Structural Characterization of Ti and Pt Thin Films on GaAs(100) Substrate

X. WU and E. S. YANG
Department of Electrical Engineering, Columbia University, New York, NY 10027

N. D. THEODORE
Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca, NY 14853

In an attempt to understand the Schottky barrier behavior of Ti/Pt/GaAs and Pt/Ti/GaAs bimetal Schottky diodes, we have investigated the interfacial morphology of Ti and Pt thin films on GaAs(100) substrate. The characterization was based on coverage profiling of Auger electron spectroscopy in conjunction with transmission electron microscopy. Emphasis was placed on film uniformity and atomic interdiffusion. The results showed Ga and As outdiffusion in Pt/GaAs interface and some oxygen incorporated in Ti film, but no evidence of clustering for both metal/GaAs systems.

Key words: Ti & Pt on GaAs, metal thin film, interfacial morphology.

Recent experiments on Ti/Pt/GaAs and Pt/Ti/GaAs bimetal Schottky diodes revealed that Fermi-level position in these devices was not fully determined until the interlayer metal exceeds 10 Å. By inserting a thin layer (0–50 Å) of metal A between the top metal B (400 Å) and the GaAs, the Schottky barrier of the device was seen to vary substantially. It evolved from the metal B limit to that of the metal A as the thickness of the intervening metal layer increases. The most interesting point was that such a transition extended over more than 10 Å, much greater than we expected. It appears that the top metal, even though separated several monolayers away from the substrate, can still affect the Fermi-level position at the semiconductor surface. This result is in contrast to the previous electron photoemission studies of thin films on GaAs, which have shown that the Fermi level was pinned at a sub-monolayer coverage. This new phenomenon has been speculated due to the finite metal screening length. However, it may also be explained by cluster formation of the intervening metal as well as atomic interdiffusions among the three materials. Therefore, it is necessary to investigate the interface morphology of Ti and Pt on GaAs before a final conclusion can be reached.

In this letter, we report our experiment on the structural characterization of Ti, Pt/GaAs systems. The analysis was based on measurement of Auger electron spectroscopy (AES) and was complemented by transmission electron microscopy (TEM). Such combination provides reliable information on film uniformity which is important to the understanding of bimetal Schottky behavior.

The deposition and measurement were carried out in an ultra-high vacuum system equipped with AES. The samples were made from GaAs(100) substrate, which was nominally undoped with \( n = 10^{16} \text{ cm}^{-3} \). The wafer was initially degreased using trichloroethylene, acetone, and methanol followed by two etching steps: (a) \( \text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} \) (20:7:973) for 1 min; (b) \( \text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O} \) (10:1:1) for 1 min. The Ti and Pt thin films were deposited in a differentially pumped evaporation chamber, which is connected to the main analysis chamber through a loadlock. The base pressure in the evaporation chamber was kept <5 × 10^{-9} Torr. During the evaporation, the pressure rises but never exceeds the 10^{-8} range. Prior to the metallization, the sample was heated to 550 °C for 5 min to desorb the chemically formed oxide on the GaAs surface. This heat treatment leaves behind a small amount of oxygen detected by AES although X-ray photoelectron spectroscopy (XPS) showed no oxygen present. The metal deposition was made by e-beam at room temperature. A quartz crystal was employed during the evaporation to monitor the film thickness. After the evaporation, the sample was immediately transferred in-situ to the analysis chamber, where the AES measurements were performed. Such evaporation-measurement sequence was repeated for thicker coverages by successively adding more metal onto the sample surface.

AES signal peak-to-peak intensities of Ga \( LMM \) and As \( LMM \) are shown in Fig. 1 as a function of Ti coverage up to 45 Å. Along with the substrate signals Ti \( LMM \) and oxygen \( KLL \) signals are also recorded. All components have been normalized according to their Auger sensitivities. It can be readily seen from the figure that both Ga and As signals attenuate exponentially with the increase of Ti coverage. The characteristic decay length is determined to be 12.5 Å and 14.1 Å for the Ga and the As respectively. These numbers are in good agreement with the electron escape depth at the corresponding energies. This signal behavior indicates that there...
Fig. 1 — Variations of AES peak-to-peak intensity of Ga, As, Ti, and oxygen as a function of Ti coverage. All components have been normalized corresponding to AES sensitivities. A uniform growth of Ti overlayer is apparent from the exponential decay behavior of the substrate signals.

There is no island structure in the Ti film for a thickness range of $<45\AA$ since a partial coverage up to 90% can be detected. In the case of island formation, part of the GaAs surface will remain exposed to the incident electron beam even after a considerable amount of Ti has been deposited. This will lead to a different overall intensity variation in which the signal attenuation will level off rather than exponentially decreased. For the same reason, the substrate atom outdiffusion appears to be very limited here as well. This conclusion comes not only from the perfect match of the electron escape depth, but also from annealing. An in-situ annealing of the sample at $300^\circ$C for 5 min does not change the GaAs signal intensity as shown in Fig. 1.

From AES data alone, it is difficult to tell the detailed interface morphology at very low coverage ($<5\AA$) because of the limited depth resolution. Therefore possible clustering of Ti during initial growth still exists. However, this possibility was ruled out by Ludeke et al. using XPS. They reported no evidence of Ti clustering at monolayer range, although some interfacial reactions between Ti and GaAs were observed. A close look of the data in Fig. 1 shows that the attenuation of the Ga and As signal appears to be little faster in the first 3Å. This was attributed to the chemisorption of chamber residue oxygen on the Ti—a well known difficulty in preparing truly clean Ti film because of its high reactivity. The reaction of Ti oxide is further evident in the AES spectra as the growing intensity of oxygen signal along with the Ti. The composition of this oxide and its detailed chemistry are not discussed here.

The result of the AES profiling for Pt/GaAs is shown in Fig. 2. Similar to the Ti/GaAs situation the Ga and As signals decrease exponentially with the subsequent deposition of Pt, suggesting a laterally uniform growth of Pt overlayer. But this time we found a rather large decay length for both substrate elements. Moreover, for a given Pt coverage, if we let the sample sit for a while (~15 min), then repeat the measurement, the signal intensity of Ga and As appears to increase slightly. This is an indication of Ga and As outdiffusion perhaps accompanied by reactions as well. This substrate outdiffusion is further enhanced at elevated temperatures. The in-situ annealing ($300^\circ$C for 5 min) results in a significant increase of Ga and As signals as shown in Fig. 2. Compared with As, Ga diffuses faster into Pt. This is consistent with the large difference in the electronegativities of these elements and some previous investigations using other spectrosopies. With Rutherford backscattering spectrometry, Sands et al. and other workers have identified that the reaction between Pt and GaAs, if complete, would result in a layer sequence of Pt/PtGa/PtAs$_2$/GaAs. However, most reactions have been observed at high temperatures ($>300^\circ$C). At room temperature Pt

Fig. 2 — The AES coverage profile of Pt/GaAs(100) interface. The significant increase of Ga and As signals after annealing (at 45Å of Pt) indicates strong substrate outdiffusion.