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Electronic structure and Schottky-barrier formation of Ag on n-type GaAs(110)

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The electronic structure and Schottky-barrier formation of the Ag/[cleaved n-type GaAs(110)] interface are studied at room temperature by using ultraviolet and x-ray photoemission spectroscopy. It is found that more metal coverage is needed to pin the surface Fermi level with Ag than with most other metals. The Schottky barrier is resolved as 0.83 ± 0.1 eV high (compared to 0.90 ± 0.1 eV for Cu/[n-type GaAs(110)] and 0.92 ± 0.1 eV for Au/[n-type GaAs(110)]). At the early stage of Ag deposition, the so-called atomiclike Ag $5s$ states and Ag $3d$ core levels are observed, which may imply that the interaction between Ag and GaAs is weak and raises the possibility that the Ag atoms may form clusters during the initial stages of metal deposition. It is found that the Ag valence-band photoyield has a maximum at a coverage of $10\sim30$ Å. This photoyield enhancement is explained in terms of Ag clustering and the Stranski-Kristanov growth pattern. In the framework of the unified defect model, it is proposed that the heat released due to the Ag-Ag interaction is responsible for the creation of the defect levels which pin the Fermi level in the Ag/[n-type GaAs(110)] interface. Thus, defects are produced under the clusters but not on the open GaAs surfaces not covered by Ag; this leads to the increased amount of metal needed to complete the surface Fermi-level pinning.

I. INTRODUCTION

To probe the process and mechanism of band bending during the Schottky barrier formation, electron spectroscopy techniques have been widely used to study how the semiconductor valence-band and core-level spectra change with increasing metal deposition. So far, less attention has been paid to the evolution of the electronic structure of the deposited metal overlayer. A careful study of the changes in the electronic structure of the deposited metal, especially at very low metal coverages, may shed light on the understanding of the physics and chemistry of the metal-semiconductor interface, including the mechanism responsible for the Schottky barrier formation. In this paper, we report on studies of the Ag/GaAs(110) interface, which can serve as a model system for the nonintermixing, nonreacting metal/III-V interface.

II. EXPERIMENTAL

The GaAs samples used in the experiments were n-type with a doping level of $10^{17}/\text{cm}^3$. The samples were cleaved *in situ* in a chamber with a base pressure better than 2×10^{-10} Torr. As the radiation source, we used He I ($h\nu=21.1$ eV) and He II ($h\nu=40.8$ eV) for ultraviolet photoemission spectroscopy (UPS) and synchrotron radiation ($h\nu=80$ eV and 100 eV) and Al $K\alpha$ x rays ($h\nu=1486.6$ eV) for x-ray photoemission spectroscopy (XPS). The energy distributions of the spectra were recorded by a cylindrical mirror analyzer. Silver was evaporated at a rate of 3 Å/min, with the sample kept at room temperature. The Ag coverage (1 ml $\approx$ 1.5 Å or 8.85×10^{14} atoms/cm^2) was determined by a quartz thickness monitor. Other experimental details can be found in the paper by Mo *et al.*[1]

III. RESULTS AND DISCUSSIONS

A. Observation and discussion of the chemisorbed atomiclike Ag 5s state

If we treat the adatoms as weak perturbations to the clean GaAs surface and subtract the clean GaAs spectrum from the spectrum with a submonolayer Ag deposit (normalized with the band bending taken into account), we obtain the contribution of the absorbate to the spectrum. We observed in this spectrum not only the Ag $4d$ peak but also a small bump separated from the $4d$ peak (Fig. 1), which we associate with the Ag $5s$ state. Restricted to the signal-noise ratio, we can only locate the bump very roughly at about 4.4 ± 0.4 eV above the Ag $4d$ level, compared with the experimentally measured difference 5.21 eV between the Ag $4d$ level and the leading edge of the Ag $5s$ level for the Ag/[n-type GaAs(100)] interface of Ludeke *et al.*[2] Since the spectroscopic data for the free atomic Ag gives a $5s$ and $4d$ level difference of 5.19 eV, only 0.02 eV smaller, Ludeke *et al.* made the following assumptions: The Ag exhibits atomic character at low coverages and the nucleation of Ag occurs at a coverage of $\sim$0.5 Å, the interaction between the Ag adatom and the GaAs substrate is very weak, and this atomiclike $5s$ level (which shifts with the growth of the Ag coverage) could act as the necessary acceptor states for the stabilization of the Fermi level.[2] Based on these three assumptions and other considerations, Ludeke *et al.* suggested their dielectric screening model.[3]

No evidence of atomiclike s state has been observed in the case of the Au/GaAs and the Cu/GaAs interface.[4,5] We believe that the observation and the location of the so-called atomiclike Ag $5s$ state is relevant to the unique behavior of the Ag/GaAs interface. However, considering the complexity of the metal-semiconductor interface

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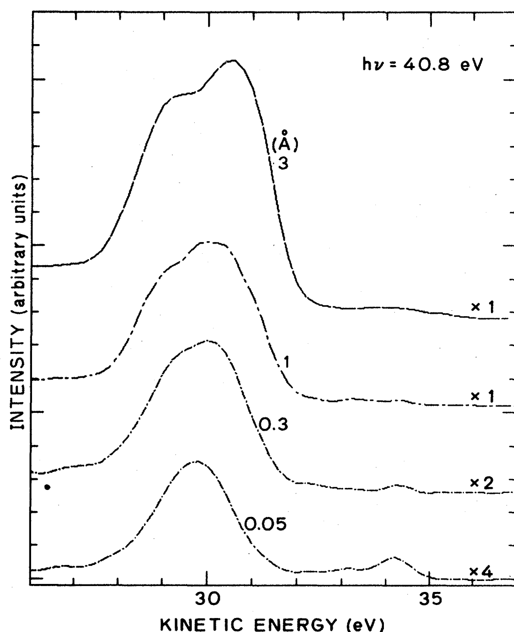

FIG. 1. UPS spectra of Ag valence electrons at various Ag coverages on n-type GaAs(110) cleaved surface.

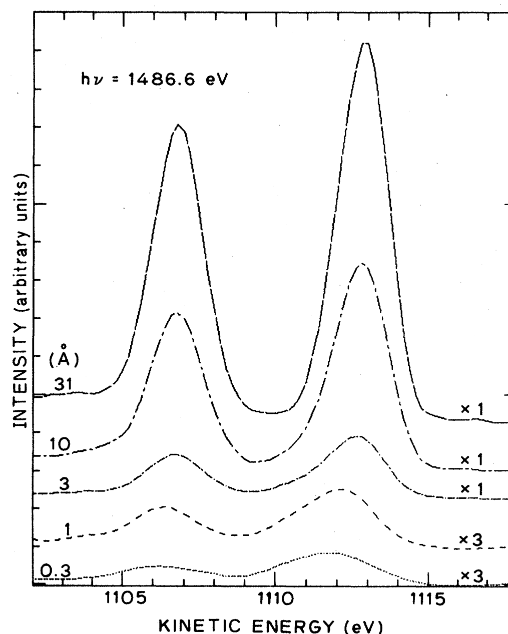

FIG. 2. XPS spectra of Ag $3d$ core levels at various Ag coverages.

and the data to be reported here, the assumptions of Ludeke *et al.* seem to be not fully justified.

(1). First, the Ag atoms may very well migrate and form small clusters in the very beginning of the deposition. This is especially likely, since Ludeke *et al.* note that the interaction between the Ag atoms and the GaAs substrate is very weak. It is also probable that some of the absorbed Ag atoms come onto the GaAs surface, not as single atoms, but in the form of small clusters. Clusters of various sizes have been studied in many metal vapors in recent years.[6] The clustering in Ag vapor is being studied.[7]

(2). The measured difference between the submonolayer Ag $4d$ and $5s$ level is determined, not only by the Ag-GaAs interaction, but also by the Ag-Ag interaction and by the surface image potential.[8,9] It seems that these three effects are of the same order.[10,11] In order to separate them, more detailed information is needed about the physics and chemistry of the metal-semiconductor interface. The conclusion that the Ag-GaAs interaction is weak is not only based on the fact that the free Ag atom and the chemisorbed Ag atom give the same difference between the $4d$ and $5s$ level. As will be shown in this paper, we have to consider a few other things in order to reach this conclusion.

(3). Although the low-coverage Ag $5s$ states observed by Ludeke *et al.*[2] and reported here seem not to be an artifact—they cannot be removed by using slightly different offsets—the reproducibility of the atomiclike Ag $5s$ states has not been well studied yet. We must therefore be very careful in reaching any conclusion from their observation.

(4). Finally, the assumption and model of Ludeke *et al.* does not shed any light on why Ag obtains the same barrier height as other noble metals (Cu and Au) and transition metals (Ni and Pd) on cleaved n-type GaAs(110).[12–14] We will discuss this problem further in subsection E within the framework of the unified defect model.[15]

B. Observation and discussion of the chemisorbed atomiclike Ag $3d$ core level

During the deposition of Ag, the XPS of the Ag $3d$ core level also shows an evolution from atomiclike to bulklike (Fig. 2). At $\Theta = 0.3$ Å (0.2 monolayer), the Ag $3d_{5/2}$ binding energy is resolved as 369.1 eV below the Fermi level. At $\Theta = 10$ Å, the same core level is 367.9 eV (with a difference of 1.2 eV) which is already bulklike.[16] Above that coverage, the Ag $3d$ does not display noticeable changes in its binding energy, spin-orbit splitting, linewidth, and line shape, and neither does the Ag $4d$ valence band. Since about 0.3 eV of the band bending in the GaAs substrate takes place at the Ag coverage of 0.3 Å, 0.67 eV ($0.67 = 1.2$ eV$+0.3$ eV-0.83 eV) of this 1.2 eV difference is presumably due to the transition from small chemisorbed Ag clusters to metallic Ag. For the Ag/[n-type InP(110)] and Ag/[p-type InP(110)] interfaces, a difference of the same order is also observed.[17] The core-level binding-energy shift for small metal clusters supported on various insulating substrates is given in Ref. 18.

C. Ag clustering

If, as we believe, the Ag atoms form clusters at the initial stage of deposition, it is unlikely that the Ag clusters will turn to an epitaxial overlayer abruptly. The valence-band evolution with Ag coverage up to 400 Å is shown by UPS. Above 10 Å, the valence-band shape does not change significantly. The He I (21.2 eV) spectra display an Ag $4d$ emission maximum at around $\Theta = 30$ Å (Fig. 3).

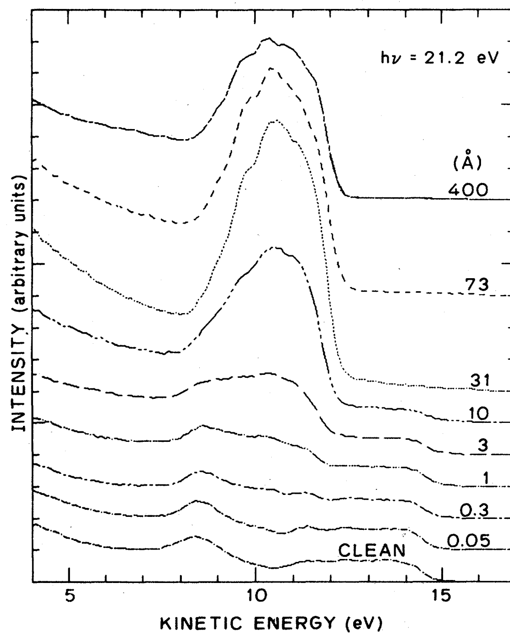

FIG. 3. Ag valence-band photoemission intensity evolution with coverage at $h\nu=21.2$ eV.

The He II (40.8 eV) spectra show an Ag 4*d* emission maximum at around $\Theta=10$ to 30 Å (Fig. 4). The relative intensity evolution is shown in Fig. 5. The valence-band evolution of the Au/[GaAs(110)] interface displays a similar Au 5*d* emission maximum, at $\Theta\approx25$ Å for He I and $\Theta\approx5$ to 25 Å for He II.[1] This coincidence implies

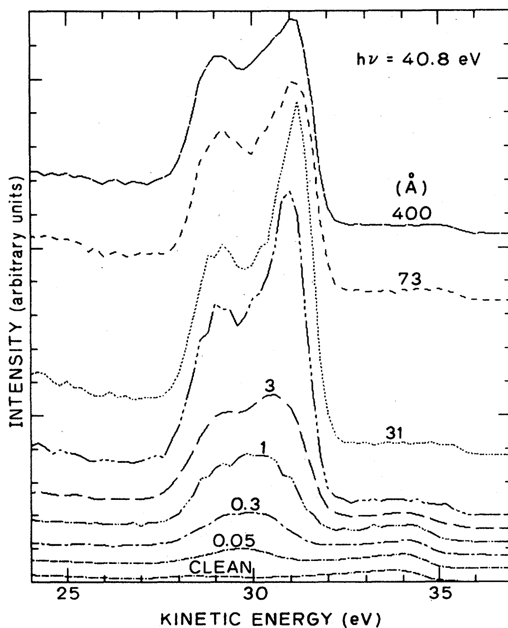

FIG. 4. Ag valence-band photoemission intensity evolution with coverage at $h\nu=40.8$ eV.

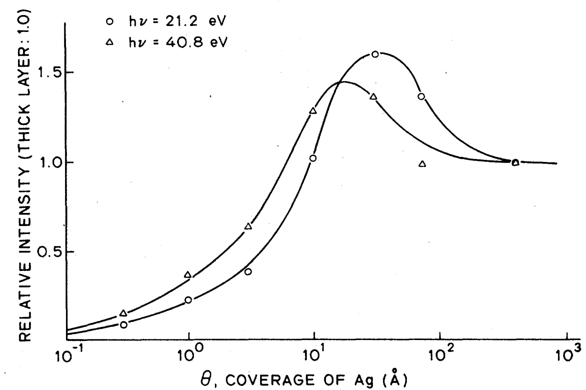

FIG. 5. Relative intensity $I(\Theta)/I(400\ \text{Å})$ of Ag 4*d* spectra at $h\nu=21.2$ and 40.8 eV as functions of Ag coverage.

that the Ag and Au clusters may continue their growth—i.e., the growth mode may be layer plus island Stranski-Kristanov growth mode[11]—to a quite high coverage in the interface. The evolution of the Ag 4*d* binding energy and the separation of the two peaks due to spin-orbit splitting is presented in Fig. 6. This is as would be expected as one goes from an "atomlike" situation to large metallic clusters.

Based on their low-energy electron diffraction (LEED) pattern and intensity analysis of the Ag/GaAs interface, Bolmont *et al.* concluded that the Ag grows as crystallites forming a nonuniform layer.[19] Schmidt-Ott *et al.*[20] observed considerably enhanced photoyield from clusters on the scale of 30—50 Å, relative to the plane photoyield for the same substance in flat morphology. Theoretical calculations also show that clusters on the scale of that size have enhanced photoyield compared to the plane.[21] Our observation of a maximum photoyield at about $\Theta=10\sim30$ Å is in good agreement with the results quoted above.

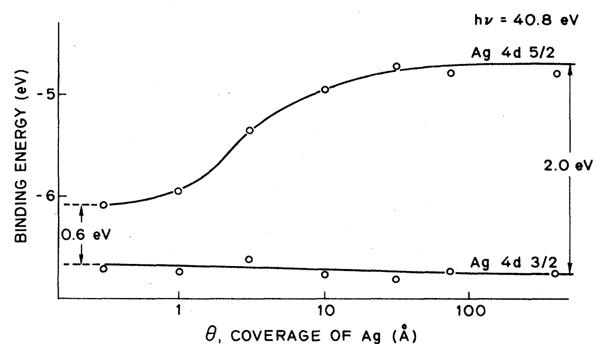

FIG. 6. Ag 4*d* binding energy and spin-orbit splitting as functions of coverage obtained by using a deconvolution technique (see Figs. 2 and 5).

D. Intermixing

The interface metal clustering and metal intermixing with the semiconductor substrate sometimes display similar features in the UPS and XPS.[1] They both change the intensity attenuation, the binding energy, the spin-orbit splitting, and the line shape. It is usually not easy to distinguish one from the other based on the photoelectron spectra only. However, two general rules may be followed.

(1). In the case of clustering without intermixing, the attenuation of Ga and As core-level emission intensity should decrease equally for Ga and As core levels. In the case of intermixing, usually characterized by alloying with Ga (Ref. 1) and/or chemical reaction with As,[5] one substrate specie moves toward the surface more than the other, thus causing a difference in the ratio of Ga to As intensity with coverage.

(2). In the case of clustering without intermixing, the binding energy, the spin-orbit splitting, and the line shape of the deposited metal core levels display an evolution from (chemisorbed) atomiclike to bulklike. In contrast, in the case of intermixing, apart from this kind of evolution, the metal core levels may have chemical shifts. Simultaneously, Ga and/or As may also display chemical shifts.[5]

The two rules for nonintermixing are fairly well observed in the UPS and XPS of the Ag/[GaAs(110)] interface. The attenuation of the Ga $3d$ and As $3d$ emission intensity of the Ag/GaAs system is fairly uniform if compared with that of the Au/GaAs and Cu/GaAs system (Fig. 7, photon energy = 1486.6 eV).

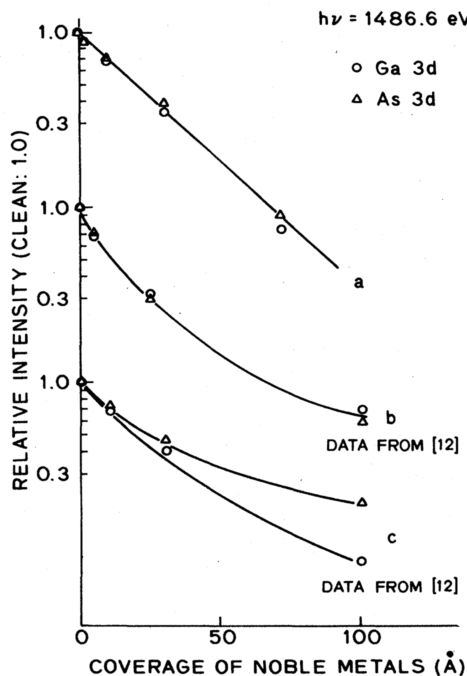

FIG. 7. The photoemission intensity attenuation of Ga $3d$ and As $3d$. (a) Ag/[n-type GaAs(110)]: uniform. (b) Au/[n-type GaAs(110)]: less uniform, indicating intermixing (Ref. 12). (c) Cu/[n-type GaAs(110)]: least uniform, indicating intermixing (Ref. 12).

E. Measurement and discussion of the surface Fermi-level pinning position

It was reported that the noble metal (Cu, Ag, and Au) overlayers on cleaved n-type GaAs(110) surfaces form Schottky barriers 0.9 ± 0.1 eV high.[13,14] Our Ga $3d$ and valence-band photoemission data (Fig. 8) give the surface Fermi-level pinning position at 0.83 eV below the conduction band minimum (CBM), i.e., a barrier 0.83 eV high, which supports the conclusion of Refs. 3 and 13 within the limits of experimental accuracy. A few authors[13,14,22–24] discuss the phenomenon in the framework of the unified defect model.

As was pointed out by several authors and discussed in this paper, the Cu/[GaAs(110)] and Au/[GaAs(110)] interfaces display chemical reaction and alloying,[1,4,5] while the Ag/GaAs interface is mostly abrupt.[2,19] Naturally, a question is raised: Are there mechanisms possible for the creation of similar defects which pin the surface Fermi level at about the same position for these three different kinds of interfaces? The answer seems to be yes, if both the interaction between adatom and substrate and the interaction between adatom and adatom are taken into account.

In the case of reactive interfaces, such as Cs/GaAs (reactive, forming strong ionic bonding), Cu/GaAs (fairly reactive, Cu replaces Ga and forms a bond with As, as well as possible Cu-Ga alloying), and Au/GaAs (also fairly reactive, Au forms an alloy with Ga, as well as possible Au-As bonds), the adatom-substrate heat of condensation plays the key role. The heat of condensation has been studied definitely only for Cs on GaAs,[25] where it is three times larger (about 60 kcal/mol or 2.6 eV per Cs atom) than for Cs on Cs (approximately 20 kcal/mol or 0.9 eV per Cs atom). The cohesive energy of GaAs is 1.63 eV per bond,[26] while the energy needed to form a vacancy in GaAs is in the order of 2 eV.[27] The heat of condensation Cs/GaAs is large enough to create a defect. In the case of noninteractive interfaces, such as Ag/GaAs shown in this paper, the interface photoemission spectra display weak interation between the adatoms and the substrate. The heat of condensation per Ag atom is not large enough to

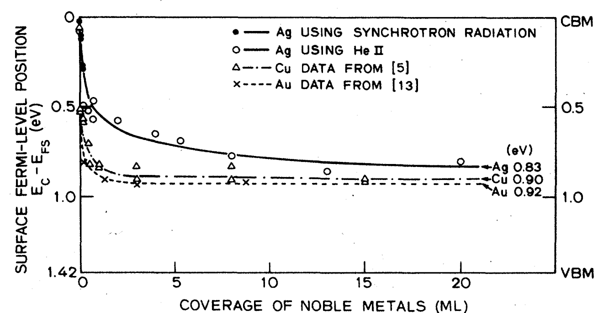

FIG. 8. Surface Fermi-level position against the noble-metal coverage (in units of monolayer) on n-type GaAs(110). The Ag data reported here were taken from three cleaved n-type GaAs(110) samples. Our data are consistent with that of Ludeke *et al.* (Ref. 3). The only discrepancy is that we observe less band bending at low Ag coverages.

create a defect. It needs several Ag atoms to form a cluster and release the energy to break the GaAs bonds to create a defect.

The Ag-Ag bond in a diatomic molecule Ag_2 is 0.85 eV per Ag atom.[28] In the solid state, the cohesive energy is 2.9 eV per Ag atom.[29] For small clusters, we assume the energy released is between 0.85 eV and 2.9 eV per atom. Since the Ag atoms are chemisorbed on a cleaved n-type GaAs(110) surface, the data quoted above for free atoms have to be modified somehow. Again, because of the complexity of the interface, we can only estimate very roughly that we may need in the range of two to ten Ag atoms to break GaAs bonds and create a defect. To test our estimation, we studied the Ga $3d$ and As $3d$ core-level shift during the Ag deposition. Comparing our data for the Ag/[n-type GaAs(110)] interface, the data of Pan *et al.* for the Cu/[n-type GaAs(110)] interface, and the data of Kendelewicz *et al.* for the Au/[n-type GaAs(110)] interface, we can clearly see that the surface Fermi levels pin at about the same energy level for these three systems. However, the pinning of the Ag/GaAs surface Fermi level requires about five times more metal coverage than the pinning of the Cu/GaAs and Au/GaAs surface Fermi levels. Because of the difficulties encountered in obtaining accurate metal evaporation rate calibration and photoemission measurements, our results should not be considered quantitatively exact. However, qualitatively, they support our suggested mechanism responsible for the creation of defect in GaAs.

It is interesting to note that prior to our work, the dielectric screening model[3] of Ludeke *et al.* is also based upon Ag clustering on the GaAs(110) surface, although it explains the surface Fermi-level pinning in terms of donor- and acceptor-type states characteristic of the clusters modified by the screening at the interface. Zunger[30] considered the role of adatom-adatom bonding, as well as that of the adatom-substrate bonding in the Al/GaAs interface in his weakly interacting cluster model, which leads to some interesting predictions regarding the properties of the Al/[GaAs(110)] interface. According to Ludeke *et al.*, under room temperature at the coverage of 3×10^{-3} ml ($2.7\times10^{12}/cm^2$), Ag adatoms are single chemisorbed atoms. Each Ag atom accepts an electron from the depletion region of an n-type GaAs(110) sample and plays the role of the nucleation center for Ag cluster formation, e.g., at the coverage of 0.25 ml ($2.2\times10^{14}/cm^2$), the average cluster size is 80 ($2.2\times10^{14}/cm^2\approx80\times2.7\times10^{12}/cm^2$). Considering the kinetics and thermodynamics of surface defect formation, Zunger points out that the density of adatom induced defect states is typically only about 1% of the adatom density. For such a system as Al/[GaAs(110)], the transition from a situation of separated Al adatoms to a situation of Al_n occurs as a phase transition at a higher coverage. A critical test of the different models presented by Ludeke *et al.*, Zunger, and us will be their different temperature dependence of the metal cluster formation and its effect on the semiconductor surface band bending. Such an experiment is in progress and will be reported later.

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