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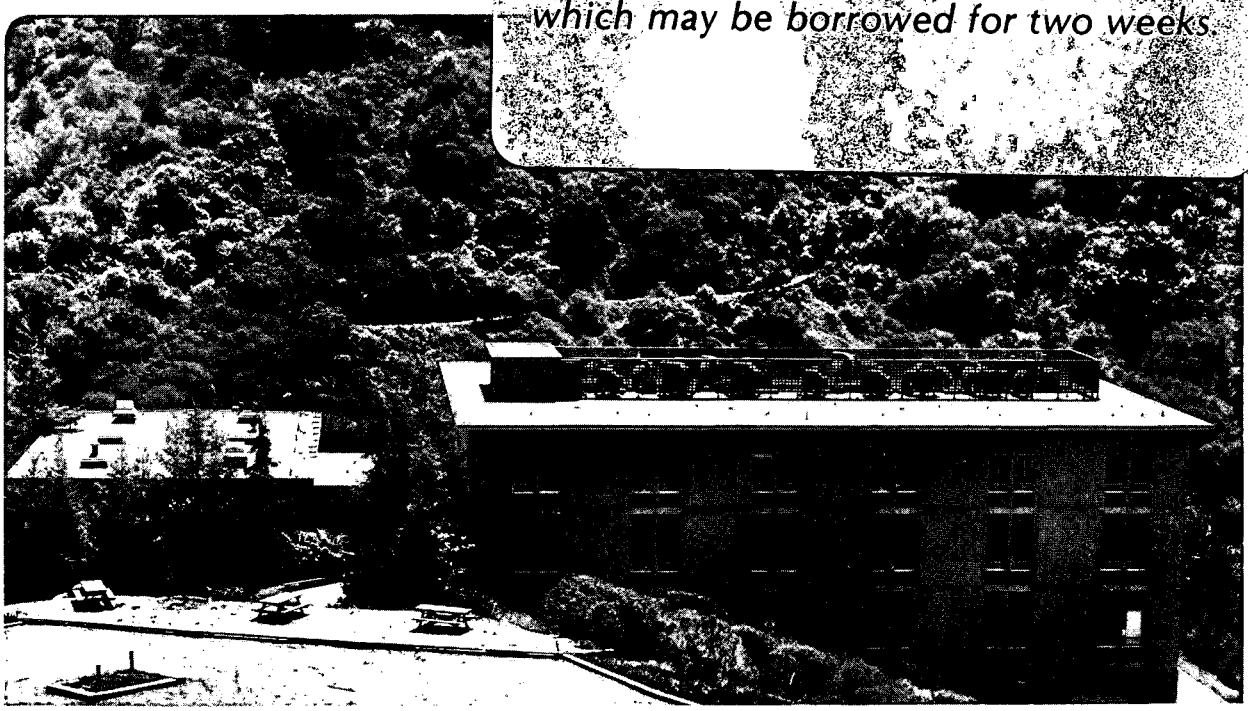

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OBSERVATION OF STOICHIOMETRY CHANGES BENEATH METAL CONTACTS ON GaAs

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The structure of metal-semiconductor Schottky contacts (Au:GaAs, Al:GaAs, and $TiSi_2$:GaAs) was investigated by high-resolution and analytical electron microscopy. In all cases investigated, a change in stoichiometry (increase of the As/Ga ratio) in the GaAs beneath the metal contact was observed. This indicates the formation of anion-rich defects at Schottky contacts on GaAs, giving strong support for the defect models of Fermi level pinning.

INTRODUCTION

Metals deposited onto semiconductors generally form rectifying "Schottky" contacts. The basic mechanism of barrier formation at these contacts is still not understood. The original Schottky model [1], predicting as barrier height the difference between metal work function and electron affinity (for n-type semiconductors), is in contradiction with experimental results [2]. In the case of GaAs, the pinning position of the Fermi level for many metals as well as for oxygen falls within a narrow range of 0.7 to 1.0 eV below the conduction band minimum (CBM) [3]. Many models have been developed to explain the observed pinning levels. They can be divided into two groups: models relating the Fermi level pinning to perfect metal-semiconductor interfaces such as semiconductor surface states [4] or metal-induced gap states [5,6], and models relating Fermi level pinning to defects in the semiconductor near the interface, such as point defects [7] or anion clusters [8]. This study shows that all Schottky contacts investigated so far show marked changes of the semiconductor stoichiometry directly beneath the interface with the metal. These results support the defect models for Schottky contact formation.

EXPERIMENTAL

In this study, three different kinds of Schottky contacts on n-GaAs were investigated: Au:GaAs, Al:GaAs, and $TiSi_2$:GaAs. The Au:GaAs contacts were deposited in-situ onto UHV-cleaved GaAs(110) [9], Al:GaAs contacts were either formed in the same way or grown by MBE on GaAs(100) [10], and $TiSi_2$:GaAs contacts were prepared by rapid thermal annealing (5 sec at 875 C) of alternate layers of Ti and Si deposited in vacuum on n-GaAs [11]. Cross-section samples were investigated by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDXS). Electrical characterization of the contacts was performed by I-V and C-V device measurements prior to the TEM sample preparation.

RESULTS AND DISCUSSION

TEM micrographs of the Au:GaAs contacts show a flat interface even after annealing (10 min, 405 C in N_2 atmosphere), with no other phase present [9]. High-resolution images of these structures reveal some rearrangement of the GaAs lattice right near the interface (Fig. 1a). Extra spots are visible in this area, as indicated by arrows in Fig. 1a. A final interpretation of these images has to be done in conjunction with computer image simulation. Detailed analytical studies by EDXS show an accumulation of As within GaAs ca. 10nm from the metal/semiconductor interface (Fig. 1b,c). This increased As/Ga ratio was observed in both the unannealed and annealed samples, with a higher As concentration in the annealed ones.

High-resolution micrographs of the MBE-deposited Al:GaAs interface show evidence for atomic rearrangements in the GaAs lattice beneath the interface (Fig. 2a). Similarly, as in the previous case, analytical work clearly showed the presence of an As-rich region in the GaAs near the interface (Fig. 2b). Qualitatively similar results were obtained for both MBE-grown and in-situ deposited structures on UHV-cleaved GaAs.

An interesting observation made during this study was the instability of the enhanced As concentration near the metal/GaAs interfaces. The highest As/Ga ratios were observable for less than 50 sec at one electron beam position. Longer observation of the same spot (beam diameter: 0.1 nm) resulted in similar As/Ga ratios as observed in the substrate, independent of the acquisition time.

In contrast to the two previously described cases, the metal/semiconductor interfaces of $TiSi_2$:GaAs contacts were very rough (Fig. 3a), due to the formation of various intermetallic phases (two orthorhombic $TiSi_2$ phases, C49 and C54 could be identified) [11]. In many areas of the interface, As precipitates were visible. The EDX spectrum of such a precipitate is shown in Fig. 3b.

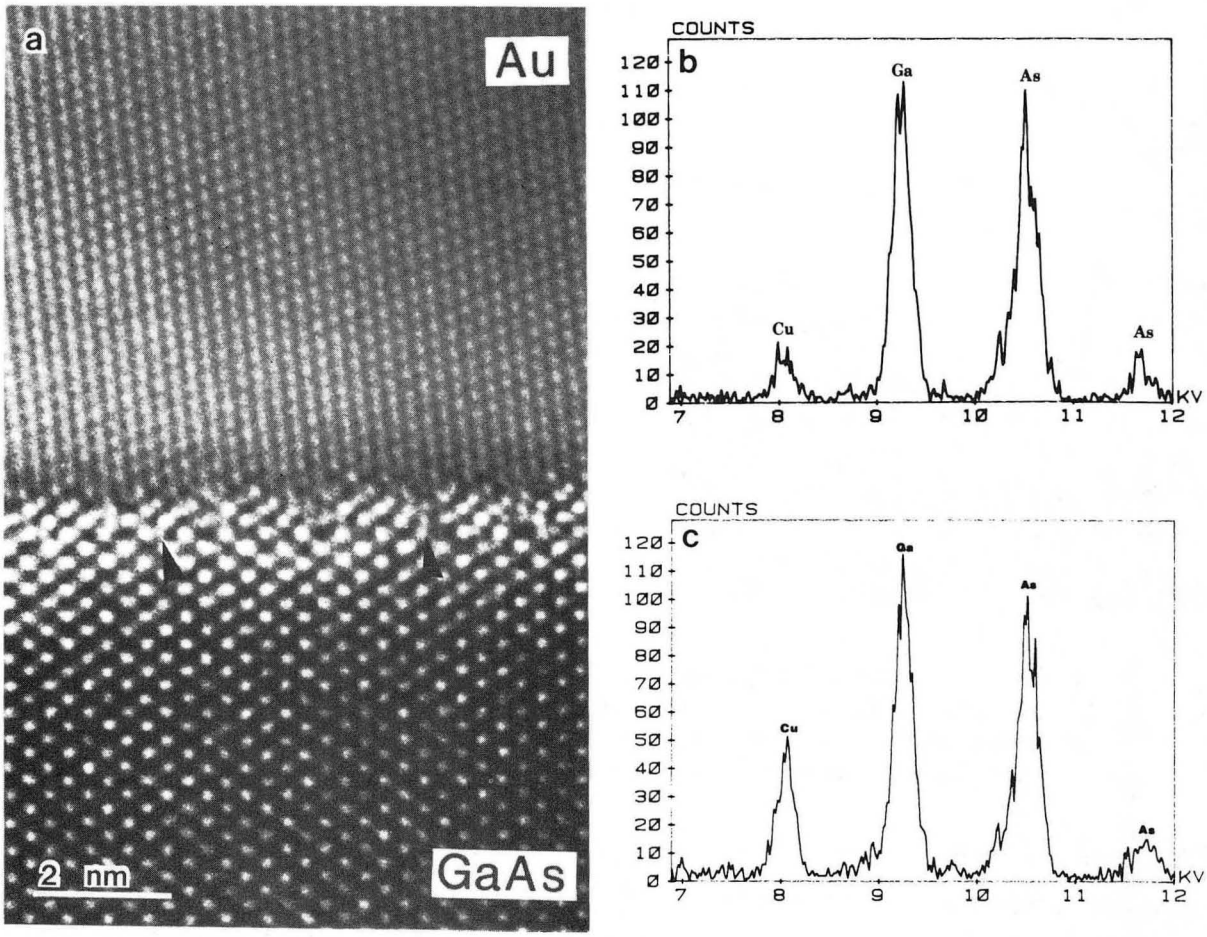

Figure 1: a) High resolution image of the Au/GaAs(110) interface annealed at 405°C for 10 min in N_2 athmosphere. Note the twisting of the $(111)_{Au}$ planes towards the $(200)_{GaAs}$ planes and the arrangement of the black dots in the GaAs near the interface in an almost regular pattern. These black dots are surrounded by white dots, suggesting some rearrangement of atoms in this area; b) EDX spectrum taken from the GaAs close to the interface with Au; c) EDX spectrum from the GaAs far from the interface. Note the increased As/Ga ratio near the interface. The Cu line is an artifact from the sample holder.

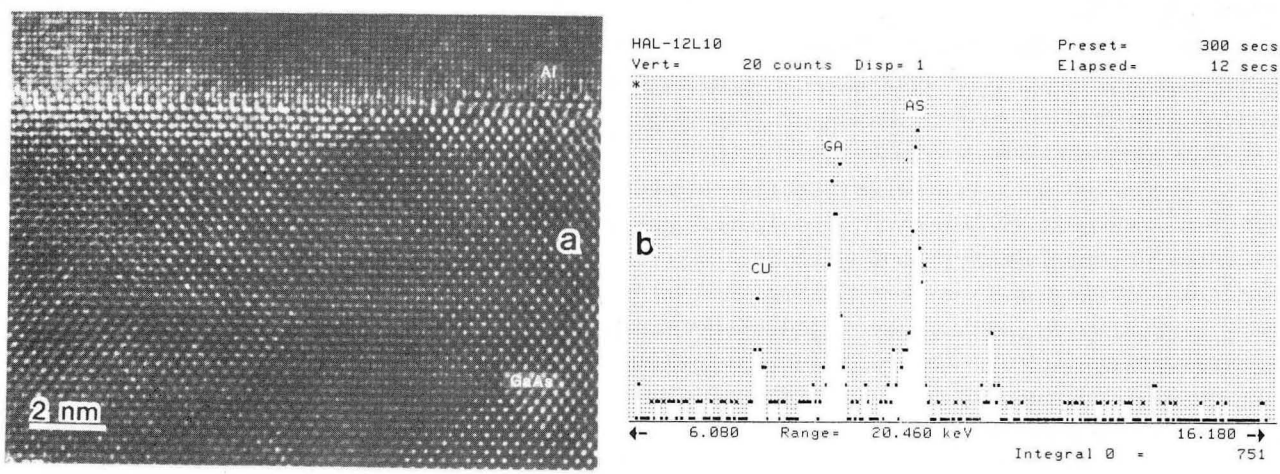

Figure 2: a) High resolution image of the Al/GaAs (100) interface grown in a MBE chamber with 25°C substrate temperaure; b) EDX spectrum taken from the GaAs close to the interface, indicating an increased As concentration.

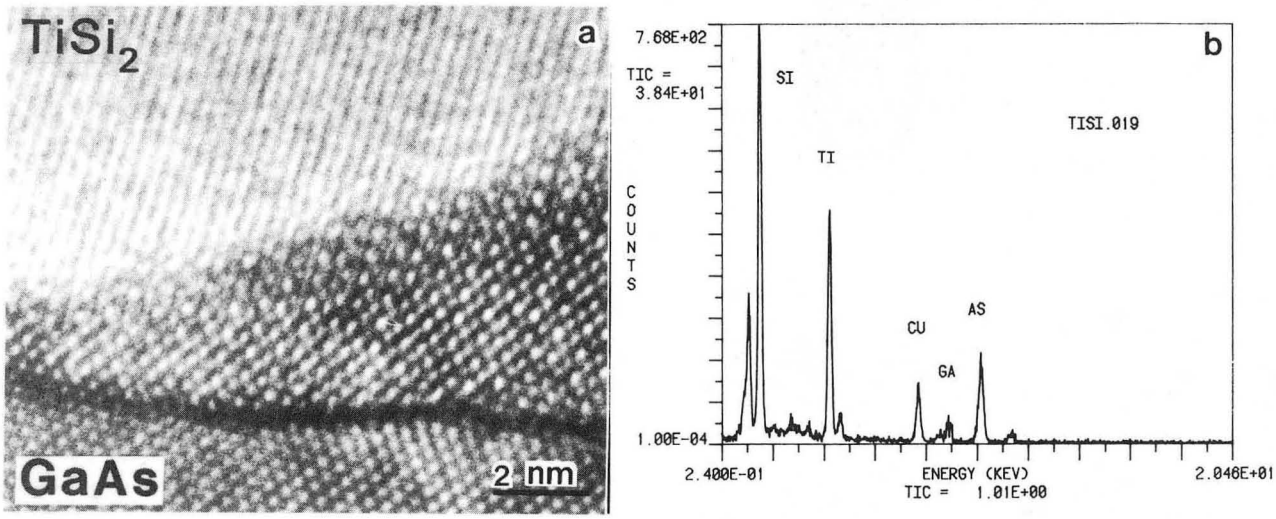

Figure 3: a) High resolution image of the $TiSi_2$:GaAs (100) interface, showing a grain of the $TiSi_2$-C49 phase. Note the overlapping of the $TiSi_2$ layer with the substrate, due to the strong ondulation of this interface; b) EDX spectrum from an As precipitate formed at the interface (see [11]).

The investigation of these three very different types of Schottky contacts on GaAs gives clear evidence for the existence of distorted regions in the semiconductor near the metal/semiconductor interface. In all cases, this lattice distortion involved deviations from crystal stoichiometry in the anion-rich direction. The observations of instabilities of the As accumulation suggest the presence of very mobile As species, e.g. As_i.

These observations show that the crystal stoichiometry can be important for metal/semiconductor contact properties of compound semiconductors. In the case of Schottky barrier formation on GaAs, the present results give strong support for those defect models which relate the observed Fermi level pinning positions to anion-rich lattice defects. These defects can be anion-rich point defects like As_{Ga} antisite defects [12] or more extended As-rich defects [8]. It should be noted that the observed pinning positions coincide perfectly with the energy levels determined for the As_{Ga} antisite defect [12]. Future work will be concerned with the direct identification of the lattice defects responsible for Fermi level pinning.

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