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Structure and electrical properties of metal-GaAs interfaces

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Abstract

The structure and related electrical properties of ohmic Au-Ni-Ge contacts, and Schottky: TiSi$_2$ and Au contacts are reviewed in this paper. Defects present in GaAs beneath the metal (anion rich - As accumulation) were suggested to be responsible for Schottky level pinning. It was shown that residual oxygen on the GaAs surface prior to metal deposition can strongly influence the interface abruptness, contact parameters and reliability of both ohmic and Schottky contacts.

Introduction

The fast development of modern device technology based on GaAs requires reliable and reproducible rectifying (barrier type - Schottky) and nonrectifying (ohmic) contacts. The physical mechanisms involved in their formation are still not well understood despite the amount of work done in this field.[1-4]

The barrier height of Schottky contacts on GaAs has been shown to be independent of the metal work function. Many models have been developed to explain the metal-independent midgap pinning levels. These include descriptions of semiconductor surface states,[5] metal-induced gap states,[1,6] anion clusters,[7] and point defects in the "unified-defect model."[8]

Because the subject of metal contacts to GaAs has attracted so much scientific interest and has such great practical importance, this paper aims to discuss a few examples of Schottky and ohmic contacts in detail in order to understand the mechanisms involved in their formation. These examples will represent the author's main interest and will include ohmic Au-Ni-Ge contacts and the following Schottky contacts: TiSi$_2$ deposited on chemically cleaned surfaces, and Au contacts treated 3 ways: (1) deposited in situ on ultrahigh-vacuum cleaved GaAs, (2) deposited on GaAs cleaved in air, and (3) deposited on chemically cleaned GaAs surfaces.

All semiconductor devices require stable and very low-resistance ohmic contacts. In fact quality of the ohmic contacts has been found to be a limiting factor in the performance of a number of GaAs-based devices. Usually the term "ohmic contact" refers to a contact that is noninjecting and has a linear current-voltage (I-V) characteristic, but in practice a contact is considered ohmic if the voltage drop across it is much smaller than that across the device. The criteria of a "good" ohmic contact is to make the contact resistance height as low as possible. This can be achieved either by using specific compounds with low barrier heights or by doping the semiconductor layer adjacent to the contact to increase the probability of tunneling.[9]

Experimental

The study was carried out by transmission electron-microscopy (TEM) methods: microdiffraction, bright-field, 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 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, GaAs/TiSi$_2$, and GaAs/Au-Ni-Ge interface stripes 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 µm. 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 100 µm 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. Electrical characterization of the contacts was performed by I-V and C-V (capacitance-voltage) electrical device measurements prior to the TEM study.

Au-Ni-Ge is the most widely used and extensively investigated contact system in the production of various GaAs devices.[10-15] In our study Au-Ni-Ge contacts were prepared by electron-beam evaporation of a 150-nm-thick Au-Ge layer (12% Ge), followed by deposition of a 50-nm-thick Ni layer and a 500-nm-thick Au layer. Four kinds of substrates were used: Si-doped horizontal Bridgeman-grown (100) GaAs, and LPE-grown n-$Ga_{1-x}Al_xAs$ (x = 10%, 22%, and 35%) doped with Te. The doping level for the last three samples was 10^{17}-10^{18}/cm^3. The substrate was not intentionally heated during the deposition. For alloying, the samples were annealed for 5 min at 450°C. The contact resistance of the alloyed contacts was (2-7) x 10^{-6} Ωcm^2 for n-GaAs and 10^{-4} Ωcm^2 for n-GaAlAs. TEM observations of the unalloyed Au-Ni-Ge contacts showed a layered structure consisting of Au, Ni, and Au-Ge layers, with thicknesses verified by TEM to be close to the intended values. No compound-phase formation among these layers in the as-deposited state was observed by Kuan.[11] However, in the author's work[10] two phases were occasionally observed at the interface with GaAs: AuGa (13% Ga) and NiAs. It was suggested that these phases were formed during the layer deposition; however, the possibility of local heating during sample preparation for the TEM study was considered. (Cross-section sample preparation involved heating for 1 h at 100°C for the epoxy-hardening process.) All layers were polycrystalline. In most cases the interface with GaAs was atomically flat.

After alloying in all four cases (GaAs and $Ga_{1-x}Al_xAs$), the interface with the substrate was not flat (Figure 1a). Protrusions extending up to 0.3 µm into the substrate were found in our study (Figure 1b). Selected-area diffraction (SAD) or convergent-beam
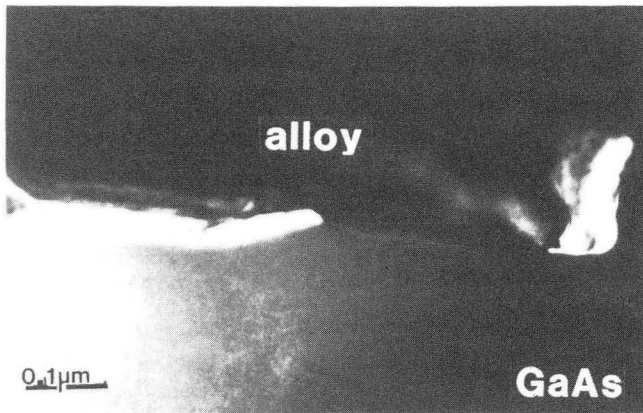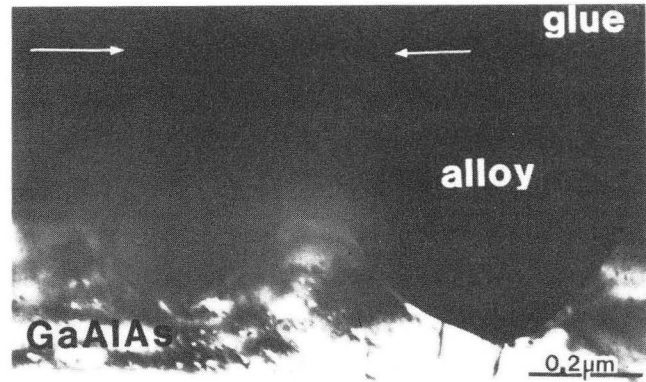
XBB 862-882A

Figure 1. a) Grains of different phases present on the alloy/GaAs interface.

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Figure 1. b) Protrusions on the alloy/GaAlAs interface.

electron diffraction (CBED) showed the different compositions of particular grains: Au, AuGa (13% Ga), NiAs, and a Ni-Ge-As ternary phase. The last phase was described by Kuan[11] as Ni_2GeAs, and it was found to be correlated with changes in contact resistivity. The formation of this phase by diffusion of Ge from the NiGe phase to the NiAs phase was believed to lower the contact resistance from greater than 10^{-4} Ω cm^2 down to about 1 x 10^{-6} Ωcm^2. It was argued that the formation of an n$^+$ layer, where the current transport dominated by tunneling, was very unlikely. However, in our study[10] Ge was found in the semiconductor substrate at distances of about 0.1 µm from the interface. It was not possible to detect Ge by EDX in any area where Au grains were present on the interface, because the GeK$_\alpha$ (9.81 KeV) and AuL$_\alpha$ (9.7 KeV) lines overlap, so that the low intensity of the Ge as a dopant does not allow reliable separation of these two lines. Only in the case of the absence of Au from the interface was Ge detected. Therefore both the formation of the ternary Ni-Ge-As phase and a possible Ge-doped n$^+$ layer were believed to be responsible for the low contact resistance.[10]

For the $Al_xGa_{1-x}As$ substrates, a higher density of triangular protrusions into the semiconductor was observed upon annealing. For these samples Ni was more often segregated into grains near the top of the contact surface. While for GaAs samples the highest Ni concentration was found at the semiconductor/metal interface. Obviously there is a strong interaction between Al and Ni in this system.

Braslau[14] has evaluated the effects of inhomogeneities at the contact interface and concluded that in alloyed contacts the measured resistance is dominated by the spreading resistance of the "good contact" protrusions. Those "good contact" protrusions are expected to be surrounded by a highly doped n$^+$ layer. For this model, the contact resistance (i.e. determined by the spreading resistance) would be inversely proportional to the size and density of the conducting areas.

In our study a different protrusion density was observed on GaAs and $Ga_{1-x}Al_xAs$ for Au-Ni-Ge contacts (with the highest density in the last case). So it was possible to check Braslau's protrusion model of low contact resistance. From the TEM observations a much lower contact resistivity would be expected using Braslau's model for contacts formed on $Ga_{1-x}Al_xAs$. The measured resistance for this contact was $(2-7) \times 10^{-4} \, \Omega cm^2$, and the calculated resistance was $2 \times 10^{-5} - 3 \times 10^{-8} \, \Omega cm^2$ on the basis of TEM results for different Al contents. For n-GaAs the measured resistance was $(2-6) \times 10^{-6} \, \Omega cm^2$, and the calculated resistance was $3 \times 10^{-6} - 2.8 \times 10^{-5} \, \Omega cm^2$. The differences between the measured and calculated values imply either that Braslau's model does not apply to GaAlAs contacts of the type investigated by us[10] or that there is a fundamental difference in the protrusions created for GaAs and GaAlAs. Electron-energy-loss spectroscopy (EELS) reveals the presence of oxygen in all contacts, especially in those formed on GaAlAs. The presence of oxygen is not desirable, because oxygen-rich compounds can form insulating areas between the contact material and the semiconductor.

Evidence for strain was observed on the interface due to the presence of various compound grains. This strain led to the different defect formations on the interface, such as dislocations and stacking faults. The presence of so many different compounds and defects on the interface makes such contacts not reproducible or reliable, especially in large-scale integration (LSI) technology. Aging of Au-Ni-Ge contacts can be explained either by defects present on the interface or (as suggested by Kuan) by a decrease in the density of low-resistance Ni_2GeAs areas.

Very interesting observations for Au-Ni-Ge contacts on GaAs were made by Callegari et al.[16] They showed that sputter precleaning of the GaAs substrates prior to the deposition of the Au-Ni-Ge films substantially improves the uniformity and thermal stability of the ohmic contacts. The contacts remain stable up to 600°C and do not deteriorate after thermal treatment at 410°C for 57 h. Good uniformity was achieved across a wafer, making the process very attractive for LSI technology. Unfortunately TEM studies were not done on these samples; therefore the structure of the alloy/GaAs interface is not known. X-ray diffraction was applied to the blanked sample, annealed at 410°C subsequently after contact formation at 440°C. Diffraction peaks corresponding to Au_3Ga and Ni_2GeAs were observed. According to these studies Ge atoms diffuse into the Ga vacancy sites, forming a heavily doped n^+ layer at the metal/GaAs interface, giving low contact resistance.

As can be seen from this review, the unambiguous understanding of such multicompound contact structures is hardly possible. It is clear that surface preparation prior to the metal deposition can play a significant role in the reliability and stability of the contacts.

$TiSi_2$/GaAs Schottky contacts

Metal silicides were widely adapted for both ohmic and Schottky contacts in the silicon LSI technology for lowering the contact resistance and controlling Schottky barrier heights as well as for gate materials in metal-oxide-semiconductor (MOS) devices.[17-20] Among the refractory metals Ti is the most popular candidate. The successful use of titanium silicides as contacts on Si suggested the possibility of their application as Schottky contacts on GaAs. Such contacts were prepared by deposition of alternate layers of titanium and silicon on n-type GaAs.[21,22] Halogen-lamp annealing was performed for 5 sec at 800°C, 825°C, 875°C, or 950°C for the alloying treatment. Two different atomic ratios of Ti and Si, 1:2 and 1:3, were investigated. The Ti:Si composition with a 1:3 ratio annealed for 5 sec at 875°C resulted in good Schottky contacts. The barrier height and ideality factor for these samples were 0.8 eV and 1.15, respectively. The samples with lower Ti:Si ratios or the same ratios annealed at other temperatures did not have as ideal contact parameters as in the first case. TEM observation of the cross-section samples showed the layered structure in unalloyed samples. EDX spectra showed the presence of Ti or Si lines in each respective layer, without intermixing between elements. The interface of the first Ti layer with GaAs was very flat and abrupt.

The structure of contacts annealed for 5 sec at 875°C with each composition was studied. Distinguishable layers were observed in the samples with lower Ti:Si ratios (see Figure 2). The interface with GaAs for these samples was very rough. Many grains with different compositions were found on the interface with the semiconductor, as well as in other parts of the contact. Two orthorhombic $TiSi_2$ phases, C49 and C54, were found, with the C49 phase making up the majority in the volume of formed contacts. These two phases were found to be formed in $TiSi_2$ thin film on silicon substrates, as published by Beyers et al.[20] Besides these two phases, grains of pure Ti and Si were observed occasionally, and the precipitates of As[23] were found in many places on this interface (Figure 3) as confirmed by EDX study. The first layer adjacent to the GaAs was very irregular in thickness, ranging from a single nm to 100 nm, and it consumed the whole first layer of Ti and 2/3 of the deposited Si. One-third of the remaining Si ($\sim$25 nm thick) was amorphous (white contrast marked by "b" on Figure 2), and a systematic study by EELS showed the presence of oxygen,
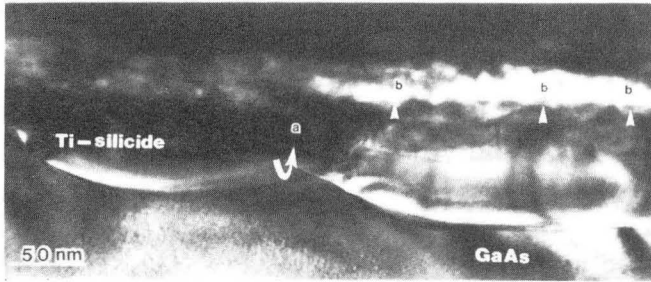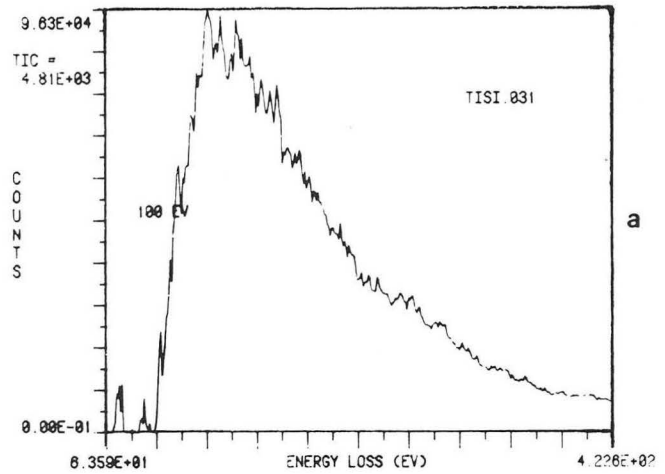
Figure 2. The titanium silicide/GaAs interface after annealing at 875°C (Ti:Si ratio 1:2); marked by arrows: a) As precipitate, b) oxide layer (formed in the previous Si layer). XBB 862-885
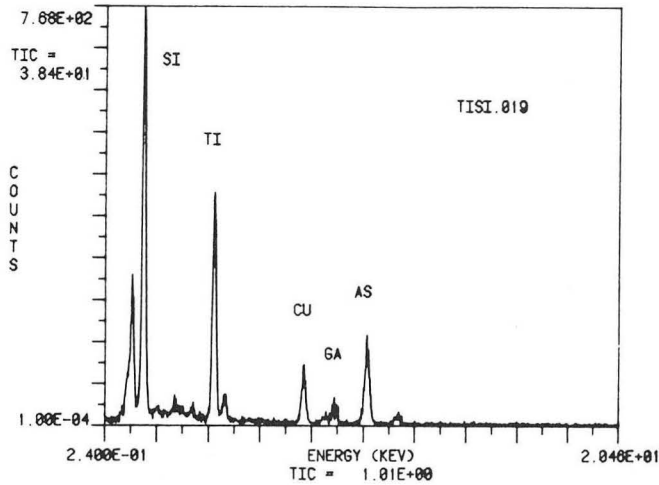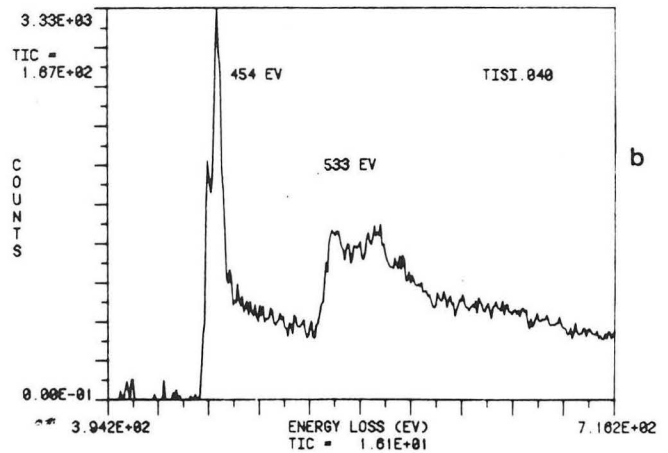

a

b

Figure 3. X-ray spectrum from As precipitate (marked by (a) on Figure 2). TiK_α and SiK_α are from a silicide grain. The intensity of the AsK_α line (in GaAs both GaK_α and AsK_α lines are almost equal intensity with As slightly lower) dominates the GaK_α line; Cu lines are artifacts from the microscope holder. XBL 858-3223

Figure 4. Energy-loss spectra from the area marked by (b) on Figure 2: a) SiL_α edge (100 eV); b) TiK_α (454 eV) edge and OK_α (533 eV) edge. XBL 861-166A

silicon, and titanium in this layer[23] (Figure 4). This would suggest that the remaining Si and diffused Ti oxidized during annealing. It is not surprising that the oxide layer was formed, because both Si and Ti are very reactive and oxidize easily in atmospheres containing residual oxygen during heat treatment. The third layer (Ti in the unannealed case) consisted of many grains of different composition: $TiSi_2$ C49 and C54 phases, and Ti. The top Si layer consisted of two sublayers of partially crystalline Si and an amorphous layer that turned out to be a silicon oxide layer.

For the higher Ti:Si ratio, after the same annealing treatment the distinction between all four layers almost disappeared in many places. Only isolated islands of silicon oxide were found in both former Si layers. The phase C54 made up the majority of the phases found in the volume of the contact; however, the C49 phase was also found, and occasionally Si, Ti, and As (present only on the interface with GaAs) were found as well.

The results show that titanium silicide contacts are not a homogeneous $TiSi_2$ phase. However, good electrical properties were achieved for the 1:3 Ti:Si ratio in spite of the very incomplete reaction and rough interfaces. Different electrical properties are attributed to the higher volume fraction of the C54 phase;[22] however, a more systematic investigation revealed the presence of oxygen in former Si layers.[23] In contacts with poor electrical properties, continuous oxide layers were found between the layers containing the $TiSi_2$ C49 and C54 phases. In contacts with good electrical properties, only separate islands of silicon oxide were observed within the former silicon layer.

4

Another important feature of these contacts was the accumulation of As on the interface in the form of precipitates. This observation, combined with our other studies, is evidence that the presence of As can play an important role in the formation of Schottky barriers.
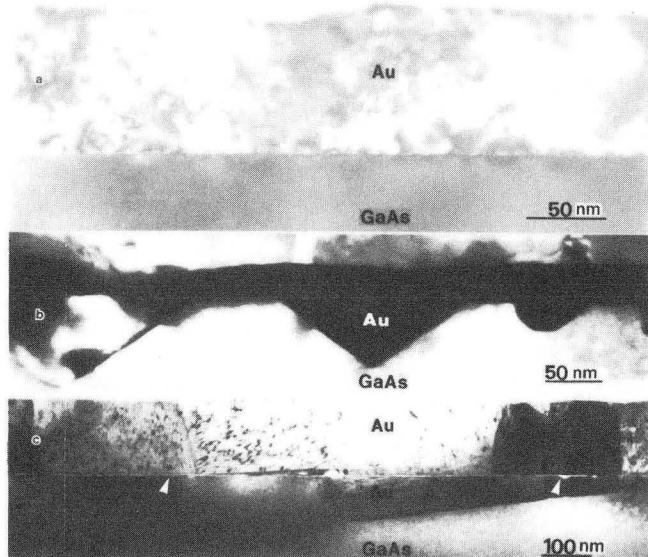
Au contacts

Multicompound alloys as either ohmic or Schottky contacts on GaAs usually form many phases on the interface. Therefore it is not easy to explain and understand which morphological and chemical characteristics are important in achieving good electrical characteristics in such complex contacts. This is one of the reasons why fundamental investigations typically use single metals. Gold is one of the examples of the single metal. It is also of practical importance as it is used in the fabrication of gallium arsenide devices, both as a component of an alloy in ohmic contacts (see Au-Ni-Ge, discussed above) and as single-metal Schottky contacts.[24-26]

In our study we wanted to avoid any unintended contamination, like oxygen contamination, which could influence the contact properties. Therefore, gold contacts were formed on well-defined (110) GaAs surfaces prepared by cleavage in UHV. Such ideal contacts were compared with Au contacts deposited on (110) GaAs surfaces cleaved in air and on chemically cleaned (100) surfaces used in device production. Bulk n-GaAs bars (Si concentration $\sim 1 \times 10^{17}/cm^2$) were placed in a UHV chamber that was baked out to obtain a vacuum of $\sim 2 \times 10^{-10}$ torr. The bars were cleaved along their {110} planes. On such prepared substrates Au was deposited in situ using a resistance-type evaporator without breaking the vacuum and without additional heating.[27] The other Au diodes were deposited on the samples cleaved in air in the same vacuum chamber with a pressure of $\sim 10^{-7}$ torr. The Au thickness for these two types of diodes was {100}nm. These two types of samples were annealed for 10 min at 405°C. The third type of sample was Au layers deposited by electron-beam evaporation on chemically cleaned samples.[28]

There were no detectable differences in the abruptness of the interface for all three types of as-deposited samples.[28-30]

After annealing, the interface abruptness of the three types of contacts differed distinctly; however, no other compounds besides Au were found. Many protrusions appeared on the interface of both types of air-exposed samples (Figure 5), but not for UHV-cleaved samples. These protrusions consisted of twinned gold and some GaAs, which was probably formed from Au_2Ga and As accumulated near the interface as a result of the reversible reaction proposed by Yoshiie.[31] Even more complicated interfaces were observed for the annealed gold layers deposited on chemically prepared (100) GaAs wafers. An oxide layer was observed on the interface (Figure 5c). Islands of epitaxial Au were present on the interface below this oxide layer, probably as an effect of diffusion through the pinholes present in the oxide. Oxygen was detected in chemically prepared samples and in samples cleaved in air but it was not present on UHV-prepared samples (Figure 6). The interfaces formed on the clean cleaved surfaces were the only interfaces to remain flat after annealing. This demonstrates that the formation of rough interfaces is not the result of annealing at elevated temperatures alone, but it is strongly affected by impurities present at the surface before metal deposition. Although the different sample preparation techniques were not found to strongly influence the barrier height, which remains almost the same (0.87 eV for UHV-cleaved and 0.83 eV for air-exposed samples), but the electrical characteristics of air-exposed samples can age with time and measurement conditions, whereas UHV-cleaved samples do not. This difference is very important for the reliability of devices built on oxidized surfaces.

Besides impurities, the stoichiometry of GaAs beneath the contacts plays an important role in the contact formation. An accumulation of As in the GaAs within 10 nm of the interface was observed in unannealed and
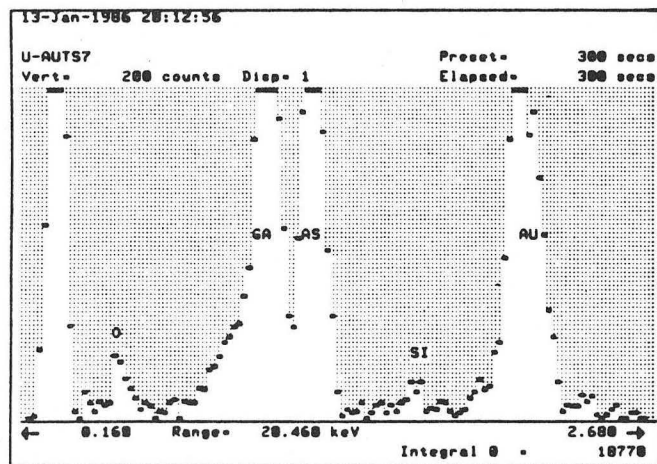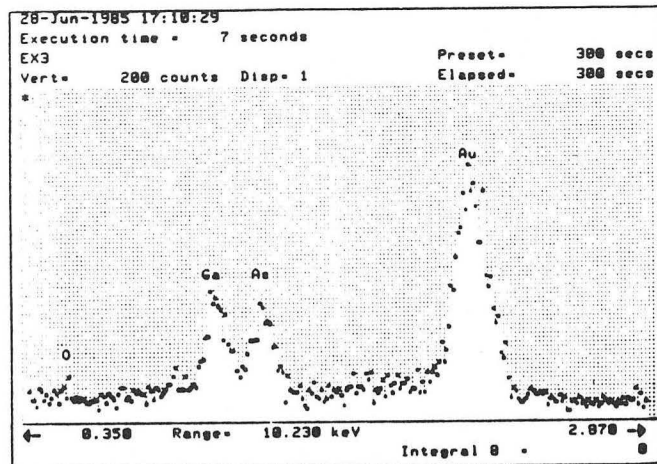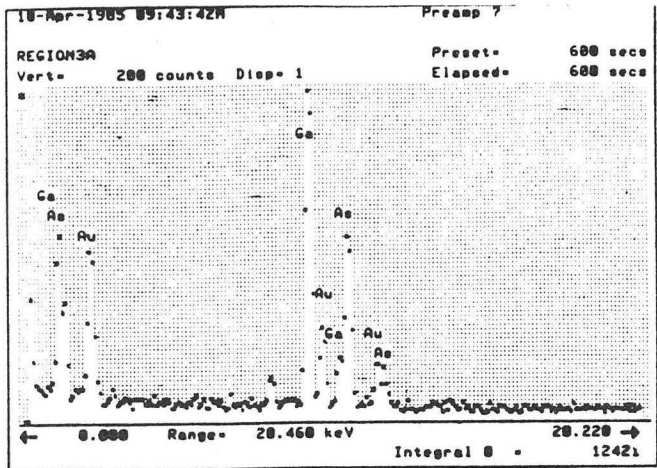

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Figure 5. The Au/GaAs interface abruptness after annealing for 10 min at 405°C: a) Au deposited in situ on a UHV-cleaved GaAs surface; b) Au deposited on the GaAs surface cleaved in air, many protrusions are formed; c) Au deposited on a chemically cleaned surface; note the Au island beneath the oxide layer (white band marked by arrow).

Figure 6. X-ray spectra from the Au/GaAs interfaces; a, b, and c are as in Figure 5.

annealed samples.[29,30] An interesting phenomenon was observed on the periphery of Au contacts annealed at 405°C. Diodes annealed at this temperature changed to ohmic behavior.[27,32] This has been shown to be caused by leakage currents at the periphery of the devices. TEM micrographs revealed the existence of elongated Au crystallites on the GaAs surface at the periphery of the contacts. Analytical microscopy in plan view established that these elongated Au crystallites are Ga-rich and are most probably responsible for the ohmic behavior of these contacts.

Mesa-etching of the annealed contacts removed the current path at the periphery of the contacts (1-3 μm of periphery removed), 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/Gas diodes.

Summary

These examples of ohmic and Schottky contacts show that the physical mechanism involved in their formation is very complex and not easy to understand in the case of multi-compound formation on the interface. The example of gold, which can form both kinds of contacts, suggests that the deposition method can play an important role. Deposition from the vapor phase obviously releases enough energy to form defects rich in anions that appear to be responsible for the Fermi-level pinning near the midgap. On the other hand, gentle Au deposition by the flow of Ga-rich Au out of the Au layer leads to low defect densities and "ohmic" interfaces. These results clearly show, for the first time, that a near-perfect Au/GaAs interface does not necessarily show Fermi-level pinning. However, two models for Schottky contact formation, the "effective work-function model"[33] ascribing the barrier to anion microclusters, and the "unified-defect model,"[34] are both consistent with the results of this study. In the case of Au and titanium silicide, accumulation of As was found in the vicinity of the interface with the metal or alloy. Therefore the defects responsible for Fermi-level pinning are believed to be anion-rich. For example, anion antisite defects, which have bulk energy levels similar to the Fermi-level pinning positions,[35] may be responsible for Schottky barrier formation.

Another issue of this review is the importance of the surface preparation of GaAs prior to the Au deposition. It was shown that, even in such complicated contacts as ohmic Au-Ni-Ge, uniformity and thermal stability could be achieved by appropriate surface preparation. The examples discussed in this paper demonstrate clearly that even small amounts of oxygen present on the wafer before metal deposition can strongly influence contact parameters and reliability.

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