# On the role of "derelaxation" of the (110) surface of GaAs in the formation of an Ag–GaAs Schottky barrier at 10 K

V. Yu. Aristov, I. L. Bolotin, and V. A. Grazhulis

*Institute of Solid-State Physics, USSR Academy of Sciences*

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Using the method of ultraviolet photoemission spectroscopy, we have investigated electronic states at the (110) surface of $n$-type GaAs at 10 K and 300 K during the deposition of silver films under ultrahigh vacuum conditions ($\approx 4\cdot 10^{-10}$ torr). It is found that at 300 K the surface band bending takes place gradually as the coverage $\theta$ (expressed in monolayers) increases, attaining a value of $\approx 0.8$ eV at $\theta \approx 5.5$, and tending to increase even more thereafter. No peculiarities are observed in the vicinity of the Fermi level at this temperature other than the formation of a metallic edge. At 10 K the band bending takes place much more rapidly in the initial stages of deposition than at 300 K, and the Fermi level is pinned at an energy $\approx 0.5$ eV below the conduction band edge if $\theta \gtrsim 0.1$. At 10 K the occupied surface states (characteristic of a cleaved surface) disappeared, accompanied by the appearance of new surface states, apparently observed for the first time; these states are located $\approx 0.5$ eV below the valence band edge. From the aggregate of experimental results we have obtained, we have come to the conclusion that at 10 K the adsorption of Ag on a GaAs (110) surface causes the surface to "derelax"; this effect is accompanied by the appearance in the forbidden band and near the edge of the valence band of surface states which are characteristic of an unrelaxed surface. As a consequence of this, the Schottky barrier at 10 K forms according to the Bardeen model (i.e., the Fermi level is pinned at intrinsic surface states of the derelaxed surface).

## 1. INTRODUCTION

It is well-known that clean (110) surfaces of cleaved $A^{III}B^{V}$ crystals do not possess surface states (SS) in the forbidden band of the electron spectrum (see, e.g., the review Ref. 1 and citations therein). Numerical calculations[1,2] carried out on the GaAs (110) surface have prompted the suggestion that the SS are "expelled" from the forbidden band in the process of surface relaxation, since electronic calculations on the unrelaxed surface give peaks in the SS density within the forbidden band and near the valence band edge (Fig. 1). The validity of conclusions based on these numerical calculations could be tested by the direct observation of SS on both unrelaxed and relaxed surfaces. Obviously, it is necessary to create both types of surface states and study their electronic properties in order to carry out such a test.

As we have already noted, clean surfaces of cleaved $A^{III}B^{V}$ compounds are in the relaxed state immediately after cleaving. However, this relaxation can apparently be eliminated by surface adsorption of atoms of, e.g., metals. In particular, there are indications that adsorption of Al, Au and Sn at the surface of GaAs (110) leads to its partial or complete derelaxation of the latter. However, this question has not been studied in detail.

We note that in practically all the papers devoted to the study of "metallized" surfaces of cleaved semiconductor crystals, the investigations have been carried out in the temperature range 80 to 400 K. These studies show that the surface band bending (i.e., the Schottky barrier) depends only weakly on the type of metal adsorbed (especially at high temperatures); however, the rate of formation of the Schottky barrier changes as a function of the substrate temperature.[4,6,7] The value of the Schottky barrier at 300 K can be explained, for example, by the appearance of defects in the GaAs (110) system upon adsorption of metal; these defects pin the Fermi level in the forbidden gap. At lower temperatures, there is no definitive explanation of barrier formation. It is important to emphasize that in fact much remains unclear regarding the question of how the surface electronic spectrum forms in the initial stages of adsorption of metal atoms, even in the case of such a classical system as GaAs. The principal reason for this lack of clarity, in our opinion, is connected with the fact that practically all the investigations were carried out in regions of insufficiently low temperatures (80–400 K), for which the adsorbing atoms could interact with the surface, form defects there, diffuse deep into the crystal and along the surface, form clusters, etc. All these processes overwhelmingly complicate the system, especially

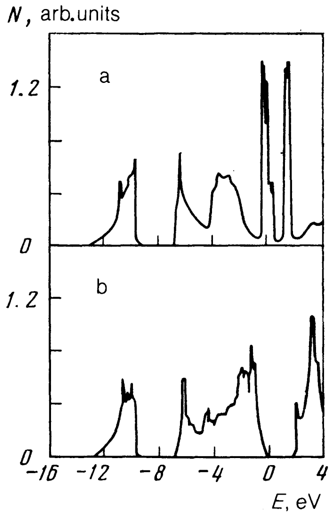

FIG. 1. Calculations (Ref. 2) of the density of surface states at the (110) surface of GaAs: (a)—unrelaxed surface, (b)—relaxed surface. $E_v = 0$ is the edge of the valence band.

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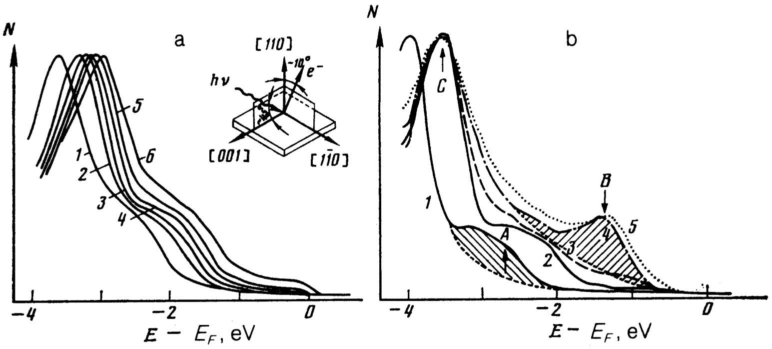

FIG. 2. UPS spectra near $E_F$ as a function of the magnitude of $\theta$ and the substrate temperature: (a) $T = 300$ K; 1—$\theta = 0$; 2—$\theta = 0.03$; 3—$\theta = 0.12$; 4—$\theta = 0.4$; 5—$\theta = 1.1$; 6—$\theta = 3.3$; (b) $T = 10$ K; 1—$\theta = 0$; 2—$\theta = 0.1$; 3—$\theta = 0.25$; 4—$\theta = 1.1$; 5—$\theta = 1.9$. All spectra are normalized to the intensity of the valence band peak (peak $C$). In the inset of (a) we show the sample geometry relative to the incident photons and the analyzed electrons. The dashed curves in (b) delineate the spectral regions corresponding to peaks $A$ and $B$.

if they take place at the same time, and make the experimental results difficult to interpret.

Low temperature (close to helium) investigations are of exceptional interest in connection with this problem, since in the region of low temperatures the phenomena listed above can be suppressed for the most part. In this way we obtain better characterized physical systems whose fundamental electronic characteristics can be clearly exhibited. Motivated by these considerations, we have begun a cycle of low-temperature studies. Certain results pertaining to various semiconductor-metal systems have been published previously[8–14]; in particular, it was shown in Ref. 8 that at low temperatures quasiamorphous layers of silver grow on the GaAs (110) surface due to the absence of diffusion.

In this article, we present (and discuss) results pertaining to the GaAs (110) + Ag system, obtained by the method of ultraviolet photoelectron spectroscopy (UPS), which in our opinion confirm the correctness of the numerical calculations carried out earlier in Refs. 2 and 3 for the GaAs (110) surface (see Fig. 1).

## 2. EXPERIMENT

The basic details of our experiments were described in Ref. 9. Here we note only that all the studies were carried out using an "ESCALAB-5" electron spectrometer with a hemispherical energy analyzer and capillary gas-discharge helium radiation source. During the experiments the pressure in the chamber never exceeded $10^{-9}$ torr; the total pressure of the remaining gases (other than helium) was below $5\cdot 10^{-10}$ torr. We used samples of $n$-type GaAs with impurity concentrations $\approx 6\cdot 10^{17}$ cm$^{-3}$. Silver (99.9999 at. %) was deposited on the GaAs (110) surface, which was cleaved at room temperature and held at 300 or 10 K. The coverages reported in this paper are expressed in monolayers ($\theta = 1$ corresponds to $8.86\cdot 10^{14}$ at/cm$^2$). The deposition rate was regulated in the interval $3\cdot 10^{-4}$ to $2\cdot 10^{-2}$ Å/sec and was measured by a quartz thickness gauge. The inset to Fig. 2a shows the geometry of the sample relative to the incident photons $h\nu$ and the electrons $e^-$ to be analyzed. Our measurements of the magnitude of the band bending were based on the shift of the peak $C$ (see Fig. 2b), which corresponds to the maximum density of volume electronic states in the region of the spectrum shown in the figure.

## 3. RESULTS

In the measurement process we used the change in the spectrum obtained by UPS in the vicinity of the Fermi level $E_F$. Figure 2 shows a characteristic UPS spectrum as a function of silver coverage $\theta$ for depositions at 300 K and 10 K. It is clear that these two spectra differ significantly in their behavior. Thus, at 300 K we find a shift of the entire spectrum as a whole toward the $E_F$ side, which suggests a gradual upward bending of the bands. In this case, when $\theta \gtrsim 1$, we observe the formation of a metallic edge near $E_F$. In contrast, at 10 K (Fig. 2b), a more sudden shift of the spectrum takes place in the direction of $E_F$; the maximum shift ($\approx 0.5$ eV) has already occurred for $\theta \approx 0.1$. In this case, the shape of the spectrum in the energy region shown in the figure is practically unchanged during the deposition process; we observe a decrease in the amplitude of the SS peak obtained immediately after cleaving the sample (peak $A$, which is practically invisible for $\theta \gtrsim 1$) and the appearance and growth of a new peak $B$ in the energy region roughly 1.4 eV below $E_F$. It is clear from Fig. 3 that the growth of the peak $B$ ceases for $\theta \approx 1$–1.25. Further increases in the coverage lead to a decrease in the peaks $B$ and $C$; for $\theta \gtrsim 4$ these peaks are practically invisible against the background level.

Our results for the change in band bending are shown in Fig. 4. It is apparent that at 10 K very small coverages lead to significant band bending. Actually, even at $\theta \approx 0.01$ the band bending reaches 80% of the maximum for this value of temperature ($\approx 0.5$ eV); the latter is already attained for $\theta \approx 0.1$. At 300 K, the band bending takes place somewhat more slowly; in our measurements it attained a maximum value $\approx 0.8$ eV and had a tendency to increase even more.

In Fig. 5 we show two spectra obtained at 10 K on a sample with $\theta \approx 2.4$. One of them was taken immediately after deposition at 10 K, while the other was taken on the same sample but after it was warmed to 300 K and then recooled. It is clear that the peak $B$ mentioned above has disappeared; in addition, a certain shift of the peak $C$ toward

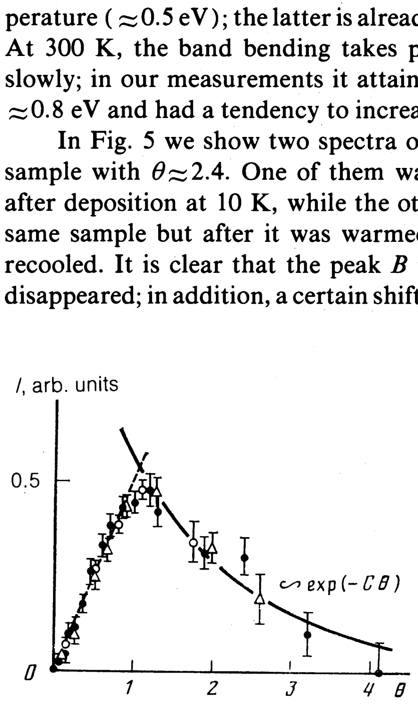

FIG. 3. Dependence of the amplitude of peak $B$ on the degree of coverage $\theta$. The results of three experiments are presented.

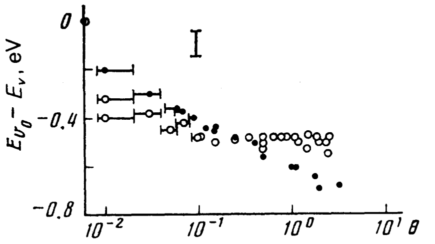

FIG. 4. Dependence of the magnitudes of the surface band bending as a function of substrate temperature and coverage $\theta$. The error in determining the magnitude of the band bending is shown in the upper part of the figure. Results are presented for 300 K (●) for three samples and for 10 K (○) for four samples.

the side of increasing band bending is noticeable. It should be noted that the final value of the band bending and the shape of the spectrum correspond to what would have been obtained if the deposition had occurred up to $\theta \approx 2.4$ but at a constant temperature of 300 K.

## 4. DISCUSSION OF RESULTS OBTAINED

The results presented above can be explained in the following way: previous theoretical (see, e.g., Refs. 2, 3) and experimental (see citations in Ref. 1) papers have shown that a relaxed GaAs (110) surface has a peak in the density of occupied SS which lies at 1–1.6 eV below the edge of the valence band. In our experiments we find this peak (*A* in Fig. 2b) $\approx 2.9$ eV below $E_F$ for a cleaved surface, i.e., $\approx 1.5$ eV below the valence band edge $E_v$. The calculations of Ref. 2 (Fig. 1a) show that for an unrelaxed GaAs (110) surface this peak should be found near the edge of the valence band. Ag deposition at 10 K (Fig. 2b) gives a new SS peak (peak *B*) at $E \approx -1.4$ eV relative to $E_F$. Because in this case the whole spectrum is shifted in the direction of $E_F$ by $\approx 0.5$ eV, the position of peak *B* is found to be roughly 0.5 eV below the edge of the valence band. This value corresponds to the position of the maximum in the density of occupied SS for an unrelaxed GaAs (110) surface, which follows from the calculations of Ref. 2.

Hence, it is reasonable to assume that in the course of Ag deposition on a GaAs (110) surface kept at 10 K we are seeing derelaxation of the surface accompanied by the appearance and growth of SS peak *B* corresponding to an unrelaxed surface, and the disappearance of SS peak *A* which corresponds to an atomically clean relaxed surface. In favor of this assumption we offer the following observations. First of all, it is clear from Fig. 5 that as the coverage increases the amplitude of the peak *B* first grows linearly (up to $\theta \approx 1$) and then falls exponentially. The linear growth of peak *B* up to $\theta \approx 1$ suggests that for small $\theta$ and low temperatures the silver atoms do not diffuse and are distributed statistically on the sample surface. Evidently, the fraction of unrelaxed surface (and consequently the density of SS for this surface) is proportional in this case to the area covered by silver. For $\theta \gtrsim 1$, the "screening" of the metal-semiconductor boundary by the silver film begins to play a role, which is manifested in an exponential decrease in the intensity of peak *B*.

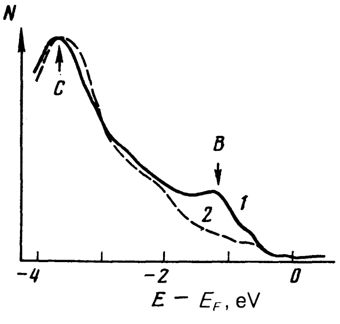

FIG. 5. The effect of warming to 300 K on the spectrum of a sample obtained by deposition up to $\theta \approx 2.4$ at 10 K. Both spectra are plotted at 10 K; 1 is immediately after deposition at 10 K, 2 is after heating to 300 K and then recooling.

Let us estimate the effective mean free path $l^*$ of electrons with energy $\varepsilon \approx 20$ eV in a silver film. Taking into account the fact that the film is quasicontinuous[8,9] and not island-like, it is easy to show that in the function

$$I \propto \exp\{-C\theta\} \qquad (1)$$

we have

$$C=\alpha d/l^*.$$

Here, $I$ is the intensity of photoelectrons emerging from the boundary (in our case it corresponds to peak *B*), $d$ is the mean spacing between neighboring monolayers in the silver film, $\alpha$ is a coefficient which equals the ratio of atomic planes of the substrate at the GaAs (110) surface to the Ag atomic planes in a plane parallel to the film surface [$\alpha \approx 0.64$ if we assume that the number of silver atoms is roughly equal to their number on a silver (111) plane]. Setting $\alpha \approx 0.64$, $d \approx 2.9$ Å (the closest spacing between atoms in condensed silver) and using the data shown in Fig. 3, we obtain $l^* \approx 2.8 \pm 0.3$ Å. The experimental points are well described by an exponential function with this exponent (Fig. 3, solid curve). We note that the scale on the vertical axis of Fig. 3 was chosen so that for $\theta = 0$ the exponential approaches 1. In order to verify this result we plotted the dependence of the amplitude of peak *C* on $\theta$. It was found that it also was well-described by Eq. (1), with a value $l^* \approx 2.5 \pm 0.3$ Å using the same assumptions about the quantities $\alpha$ and $d$. This value of $l^*$ agrees well with analogous values which we also obtained for small $\varepsilon$ and low temperatures in Ref. 14.

In favor of the assumption that the GaAs (110) surface is derelaxed at 10 K in the process of deposition of silver we submit the following fact: it follows from Ref. 3 that the peak of unoccupied SS of an unrelaxed GaAs (110) surface lies at $\approx 0.5$ eV below the conduction band edge $E_c$. Therefore, the band bending we observed in the process of silver deposition, which at 10 K had a value $\approx 0.5$ eV for $\theta \gtrsim 0.1$ (Fig. 4), may be regarded as the appearance in the forbidden band of the unrelaxed SS at an energy $\approx 0.5$ eV below $E_c$ (due to the surface derelaxation) and the pinning of the Fermi level at this energy.

A final argument in favor of our model is provided by the results of experiments in which the samples are warmed to 300 K after deposition at 10 K. It is clear from Fig. 5 that such warming leads to the irreversible disappearance of the peak *B*, while the spectrum itself (with regard to the shape and position of the peak *C*) develops the characteristics of spectra corresponding to deposition at 300 K to the same coverage $\theta$. In this case, as was shown in Ref. 8, the film becomes island-like, and "uncovers" a large part of the surface.

Summarizing what we have discussed, we can make the following assertions:

1. When we deposit Ag on a GaAs (110) surface up to a coverage of $\theta \lesssim 0.1$ at 10 K, we observe a sharper dependence of the band bending on $\theta$ compared to results obtained at 300 K.

2. Further deposition ($\theta \gtrsim 0.1$) leads to pinning of the Fermi level at a position $\approx 0.5$ eV below $E_c$. In contrast, the band bending reaches $\approx 0.8$ eV ($\theta = 5.5$) at 300 K and has a tendency to grow further as growth continues. This value is in agreement with what is observed in Ref. 15 (where for $\theta \approx 10$ a value of 0.9 eV was obtained).

3. During the deposition of silver at 10 K, we observed the appearance of a new peak of occupied SS, located at 0.5 eV below the edge $E_c$; at the same time, the SS peak for a clean GaAs (110) surface disappeared.

4. Assertions 1–3 above can be explained by derelaxation of the GaAs (110) surface at 10 K caused by the Silver deposition.

5. Evidently, at 10 K the formation of a Schottky barrier proceeds via the Bardeen model (in which the Fermi level is pinned at intrinsic SS of the derelaxed surface).

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