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Publication Date

1987-02-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

APR 22 1987

Presented at the Conference on Physics and
Chemistry of Semiconductor Interfaces,
Salt Lake City, UT, January 27-29, 1987

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January 1987

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CONTACTS ON GaAs

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This work was done with support from the U.S. Department of Energy
under Contract No. DE-AC03-76SF00098

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Abstract

This paper reports a study of the structural and analytical properties of Au and Al contacts on GaAs and their change in the range of temperatures where the Schottky barrier height changed. The annealing of Au contacts above 290°C caused the Schottky barrier height to decrease, an effect opposite to that of Al, where the Schottky barrier height increased upon annealing. An increase in As in the GaAs under the as-deposited metal was consistently found in both cases, whereas annealing seems to change the As/Ga ratio in an opposite way for Au and Al. The orientation relationship of the Au contacts changed upon annealing, which was not observed with the annealed Al. The orientation relationship depended strongly on the surface preparation before the metal deposition and on the annealing environment. It was proposed that the presence of As at the interface can determine the orientation relationship between metals and GaAs.

I. Introduction

The basic mechanisms of formation of ohmic and barrier-type ("Schottky") contacts on GaAs are still a subject of controversy, despite intense investigations in this field [1]. All experimental data agree that the barrier height for all measured metals on GaAs falls within a few tenths of an eV in the midgap region. Measurements of barrier heights for many metals deposited in situ on UHV cleaved GaAs by I-V and C-V characteristics by Newman [2] seem to be very consistent. They show the same ideality factor $n = 1.05$ independent of reactivity of particular metals. The lowest barrier height found on n-GaAs was for Cr ($\phi_b = 0.67$ eV), and the highest was for Au ($\phi_b = 0.92$ eV). In this paper the correlation between electrical and structural properties will be discussed, particularly for Au, which is considered non reactive metal in a closed system [3], and for Al, which is known to form ternary phases with GaAs for all concentrations of Al.

II. Au-Schottky Contacts

1. Electrical Characteristics

The barrier height for Au deposited on UHV cleaved GaAs surface at room temperature is $\phi_b = 0.92$ eV [4]. This value changes to $\phi_b = 0.8$ eV upon annealing at 290°C. After annealing above ~360°C, Au contacts no longer show any rectifying behavior; they show ohmic behavior, which is associated with the periphery of Au contacts [4-6]. (This problem will be discussed later.) After mesa-etching or sputtering [7] when the periphery was removed, the decreased barrier height of 0.8 eV was still observed, and it did not change when annealing (and mesa etching after

this) was performed at higher temperatures. This noticeable change from 0.92 eV to 0.8 eV will be compared to the Au structure and composition change upon annealing.

2. Structural Characteristics

The study was carried out using both transmission electron microscopy (TEM) and analytical electron microscopy methods. Plan-view and cross-section TEM specimens were observed in JEOL 200CX electron microscopes (with high-resolution polepiece and analytical polepiece) and the atomic resolution microscope (ARM) in Berkeley.

The structure of 100-nm-thick Au layers was compared for contacts formed three ways: (1) on ultrahigh-vacuum (UHV) clean, cleaved samples; (2) on samples cleaved in air; and (3) on chemically cleaned GaAs substrates.

The as-deposited Au layer was found to be polycrystalline in all three cases, with grain diameters in the 10–50 nm range. The largest grain size was found in UHV-deposited Au samples (Fig. 1a). Some of these grains were twinned along {111} planes. Such unannealed Au layers observed in cross sections show atomically flat interfaces with GaAs [5]. Some of these grains, particularly in UHV-cleaved samples, were in the (211) or (011) orientation parallel to the (011) GaAs substrate orientation, but generally the grains were randomly oriented, resulting in diffraction patterns with textured rings (Fig. 1b). The differences between these samples appeared after annealing.

For the samples formed on the atomically clean GaAs surface and subsequently annealed for 10 min at 405°C in a N₂ atmosphere, the Au

layer was almost monocrystalline, with the smallest grain size ~ 500 nm. Most of the grains were elongated along $[01\bar{1}]_{\text{GaAs}}$. Their orientation relationship towards the substrate was $(211)_{\text{Au}}$ slightly tilted from $(011)_{\text{GaAs}}$ with $[02\bar{2}]_{\text{Au}}$ rotated slightly from $[02\bar{2}]_{\text{GaAs}}$ and $[\bar{1}11]_{\text{Au}}$ rotated slightly from $[200]_{\text{GaAs}}$. In a few cases the orientation relationship was $(011)_{\text{Au}} \parallel (011)_{\text{GaAs}}$. Two neighboring grains could differ in orientation. On the dark-field image in Fig. 2 the (211) -oriented grains were in the reflecting position and the (011) oriented grains were not. Both of those grains were elongated along common $[01\bar{1}]_{\text{GaAs}}$ direction.

Prism-shaped features parallel to the same $[01\bar{1}]_{\text{GaAs}}$ were observed within the grains or on the grain boundaries. Their nature was discussed previously [8].

The interface with GaAs in these samples remained flat upon annealing. This was the first observation of a flat and abrupt interface for Au/n-GaAs diodes annealed at these temperatures [8]. Even for these "perfect" interfaces a lattice distortion ~ 0.5 – 1 nm thick was observed in the interfacial region (Fig. 3). The atomic arrangement in this area obviously is different from that in the bulk semiconductor, and the presence of point defects and even the possibility of dislocation formation can be considered.

For samples cleaved in air and annealed at 405°C for 10 min in N_2 atmosphere, many small grains, highly twinned and dislocated with irregular shapes, were observed in plan-view samples. The larger grains had two different shapes: triangular and rectangular (Fig. 4). These two grain shapes differ in their orientation relationship to the GaAs

substrate. The triangular-shaped grains were $[011]_{\text{Au}} \parallel [011]_{\text{GaAs}}$. Holes were often present in the Au layer adjacent to one side of the triangular grains. These holes might have been GaAs particles embedded in the Au layer [8]; these particles were preferentially etched during the sample preparation. The rectangular grains were $(211)_{\text{Au}}$ slightly tilted from $(011)_{\text{GaAs}}$. The longer axis of the rectangular grains was elongated along $[01\bar{1}]_{\text{GaAs}}$. The presence of these grains is reflected by the interface morphology.

In cross sections two different shapes of protrusions were found extending into the GaAs: (1) triangular protrusions whose sides were delineated by GaAs $\{111\}$, and (2) multifaceted protrusions delineated by GaAs $\{111\}$, $\{110\}$, and $\{100\}$. The details of these studies were presented in earlier work [6,8].

For comparison to diodes used in typical commercial GaAs processing technology, diodes were formed by electron-beam evaporation on chemically prepared (100) GaAs substrates. For these samples annealed at 405°C for 10 min in flowing forming gas (95% Ar and 5% H_2), observed in plan-view, characteristic long Au grains elongated along only one $\langle 110 \rangle$ direction were observed (Fig. 5). These long grains were seen in cross section as monocrystalline grains (Fig. 6) protruding through the existing oxide layer into the GaAs substrate [6,8].

The orientation relationship for all samples will be discussed in a separate chapter.

3. Rectifying Behavior of Au Deposited and Annealed In-Situ in UHV

To observe how the formation of new phases at the interface can influence the Schottky barrier height, another experiment was performed on thin Au layers. It was known from the phase diagram [3,9] that annealing of Au/GaAs in an open system will lead to the formation of Au-Ga phases. Therefore, 10 nm of Au was deposited in situ on UHV-cleaved GaAs samples in the form of dots (as was done for 100 nm of Au discussed previously [5]) and annealed in situ in UHV for 10 min at 405°C. After the sample was cooled down, 90 nm of Au was deposited through the same mask in the UHV system. Plan-view and cross-section samples were prepared from the areas where annealed and unannealed samples were overlapping.

The 10 nm thick Au layer clustered during UHV annealing and protruded into the GaAs substrate. The unannealed 90 nm-thick Au (deposited later) forms a uniformly thick layer that covers both the protrusions and the areas between them (Fig. 7). These protrusions were large grains of Au embedded in a newly formed AuGa_2 phase ($a = 0.607 \text{ nm}$) that separated Au from GaAs. (In a few cases a Au_7Ga_2 phase ($a = 0.77 \text{ nm}$, $c = 0.875 \text{ nm}$) was found as well.) It was not surprising that these phases were formed because annealing in an open system (e.g., vacuum) leads to the dissociation of GaAs and the evaporation of As. (A special experiment where GaAs was annealed in-situ in the HVEM microscope with an N_2 environmental cell, at 120 mbar pressure and 400°C and above showed that As was depleted from the GaAs surface a few nanometers deep.) Therefore, excess Ga forms the chemical reaction with Au. Formation of an AuGa_2 intermediate layer makes a perfect match between GaAs, AuGa_2 , and

Au.

I-V characteristics were measured on those diodes (dots) where in situ annealed and unannealed Au were overlapping. To avoid any confusion with the periphery, mesa etching was performed on these diodes before I-V measurements. The measurements showed rectifying behavior of the diodes despite the formation of other phases on the interface. The measured barrier height was 0.93 eV [10] similar as it was measured for the unannealed samples described earlier. This is a very important finding, that formation of new crystallographic phases does not significantly influence the Fermi-level pinning.

4. Stoichiometry Changes under Au Contacts to GaAs

An analytical electron microscopy (EDX) study of cross-section Au/GaAs samples consistently showed an increase of the As/Ga ratio near the interface with Au. This was observed in as-deposited and annealed samples, with even higher As/Ga ratios in the latter case. As was mentioned before [11], the additional As near the interface shows metastable behavior and can be observed only in freshly prepared samples for a short time. This behavior was not observed when EDX spectra were accumulated on GaAs far from the interface.

To avoid any artifacts during the experiment (e.g., secondary excitation from heavy Au), cross-section samples were prepared from Au/GaAs interfaces when a thin Au foil was only mechanically pressed on GaAs. Measurements identical to those done previously (with short and long acquisition times) were repeated on those samples. In this case, the same As/Ga ratio was observed both far from and close to the interface,

and no acquisition time dependence occurred. The result of this experiment confirms the observation of As accumulation near the interface under the Schottky contacts. The instability of the additional As suggests that those As atoms are bonded differently near the interface compared with As in the bulk substrate, and the interfacial area can have a high concentration of As-rich defects. From this we conclude that metastable, As-rich defects are formed near the interface during metal deposition.

Figure 7a gives the clear evidence for the existence of distorted regions in the semiconductor near the Au/semiconductor interface. This area shows the deviation from crystal stoichiometry in the anion-rich direction. Similar results of As enrichment near the interface were observed on Al/GaAs and $\text{TiSi}_2/\text{GaAs}$ interfaces [11]. This observation can be significant for the mechanism of Schottky barrier formation.

5. Ohmic Contacts-Periphery and Au Diodes

As was shown in [4], I-V characteristics change their character by four orders of magnitude upon annealing, and the diode does not show rectifying behavior. This change was attributed to the presence of elongated crystallites on the periphery of the Au diodes [5,6].

Figure 8 shows such a periphery of an Au diode in as-deposited samples and in annealed ones before and after mesa etching. These crystallites are elongated along the $[01\bar{1}]$ direction, and they disappear after chemical etching (or sputtering). The GaAs after etching, under the elongated crystallites shows the few-micron step into the bulk substrate (Fig. 8c,d), either suggesting a different diffusion path for the

etchant beneath the crystallites or indicating some stress present on the periphery (such as an action similar to etching near the dislocation, leading to etch-pit formation).

Cross-sections from these crystallites are shown in Fig. 8e. They are partly embedded into GaAs, and the lattice image shows the Au lattice. The EDX data taken of the area under the embedded crystallites showed an increase of As, as was observed in the central part of the Au diode. Similar concentrations (less than 5%) of Ga were observed in both the central part and the peripheral crystallites. As was observed from the air - exposed samples, the presence of protrusions in the middle part of the diode does not change the electrical characteristics of the diode. This would mean that protrusions at the periphery act in a different way than these observed in the central part of diodes in air-exposed samples, but their action is still not fully understood.

III. Al Schottky Contacts

1. Al Deposited in situ on UHV-Cleaved Surfaces

Al deposited in situ on UHV-cleaved GaAs forms Schottky contacts with barrier height of 0.8 eV. After ex situ annealing for 10 min in N₂ atmosphere at 360°C or above the barrier height increases to 0.89 eV [12]. This contrasts with the behavior of Au, where the barrier height decreases upon annealing. Mesa etching of Al diodes did not change the electrical characteristics. Elongated crystallites at the periphery of the diodes were not observed upon annealing, as were observed for Au.

For Al deposited on UHV-cleaved GaAs, it appears that the interface with GaAs remains flat and that the Al (11 $\bar{1}$) planes form a 10° angle

with the GaAs (111) planes (Fig. 9a). This angle remains constant for grains with different orientations, as can be seen in Fig. 9b. Upon annealing at 375°C in N₂ for 10 min the interface remains flat. In some areas a very thin layer (50–100Å) of AlGaAs was formed.

The formation of AlGaAs did not occur uniformly. There were large areas where this phase was not detected even by (200) dark-field imaging, which is most sensitive to the structure-factor change. The particular grains of Al above AlGaAs or in intimate contact with GaAs did not change the orientation relationship upon annealing. The same 10° angle between (111) GaAs (or AlGaAs) planes and (111) Al planes was observed in annealed samples as in unannealed ones. This 10° rotation angle was already observed in annealed Au (see Fig. 3).

2. Al Grown in an MBE Chamber

Before Al deposition in an MBE chamber (base pressure $<1 \times 10^{-8}$ Pa), GaAs crystals were cleaned either by sputtering or by heating in the As beam at 600°C to remove the oxide. Subsequently an n-type GaAs buffer layer was grown to a thickness of 0.2–0.5 μm. After this procedure the substrate was cooled to the desired temperature, and Al was deposited without breaking the vacuum. Studies were done to observe the Al structure change for different substrate temperatures (T_s) and different surface reconstructions. First discussions of these results have been published elsewhere [13,14]. Elongated domains (40–70 nm long) parallel to the interface with GaAs were observed for deposition at $T_s = -30^\circ\text{C}$, with the (1×2) surface reconstruction. The thickness of these domains varied from 5 to 20 nm. When the domains were thin (~5 nm), clusters of several domains with clear facets were observed within 20 nm of the

interface. Some of these domains were identified as droplets of β Ga. No domains were observed when the substrate temperature was kept at room temperature or above. The interface where the domains were present was rougher than the areas where the domains were not present. Even in the areas between domains, the interfacial area (0.3–0.6 nm) showed some reconstruction. The Al between the domains and above them followed the fourfold symmetry of the substrate: $(100)_{\text{Al}} \parallel (100)_{\text{GaAs}}$ with $[001]_{\text{Al}} \parallel [011]_{\text{GaAs}}$. When Al was deposited on the substrate with $T_s = 25^\circ\text{C}$ and with the (2×6) surface reconstruction, most Al grains were in the same orientation as for lower temperatures. Monoatomic steps (2–4 Å high) were observed along the interface (Fig. 10a). Some other grains showed $(110)_{\text{Al}} \parallel (100)_{\text{GaAs}}$ with $[002]_{\text{Al}} \parallel [011]_{\text{GaAs}}$. No exchange reaction was discovered with dark-field imaging.

For depositions at 150°C and above with an As-stabilized surface, $c(2\times 8)$ triangular faceted islands were observed along the interface with the $(110)_{\text{Al}} \parallel (100)_{\text{GaAs}}$ orientation, where $[002]_{\text{Al}} \parallel [022]_{\text{GaAs}}$.

Two kinds of crystallographically equivalent (110) Al grains were observed rotated 90° from each other confirming earlier work by Ludeke et al. [15]. In this temperature range, formation of AlGaAs was observed. The thickness of the AlGaAs layer increased for the samples with $T_s' = 400^\circ\text{C}$.

In order to investigate the effect of high-temperature annealing, a sample with a Ga-stabilized surface deposited at $T_s = 0^\circ\text{C}$ ($c(8\times 2)$ reconstruction) was annealed in steps of 100°C -up to 700°C .

Long domains of Ga droplets (~ 20 nm thick and ~ 1 μm long) were observed in these samples, similar to droplets observed for the other

samples with $T_s < 25^\circ\text{C}$. Annealing at higher temperatures did not remove these droplets; in fact, their size even increased.

A mixture of Al(100)- and AlGaAs(110)-oriented phases was observed in these samples (Fig. 10b), with a large variation of Al concentration (from 5–100%). This showed that a AlGaAs layer was not formed uniformly after annealing at higher temperatures. This would support similar observations on cleaved GaAs surfaces, that annealing at 375°C caused only very discrete areas of AlGaAs. Large areas did not show this exchange reaction.

3. Stoichiometry under the Al Contacts

Two kinds of Al samples were studied by EDX spectroscopy: deposited in situ on UHV-cleaved GaAs, and MBE-grown with postannealing treatment. In both cases an increase of As in GaAs was found near the interface for as-deposited samples, as was observed for other metals. Comparing both samples, lower concentrations of As were observed in the MBE-grown samples with postannealing treatment, suggesting that different concentrations of As-rich defects can be expected in annealed samples. This observation would support the idea of the dependence of the Fermi-level pinning on the concentration of As-rich defects near the interface. A discussion of this model is given by Newman et al. [12].

IV. Orientation Relationship in Au/GaAs and Al/GaAs Interfaces

The orientation relationship between Au and GaAs for as-deposited samples was almost random for all samples. The largest grains were observed for Au deposited in situ on UHV-cleaved GaAs. The difference in the orientation relationship between differently prepared samples

occurred after annealing; these differences are shown in Table I. The type I and IIa orientation relationships were observed for most grains in Au (annealed at 405°C for 10 min in N₂) deposited on GaAs cleaved in air. These two types of orientation relationships were also found in the large grains protruding through the oxide layer in the chemically prepared samples (Fig. 6b). Type IIa is related to type I by twinning along the ($\bar{1}11$) planes (which correspond to a 70.5° rotation around $[0\bar{1}1]$). The samples with the type I and IIa contained a much larger number of twins than annealed Au samples with metal deposited in situ in UHV. Twinning into the type IIa orientation provides a better lattice match and releases the existing stress. There is a good match between $(442)_{\text{Au}}$ planes, $d_{442} = 0.068$ nm, and $(800)_{\text{GaAs}}$ planes, $d_{800} = 0.070$ nm).

Type IIb is related to type IIa by a 90° rotation around $[\bar{4}11]$ and gives a perfect match between the $(220)_{\text{Au}}$ planes with $d_{220} = 0.114$ nm and $(400)_{\text{GaAs}}$ with $d_{400} = 0.1413$ nm. The match between the $(110)_{\text{GaAs}}$ planes and $(100)_{\text{Au}}$ was expected because the lattice constants of GaAs and Au are related by $\sqrt{2}$. The 45° rotation on $(100)_{\text{Au}} \parallel (100)_{\text{GaAs}}$ with $[001]_{\text{Au}} \parallel [011]_{\text{GaAs}}$ should occur to fulfill the smallest misfit at the interface. This type of relationship was observed in Al samples (lattice constant close to Au) deposited in an MBE chamber on $(100)_{\text{GaAs}}$ [14] and on $(011)_{\text{GaAs}}$ [16]. Type IIb was observed in most cases for Au deposited on UHV-cleaved GaAs with in-situ postannealing. In these samples the formation of two types of Au-Ga phases was observed related to the two types of relationship with Au (type I and IIb). In the large grains protruded into the GaAs substrate, type IIb was observed, e.g., $(011)_{\text{GaAs}} \parallel (011)_{\text{AuGa}_2} \parallel (\bar{4}11)_{\text{Au}}$ with $[01\bar{1}]_{\text{GaAs}} \parallel [01\bar{1}]_{\text{GaAs}_2} \parallel$

$[\bar{1}\bar{2}\bar{2}]_{\text{Au}}$. In the unannealed 90-nm-thick Au sitting on the GaAs between these protrusions, many grains revealed a type I orientation relationship, e.g., $(01\bar{1})_{\text{GaAs}} \parallel (1\bar{1}0)_{\text{Au}_7\text{Ga}_2} \parallel (01\bar{1})_{\text{Au}}$ with $[01\bar{1}]_{\text{GaAs}}$ with $[01\bar{1}]_{\text{GaAs}} \parallel [001]_{\text{Au}_7\text{Ga}_2} \parallel [01\bar{1}]_{\text{Au}}$. However, formation of an Au-Ga phase is not necessary to fulfill the minimum mismatch on the interface, as described by Yoshiie and Bauer [17]. The mechanism is probably more general. Our data show that the Au orientation relationship for cleaved (110) GaAs surfaces depends on both the environment in which the GaAs surface was prepared before annealing and the annealing conditions, and not necessarily on the Au-Ga phases formed. The type I orientation relationship exists in annealed Au even when Au-Ga phase is not formed, but it is characteristic for annealed Au deposited on air exposed GaAs. A possible explanation for this behavior is that the $\gamma\text{-Ga}_2\text{O}_3$ grows epitaxially [18,19] as type I orientation: $(011)_{\text{Ga}_2\text{O}_3} \parallel (011)_{\text{GaAs}}$ with $[100]_{\text{Ga}_2\text{O}_3} \parallel [100]_{\text{GaAs}}$. This oxide provides an excellent lattice match to Au: $d_{400}(\text{Ga}_2\text{O}_3) = 0.205$ nm, as compared with $d_{200}(\text{Au}) = 0.203$ nm and $d_{044}(\text{Ga}_2\text{O}_3) = 0.145$ nm, with $d_{022}(\text{Au}) = 0.149$ nm. This observation would suggest that as soon as GaAs is exposed to air, epitaxial $\gamma\text{-Ga}_2\text{O}_3$ is formed, and the deposited metal is epitaxially related to the oxide already existing at the interface. The oxide on GaAs is not a continuous layer. In the areas where the oxide is not present twinning takes place, giving a better match at the interface.

The orientation relationship in UHV-deposited Au samples annealed ex situ in N_2 (405°C , 10 min as done for air-exposed samples) was completely different (see Fig. 3b) and was described as type III. (In our first publication [6] the orientation of the Au grains was described as

$\{211\}_{\text{Au}} \parallel \{011\}_{\text{GaAs}}$. A detailed study by high resolution electron microscopy [8] showed a slight rotation of lattice planes ($\sim 60^\circ$) which are indicative for a slightly different orientation of the normal of the grains, e.g., $\{522\}_{\text{Au}}$ instead of $\{211\}_{\text{Au}}$ being parallel to $\{011\}_{\text{GaAs}}$. This orientation is related to type I by a 60° rotation around $[0\bar{1}1]$. In this way a 10° angle occurred between $\{111\}_{\text{Au}}$ planes and $\{\bar{1}11\}_{\text{GaAs}}$ planes (measured on high-resolution pictures), which was observed not only in Au samples but also in Al and Ag [20]. This 10° angle was characteristic for all three metals (with similar lattice parameters) deposited in situ on UHV cleaved GaAs and annealed in N_2 .

This behavior can be explained hypothetically by As accumulation on the interface [6,15], and an earlier observation [18] of the relationship between As and GaAs. Arsenic on GaAs accommodates its basal plane $(001)_{\text{As}} \parallel (\bar{1}\bar{1}1)_{\text{GaAs}}$ with $[030]_{\text{As}} \parallel [242]_{\text{GaAs}}$. The metal probably tries to accommodate to the accumulated As. The best match can be achieved with $[422]_{\text{GaAs}} \parallel [030]_{\text{As}} \parallel [3\bar{1}\bar{1}]_{\text{Au}}$. The match between $[422]_{\text{GaAs}}$ and $[3\bar{1}\bar{1}]_{\text{Au}}$ was observed for many grains (Fig. 3b) and resulted in a 10° angle between $\{111\}_{\text{Au}}$ and $\{\bar{1}11\}_{\text{GaAs}}$. The $\{111\}$ planes of Au and GaAs is easy to observe in a high-resolution lattice image with ARM resolution of 0.16 nm, but neither $(422)_{\text{GaAs}}$ nor $(311)_{\text{Au}}$ can be observed ($d_{422} = 0.115$ nm). In unannealed Al deposited in situ on UHV cleaved GaAs grains with different orientation (different normal of the grains) were aligned in such a way that 10° angle between $\{111\}_{\text{Al}}$ and $\{111\}_{\text{GaAs}}$ lattice planes was observed for most of the grains. The orientation relationship did not change significantly upon annealing in N_2 .

Special alignment between different metals and GaAs support the idea that this effect originates from the substrate itself and that As (discovered in our earlier study) accumulated at the interface can determine the relationship between metals and GaAs.

In the case of MBE-grown samples, when Al was deposited on GaAs at room temperature and below, Al followed the fourfold symmetry of the substrate with a 45° rotation to fulfill the best match with the substrate, e.g., $(100)_{\text{Al}} \parallel (100)_{\text{GaAs}}$ with $[001]_{\text{Al}} \parallel [022]_{\text{GaAs}}$.

For substrate temperatures of 150°C and above, Al changes the orientation relationship to twofold symmetry: $(110)_{\text{Al}} \parallel (100)_{\text{GaAs}}$ with $[001]_{\text{Al}} \parallel [011]_{\text{GaAs}}$. (The surface reconstruction shows twofold symmetry as well) A similar orientation relationship fulfilling the minimum mismatch was observed for MBE samples grown on (110) surfaces [16].

V. Conclusions

This study showed that the interface morphology, the orientation relationship, and the formation of new phases strongly depend on the surface preparation of GaAs before metal deposition and/or on the annealing environment. The metals investigated (Au and Al with lattice parameters close to each other) deposited in situ on a UHV-cleaved GaAs surface show very similar relationships with GaAs upon annealing. This relationship changes when GaAs is exposed to air before metal deposition. The variously prepared contacts frequently showed crystallographically oriented metal grains after annealing. Only in the case of annealing in UHV, new Au-Ga phases were formed.

For all investigated Schottky contacts (Au, Al and TiSi_2) an increase in the As/Ga ratio in GaAs was observed near the metal-semiconductor interface, suggesting that the stoichiometry of the GaAs under the metal/semiconductor interface can influence the Fermi-level pinning. High-resolution electron microscopy showed evidence of lattice reconstruction and defect formation in the interfacial area, supporting defect models of Schottky barrier formation.

The Schottky barrier height was the same for the samples where newly formed Au-Ga phases were found as for the as-deposited metal.

The periphery of Au contacts showed ohmic behavior in areas where elongated Au crystallites protruded into GaAs. The protrusions observed in the central area of annealed Au contacts deposited on GaAs cleaved in air did not show this behavior. It is possible that stress at the periphery of the contacts might influence electrical properties.

Acknowledgements

This work was supported by the Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

The author would like to acknowledge N. Newman for the sample preparation, electrical measurements, and very fruitful discussion; Dr. R. Ludeke for Al samples grown in MBE; Dr. W.E. Spicer, Dr. P. Petroff, Dr. E.R. Weber and Dr. J. Washburn for inspiring suggestions and discussions. Electron microscopy was carried out in National Center for Electron Microscopy. The technical assistance of C. Nelson, C. Echer, D. Ackland and D. Ah Tye is also greatly appreciated.

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Table I.
Orientation relationship between Au and GaAs.

Crystallographic axis	x	y	z
GaAs	011	100	$0\bar{1}1$
Type I	011	100	$0\bar{1}1$
Type IIa	$\bar{4}11$	122	$0\bar{1}1$
Type IIb	$\bar{4}11$	$0\bar{1}1$	$\bar{1}22$
Type III	$\bar{5}22$	455	$0\bar{1}1$

Figure Captions

Fig. 1. a) Bright-field image of plan view of the unannealed Au layer deposition in UHV on cleaved GaAs: b) diffraction pattern from the area shown in a); dots represent the $[011]$ zone axis of GaAs, and textured rings represented Au; weak spots are due to double diffraction and twin spots.

Fig. 2. a) Dark field image of plan view of the Au layer deposited in UHV and annealed at 405°C for 10 min. The grains are elongated in the $[01\bar{1}]$ direction. Grains 1 and 2 were in different reflection positions. b) Diffraction pattern from two adjacent grains (1 and 2). Three different zone-axis patterns are visible: (1) $[211]$ zone-axis pattern of gold grain 1). (2) $[011]$ zone-axis pattern of gold grain 2). (3) $[011]$ zone-axis pattern of GaAs (GaAs indices are marked in boldface).

Fig. 3. a) High-resolution image of the Au/GaAs $(01\bar{1})$ interface annealed at 405°C for 10 min in N_2 atmosphere. Note the lattice distortion in the interfacial area and the twisting of all Au planes toward the GaAs planes. A 10° angle was measured between the $(111)_{\text{Au}}$ and $(\bar{1}11)_{\text{GaAs}}$ planes. b) Diffraction pattern for the image shown in a) with zone axis $[01\bar{1}]$. Note $[3\bar{1}\bar{1}]_{\text{Au}} \parallel [422]_{\text{GaAs}}$.

Fig. 4. a) Plan view of the annealed Au layer deposited on a GaAs substrate that was cleaved in air. Both rectangular and triangular grains are present. An arrow shows the hole in the Au. b) Diffraction pattern from a large area of the sample shown in a). c) Diffraction pattern of $[011]_{\text{Au}}$ zone axis from the

triangular grain. d) Diffraction pattern of $[211]_{\text{Au}}$ zone axis from the rectangular grain. The $[111]_{\text{Au}}$ direction is rotated slightly towards the $[200]_{\text{GaAs}}$ direction. This is the same orientation relationship that was observed for most grains in the UHV-cleaved samples. (The diffraction patterns b, c, and d were taken with different focal lengths).

Fig. 5. a,b) Bright-field image of a plan-view sample of an annealed Au layer deposited on (100) chemically cleaned GaAs. Note the long grains elongated along $[01\bar{1}]_{\text{GaAs}}$. c) $[001]$ zone-axis pattern of gold from an elongated grain.

Fig. 6. a) The Au/GaAs interface after annealing at 405°C for 10 min in forming gas (95% Ar and 5% H_2). Au was deposited on a chemically cleaned (100) GaAs surface. Note the Au elongated grain island protruding through the oxide layer (white band). b) $[01\bar{1}]$ zone-axis pattern of Au and GaAs with all axes parallel to each other (type I orientation relationship) and twinned spots marked by arrows (type IIa orientation relationship). The other diffraction spots are due to double diffraction. The diffraction pattern was taken from the interface between GaAs and the grain shown in e).

Fig. 7. a) Dark-field image of Au/GaAs interface in cross section where 10 nm of Au was deposited and annealed in situ on GaAs cleaved in UHV (marked by A) followed by 90 nm of unannealed Au (marked by B). Au annealed in situ (A) clustered and protruded into the GaAs, forming the Au-Ga phases. b) The lattice image of the AuGa_2 phase formed in the areas in direct contact with

GaAs, shown by the arrow in a). c) Diffraction pattern of AuGa_2 and GaAs taken from the interface between the protrusion and the substrate.

Fig. 8. a) SEM image of the periphery (p) of an Au diode (dot) deposited in situ on UHV-cleaved GaAs. b) The periphery (p) of an Au dot after annealing at 405°C ex situ in N_2 . Note the formation of small clusters and crystallites elongated along $[01\bar{1}]_{\text{GaAs}}$. c) The periphery (p) after mesa etching; the central part of the Au dot is marked by c. d) The magnified image of c) shows a deep step into GaAs, which was formed in GaAs in the area with elongated crystallites. On the circumference where Au clusters were present, the GaAs was flat after mesa etching, in contrast to the GaAs area outside the original Au dot. e) Cross-section image of an elongated crystallite showing a slight protrusion into the GaAs.

Fig. 9. a) High-resolution image of Al/GaAs interface for Al deposited in situ on UHV-cleaved GaAs. Note the 10° angle between the $\{111\}_{\text{Al}}$ and $\{111\}_{\text{GaAs}}$ planes. b) Diffraction patterns from three differently oriented Al grains showing a 10° angle between the $\{111\}_{\text{Al}}$ and $\{111\}_{\text{GaAs}}$ planes.

Fig. 10. a) High-resolution image of the Al/GaAs (100) interface grown in an MBE chamber with a 25°C substrate temperature. Note the 0.2 nm lattice image of the Al(200) planes and the -0.4 nm step at the interface. b) High-resolution image of the GaAlAs/GaAs (100) interface. Al was deposited on the substrate with a 0°C in MBE chamber and postannealed at 700°C . Note that the

interface is more rough than in the case shown in a).

XBB 868-6149

Fig. 1

XBB 872-1375

Fig. 3

XBB 868-6153

Fig. 4

Fig. 5

XBB 872-1379

Fig. 6

XBB 872-1378

Fig. 7

XBB 872-1377

Fig. 8

XBB 868-6147

Fig. 9a

Fig. 9b

XBB 872-1376

Fig. 10

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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