au/Ga interface after annealing at 405°C for 10 min. in a N_2 atmosphere. a) UHV-cleaved GaAs with *in situ* Au deposition; b) GaAs cleaved in air; the Au was deposited under the same vacuum condition as sample a) after the sample was exposed about 2 hours in air. XBB 857-5110

Fig. 7. The Au layer on the GaAs with cleavage damage: a) bright field; As precipitate marked by arrow b) dark field; the same Moire' fringes are present on the whole Au layer. XBB 857-5111

addition, some significantly larger precipitates were formed (Fig. 7b) near the voids created on the cleavage steps (not immediately next to them but between them). The selected-area-diffraction pattern of those large precipitates shows spots characteristic of hexagonal As. The phenomenon of As precipitate formation between voids was already observed by Sands et al. on oxidized GaAs surfaces [14].

The formation of small clusters and large As precipitates, along with the increase of the As/Ga ratio in the vicinity of the interface with Au is strong evidence that most of the As accumulates in these areas and only part of the As diffuses into Au together with Ga, so that the Ga concentration in the Au layer is always larger than the As concentration. The accumulation of As in the semiconductor about 10 nm from the interface is more pronounced in annealed samples than in as-deposited samples.

An interesting phenomenon was observed on the periphery of Au contacts annealed at 405°C. Diodes annealed at this temperature changed to Ohmic behavior [9,11]. This has been shown to be caused by leakage currents at the periphery of the devices. TEM micrographs of the structure revealed the existence of elongated Au crystallites on the GaAs surface at the periphery of the contacts (Fig. 8). Analytical microscopy (EDX) in plan

Fig. 8. The periphery of Au diodes in annealed samples; the extended Au crystallites responsible for the Ohmic behavior. XBB 857-5112

view established that these elongated Au crystallites are Ga-rich, and are most probably responsible for the Ohmic behavior of those contacts. Mesa-etching of the annealed contacts removed the current path at the periphery of the contacts (1-3 μm), so that the contacts again showed Schottky behavior, with a barrier height approximately 0.1 eV to 0.15 eV below the barrier height of the unannealed Au/GaAs diodes. The decrease in the barrier height upon annealing has been attributed to the formation of a Au-Ga alloy at the interface, resulting in a smaller electronegativity overlayer as compared to the pure Au film [9,10]. Elec-

tron microscopy did not show any extended crystallites at the periphery after mesa-etching. In some cases, where the etching time was too short, the leakage current was significantly reduced in magnitude after mesa etching but was not completely eliminated. The periphery of such contacts was not as smooth as the periphery of asdeposited contacts. These findings suggest that these elongated crystallites are responsible for Ohmic contact formation, because the other areas of the contacts remain the same before and after mesa-etching.

Conclusions

Our results on unannealed and annealed UHV-cleaved and *in situ* deposited Au layers on GaAs and on air-exposed samples showed clearly that the abruptness of the interface depends critically on both the surface preparation and the annealing temperature.

Au does not form new phases upon annealing. A significant amount of Ga was observed in the Au layer, but presumably not enough to form a new crystallographic phase. The observation of significant concentration of Ga on the Au surface would explain why the surface layer of Au was melted and a flow of Au was observed in the shape of elongated crystallites on the periphery of the contacts. These crystallites were responsible for the

change from Schottky to Ohmic behavior. It is interesting to observe that, using the same metal (Au), it is possible to avoid the barrier formation at the Au/GaAs interface, if the Au is not vacuum deposited onto the semiconductor surface, but rather if it is allowed to flow out onto the semiconductor substrate at the periphery of the device. Such a process occurs during annealing of the Au/GaAs contacts. It would suggest that the different amounts of energy released during Au solidification from the vapor phase leads to the formation of the Fermi-level pinning defects with states near midgap while gentle deposition that occurs during flow of liquid Au-Ga alloy from the Au layer leads to a low defect density and Ohmic Au/GaAs interfaces.

Our observations show that crystal stoichiometry can be important for contact properties. A Schottky barrier is observed when As accumulates near the interface. These findings support both the point-defect model, the point defects probably being anion antisite, and defect-anion clusters responsible for Schottky-barrier formation.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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