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Metallization and Fermi-level movement at the Cs/GaAs(110) interfaces

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The room-temperature (RT) and 110-K low-temperature (LT) Cs/GaAs(110) interfaces have been studied with use of photoelectron spectroscopy. The overlayer metallization is investigated by following the density of states near the Fermi cutoff, the free-electron-plasma loss features, and the Fermi-level movement of *n*- and *p*-type GaAs. The criteria of metallicity are proposed. One monolayer (ML) Cs (which is the saturation coverage at RT) is not metallic at either RT or LT, and the full metallicity is established at 2 ML coverage. Development of the overlayer metallicity after the first monolayer is accompanied by a striking increase in electron scattering. The band bending (large for *p*-type GaAs but little for *n*-type GaAs) at low Cs coverages (up to 0.1 ML) is predominantly due to the surface donor states originating from the chemisorbed Cs adatoms. A one-to-one correlation is established between the number of surface donor states and that of the deposited Cs atoms before *p*-type GaAs band bending reaches a maximum value [1.25 eV at LT and 1.1 eV at RT above the valence-band maximum (VBM)]. The Fermi-level stabilization (0.75 and 0.5 eV above the VBM for *n*- and *p*-type GaAs, respectively) is due to the defects at the RT interfaces. At LT it takes place only when the overlayer becomes metallic. In this case, the defects become inefficient because of metal screening, and the metal-induced gap states are responsible for the Fermi-level pinning (0.78 eV above the VBM).

I. INTRODUCTION

One of the interesting problems in present-day metal-semiconductor interface research is the metallization of the deposited film and its effect on Schottky-barrier formation. In order to study this effect one at first has to establish acceptable criteria of the metallization of the deposited films. In the past few years, several authors have reported experimental results of characterizing the metallicity of the deposited thin film for selected systems.[1,2] Different criteria were proposed, which, however, raised some questions.[3,4] Also, the discontinuous film or interfacial reaction found for those systems makes the studies somewhat ambiguous. Cs has the least tendency to form three-dimensional cluster of all metals studied. In this regard, investigation of development of continuously distributed film at the nonreactive Cs/GaAs interface offers a model system to establish the criteria of overlayer metallization. Previous studies of the Cs/GaAs interfaces were mainly conducted at room temperature (RT). Under this condition only one monolayer of saturation coverage can be obtained.[5-8] This overlayer is not metallic as we will show later in this paper. To obtain multilayer coverages it is necessary to lower the temperature substantially below RT. The Cs additional to the first monolayer shows development of metallicity of the overlayer. Thus the Cs/GaAs interfaces formed at low temperature (LT) offer a unique possibility to study the correlation between overlayer morphology and/or metallization and the processes responsible for the Schottky-barrier formation.

Besides the morphological properties for Cs on GaAs, the unique electronic properties of Cs have attracted a lot of attention. Although Fermi levels have been found to be pinned in a narrow range when the semiconductor surfaces are covered by a variety of metals, weak dependence of the pinning position on the electronic properties, such as work function and electronegativity, of metals has been reported. The low work function and the electronegativity of Cs will set a limit to various models of Schottky-barrier formation which explicitly or implicitly consider such dependence. Recent studies of the metal/GaAs interfaces prepared at LT have provided a lot of valuable information pertinent to Schottky-barrier formation.[9-11] One important finding is the dependence of the low coverage band bending of GaAs on the metal atom electronic properties such as first ionization potential.[9,12] The extremely electron positive properties and the lowest ionization potential Cs atoms will certainly extend the trend and test the validity of the explanation in the literature.

In this paper we report a systematic photoemission study of the RT and LT (110 K) prepared Cs/GaAs interfaces. We will emphasize the development of the overlayer metallization. Through this study the criteria of the overlayer metallization are proposed, which can be used as a guideline for other metal/GaAs interface studies. Particular attention will also be put on the Fermi-level movement as a function of the Cs coverage. A quantitative relationship between the initial-stage band bending and the amount of the deposited Cs atoms is established. The Fermi-level stabilization at high coverage at RT and LT is studied. In particular, we investigate the influence of the overlayer metallization on the Schottky-barrier formation and discuss the data in terms of the current models of Schottky-barrier formation.

II. EXPERIMENTAL DETAILS

The experiments were conducted at the Stanford Electronics Laboratories with a monochromatic He discharge

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lamp as a photon source of photoelectron spectroscopy (PES). Interface preparation and photoemission measurements were performed in a standard ultrahigh-vacuum (UHV) chamber (base pressure 6×10^{-11} Torr) equipped with a double-pass cylindrical mirror analyzer. The Cs/GaAs(110) interfaces were prepared by cleaving *n*-type (Si doped, $n=4\times10^{18}$ atoms/cm^{-3}) and *p*-type (Zn doped, $p=1.4\times10^{19}$ atoms/cm^3 GaAs single crystals in (110) orientation followed by stepwise Cs exposures. A precalibrated commercial SAES getter dispenser was used as the Cs source. It had been carefully outgassed prior to evaporation. The chamber pressure was around 8×10^{-11} Torr during the Cs deposition, and contamination was not detected with photoemission. The samples were kept at constant temperature (either RT or 100-K LT) during the interface preparation and PES characterization. After cleave and each Cs deposition Ga 3*d* and Cs 5*p* core levels ($h\nu=40.8$ eV) as well as the valence-band ($h\nu=21.2$ eV) spectra were taken. The band bending of the GaAs substrate was established by the shift of the Ga 3*d* core level and the valence-band spectra.

It has been established that there is a saturation coverage for Cs deposited on the GaAs(110) surface at RT, and this saturation coverage is defined as one monolayer (here 1 ML=4.4×10^{18} atoms/cm^2).[5–8] In this work, the proportionality between the coverage and the exposure time and unity sticking coefficient of Cs on GaAs(110) through all the coverages was assumed. The RT saturation coverage was used as a reference point to obtain the absolute Cs coverage.

III. RESULTS

Figures 1 and 2 show the Ga 3*d* core-level spectra for the Cs/[*n*-type GaAs(110)] interface at RT and LT (110 K). Photoemission spectra were also taken at the RT and LT Cs/[*p*-type GaAs(110)] interfaces but not shown here for the sake of brevity. Absence of chemical reaction at these interfaces is indicated by lack of change of the core-level line shape at any coverage. This is consistent with previous studies.[6–8] The rigid shift of the Ga 3*d* peak towards the high-kinetic-energy (low binding energy) direction represents the substrate band bending induced by the Cs deposition. In contrast to the 1-ML saturation coverage at the RT GaAs(110) surfaces, more than 1 ML of Cs can stay on the surface at reduced temperature. Moreover, above the first monolayer, a new feature appears on the low-kinetic-energy side of the main peak. This is interpreted as the free-electron-plasma loss of the Ga 3*d* photoelectrons. The energy separation between the main peak and the plasma loss increases with increasing Cs coverage.

Substrate signal attenuation has proven useful to elucidate the growth of the deposited materials.[3,13] The area underneath the Gs 3*d* main peak is measured and normalized against that of the clean surface. The normalized intensities are plotted in Fig. 3 as a function of Cs coverage in terms of ML. The data points lie on two segments of straight lines with different slope. This indicates exponential decay of the substrate intensity but with

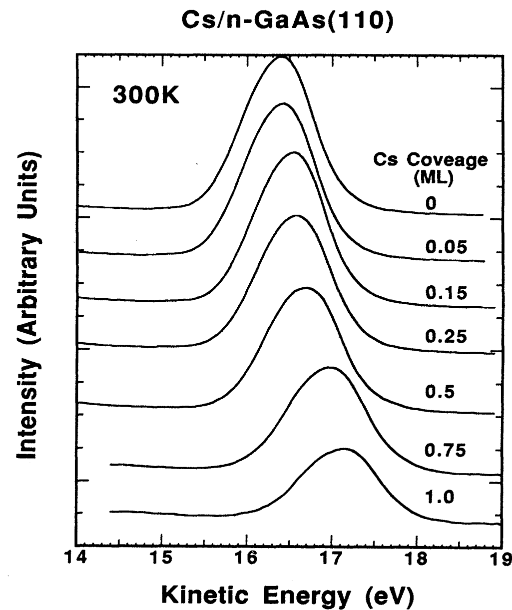

FIG. 1. Ga 3*d* core-level spectra ($h\nu=40.8$ eV) of the RT (300 K)Cs/(*n*-type GaAs) as a function of Cs coverage. The one monolayer is the saturation Cs coverage on the GaAs(110) surface at RT.

different decay length and is consistent with the laminar growth of Cs on a GaAs(110) surface. By the conventional definition of the escape depth of a photoelectron for the laminar growth mode, $I/I'=\exp[(x'-x)/\lambda]$, where I and I' are intensities with overlayer thickness x and x'

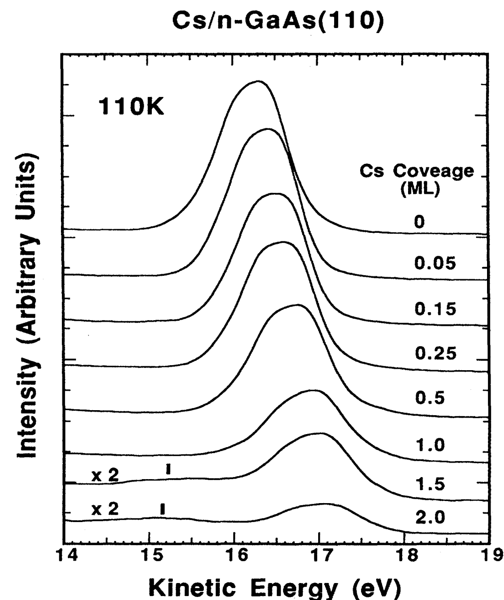

FIG. 2. Ga 3*d* core-level spectra ($h\nu=40.8$ eV) of the LT (110 K)Cs/(*n*-type GaAs) as a function of Cs coverage. More Cs can stay on the GaAs(110) surface at LT. The marked peaks on the low-kinetic-energy side are due to free-electron-plasma loss.

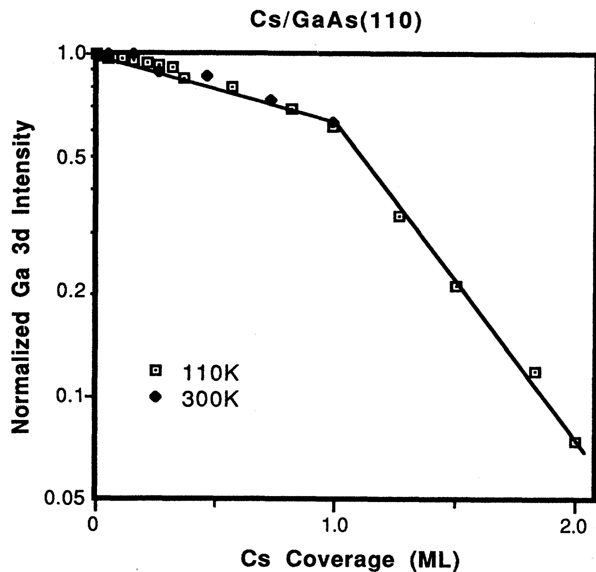

FIG. 3. Substrate signal attenuation vs Cs coverage at the RT and LT Cs/GaAs(110) interfaces. The straight lines indicate laminar growth of Cs on the GaAs surfaces at both temperatures.

and λ is the mean free path (MFP). With this equation, the MFP for the first Cs layer is estimated to be between 6.6 and 10.4 Å, depending on the diameter used for Cs atoms (neutral atom or ion with one positive charge). Faster attenuation is found with the Cs coverage over 1 ML, indicated by larger slope of the straight line in this coverage regime compared with that below 1 ML. This suggests that the MFP of the photoelectrons in the Cs overlayer above the first layer is much shorter. The MFP estimated in this case is less than 2.5 Å with the assumption that the thickness of the one layer is the diameter of the neutral Cs atom which is about 5.34 Å.

To our knowledge, it is the first case that the substrate signal attenuation rate is faster with thicker overlayer than that with the first monolayer. This is ascribed to the change of the MFP in different layers. The MFP for the first layer is similar to most other systems; whereas that of the second layer shows an abnormally low value. The MFP's of bulk alkali metals have been investigated by Smith and Fisher.[14] An abnormally small value was reported for Cs and Rb ($\sim$2 Å for 10-eV kinetic energy of the photoelectron). The MFP in the second Cs layer estimated from our data (with 17-eV kinetic energy) is consistent with their results. This also implies that the deposited Cs above the first monolayer is close to those of bulk Cs metal. The large amount of free-electron-plasma loss may be responsible for such a short MFP.[14] In contrast, the first monolayer of Cs is not metallic because of strong bonding with GaAs surface atoms.

The band bending of the substrate GaAs can be determined straightforwardly from the shift of the Ga 3d peak. More precise determination of the band bending is obtained by employing a curve fitting program. The procedure of the curve fitting and the fitting parameters has been discussed in detail in Refs. 11 and 15. The uncertainty of the band bending determination is estimated to be less than 0.05 eV. The results plotted in Fig. 4 show the surface Fermi-level position inside the band-gap for n- and p-type GaAs at both RT and 110-K LT as a function of Cs coverage. A strongly asymmetric pattern of the Fermi-level movement for n- and p-type GaAs at both temperatures is observed. Such a characteristic pattern has been reported before mainly at the LT metal/GaAs interfaces.[9–11] In the low metal coverage regime the observed band bending is large for p-type GaAs but small for n-type GaAs. Moreover, the band bending of p-type GaAs reaches a maximum (overshoot) before it drops to its stabilization value. The overshoot of p-type GaAs is as large as 1.25 and 1.1 eV above the valence-band maximum (VBM) for LT and RT, respectively. These are the largest overshoot values ever observed for p-type GaAs.

Despite some similarities of the band bending in the low coverage regime (indicated by the large band bending for p-type GaAs and small band bending for n-type GaAs), the Fermi-level stabilization values at higher coverages are different at different temperatures. At RT the Fermi levels are stabilized at two distinct positions of 0.75 and 0.5 eV above the VBM for n- and p-type GaAs, respectively. These are the same values as those obtained for many other RT metal/GaAs interfaces (such as Al, In, etc.[9,10]). In contrast, the Fermi levels are not stabilized at the LT interfaces until the coverage reaches 2 ML. In this case, only one pinning position is observed at around 0.78 eV above the VBM for both n- and p-type GaAs.

In order to get more insight into the Schottky-barrier formation processes, in particular the influence of overlayer metallization, the Cs/(p-type GaAs) interface with 1 ML Cs coverage prepared at RT (this is the saturation coverage) was also cooled down to 110-K LT. This was followed by further Cs deposition. During this process

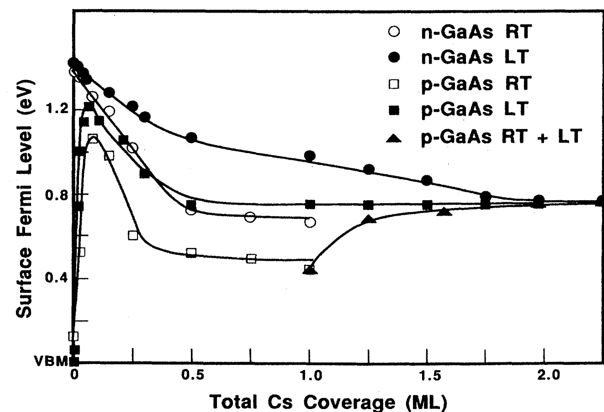

FIG. 4. The surface Fermi-level position of n- and p-type GaAs as a function of Cs coverages at RT and LT. Notice the strongly asymmetric band bending for n- and p-type GaAs in low coverage regime and different Fermi-level pinning patterns at the two temperatures.

no contamination was detected. The results of this study are included in Fig. 4. An additional movement of the surface Fermi level of about 0.2 eV due to the further Cs deposition was observed. As we will show later, this movement is accompanied by the development of the overlayer metallicity.

IV. DISCUSSION

A. Overlayer metallization

For studies involving deposition of metal atoms, it is important to develop acceptable criteria for the establishment of metallicity in the deposited films. The central question is can the deposited film by characterized by Fermi-Dirac statistics and in general demonstrate the properties of a Fermi liquid? In this paper we will propose a few criteria of metallicity which are closely tied to the metallic behavior of "free electrons." The criteria developed here are particularly applicable to PES studies. Two of them can be directly applied to most other interfaces. Later in this paper, we will show the correlation of the overlayer metallicity with other interface properties, such as Schottky-barrier formation. This is ultimately important in the metal-semiconductor studies. Cs/GaAs is used as a model system to demonstrate these criteria because of its unique properties, e.g., the continuously distributed film and nonreactive nature. Previous studies of overlayer metallization involved clustering systems (e.g., Ag/GaAs) (Ref. 1) and reactive systems (e.g., Tm/GaAs).[2] The discontinuous film and nonmetallic phase at the interface make unambiguous interpretation of these studies difficult.

At first let us look at the development of a Fermi surface as seen by PES. This is illustrated in Fig. 5, in which evolution of the density of states near the Fermi level at the RT and LT Cs/GaAs interfaces is presented as a function of Cs coverage. It is well known that the Fermi level coincides with the Fermi cutoff of the electron distribution for bulk metal at 0 K. When it is measured by PES at a temperature above 0 K, the Fermi cutoff is broadened by instrumental broadening (usually about a few tenths of an eV) and thermal broadening (usually much less than the instrumental broadening at most temperatures of interest). In this case the Fermi cutoff must be bisected by the Fermi level.[3,4] In Fig. 5, starting from 2 ML Cs coverage the Fermi cutoff is bisected by the Fermi level. This assures that full metallicity is established in the Cs overlayer in agreement with the above definition. In contrast, for 1 ML Cs/GaAs at both RT and LT this criterion is not fulfilled. We thus conclude that the 1 ML Cs is not metallic. Between 1 and 2 ML a movement of the bisector of low-binding-energy cutoff toward the Fermi level is observed and this can be con-

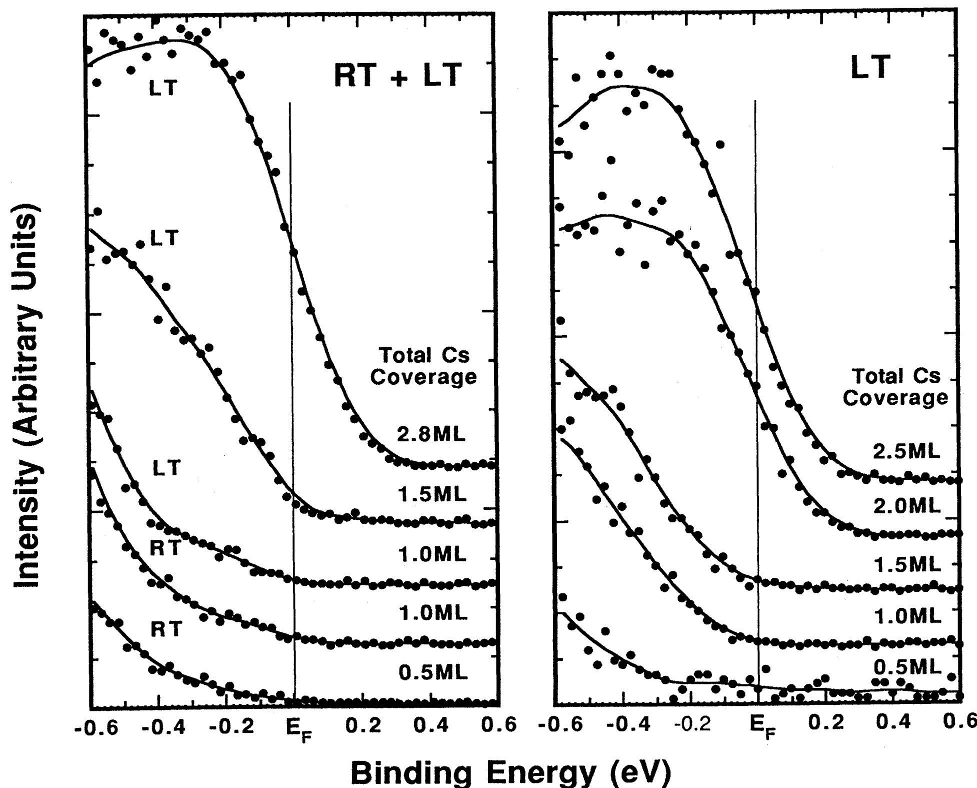

FIG. 5. Density of states ($h\nu=21.2$ eV) near the Fermi level of the RT and LT Cs/GaAs(110) interfaces. The overlayer metallization is indicated by the Fermi cutoff bisected by the Fermi level.

sidered as development of the overlayer metallicity. The left panel shows that by cooling the 1 ML Cs/GaAs prepared at RT, more Cs can be deposited on the surface and becomes metallic. This is consistent with data in the right panel, where Cs was directly deposited on the LT GaAs surface.

The second criterion is related to the Schottky-barrier formation at the metal-semiconductor interface. When the semiconductor surfaces are covered by a continuous metallic overlayer the Fermi-level positions for *n*- and *p*-type semiconductors must coincide.[16] This can be used to judge the metallization of the deposited overlayer. Using this as one criterion, one sees that the 1 ML Cs is not metallic yet since two distinctly stabilized Fermi-level positions are observed; whereas 2 ML Cs, where Fermi levels of *n*- and *p*-type GaAs are at the same place as shown in Fig. 4, becomes metallic. This is in agreement with the Fermi cutoff criterion discussed before. It is worth pointing out that this criterion can only be applied to continuous metallic film but not to strongly clustered systems such as In, Al, and Ga on GaAs. In these cases, the clusters can be large enough to possess bulk metallic properties even at submonolayer regime but no coincidence of the stabilized Fermi levels for *n*- and *p*-type GaAs has ever been observed with PES.[9] The metallization only occurs locally, and the semiconductor surface Fermi-level position is obtained principally from the nonmetallized areas. The RT Cs/GaAs also shows that the Fermi-level stabilization can be unambiguously seen before metallization takes place, although this may not be directly related to the ultimate Schottky-barrier height.

The development of the overlayer metallicity can also be monitored with the free-electron-plasma loss feature. This is illustrated in Fig. 6. No free-electron-plasma loss is seen for the Cs coverage at 1 ML, whereas this feature clearly appears and grows with the coverage above one monolayer. Notice that the energy separation between the main peak and the plasma loss feature increases with increasing coverage.[17] This can be explained in terms of the increase of the density of free electrons in the overlayer. As shown before, the presence of a large amount of free electrons reduces the MFP of the photoelectron dramatically, which is responsible for the extremely short escape depth observed for the Cs coverage above the first monolayer. The agreement between the estimated MFP above the first monolayer and that of the bulk Cs by Smith and Fisher[14] reinforces the conclusion that the full metallicity is established at 2 ML of coverage.

Work-function study has been performed recently with Cs on GaAs by Prietsch *et al.*[18] A monotonic decrease of the work function has been reported with Cs coverage up to 1 ML. After that an increase of the work function was observed, and the work function becomes stabilized around 2 ML, indicating the full metallization in the overlayer. Change of the work function from its lowest value to its final value between 1 and 2 ML is considered as the development of the metallicity of the overlayer. These data are clearly consistent with our results.

We would like to emphasize that the criteria of metallicity established for (alkali metal) GaAs interfaces can be applied to other metal/GaAs interfaces. In particular,

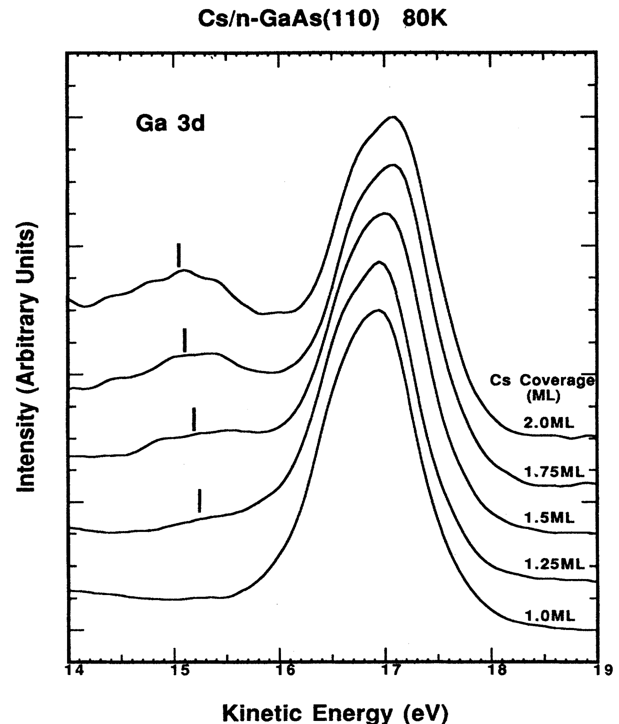

FIG. 6. Ga 3*d* core-level spectra ($h\nu = 40.8$ eV) taken at the LT Cs/(*n*-type GaAs) interface. The free-electron-plasma loss features are marked. This feature grows with more Cs additional to the first monolayer. The separation between this and the main peak also increases.

the evolution of the Fermi cutoff should be used as a fingerprint of the metallization of the deposited films. In fact, the same criteria have been used to characterize the deposited overlayer on GaAs(110) surfaces by Spicer *et al.* and Cao *et al.*, and consistent pictures have been obtained.[3,4]

B. Initial-stage band bending

Similar band bending behavior as a function of Cs coverage at both RT and LT in the low coverage regime (<0.1 ML) is shown in Fig. 4. This is characterized by the large band bending for *p*-type GaAs but small band bending for *n*-type GaAs. The same behavior has been observed at many LT's but is unusual for RT metal/GaAS(110) interfaces.[9,11] For metals deposited at LT, one common phenomenon is the uniform growth of the deposited materials with the coverage below one monolayer. They behave like individual atoms without strongly mutual interaction.

Large band bending for *p*-type GaAs and small band bending for *n*-type GaAs in the low coverage regime immediately indicates that the dominant surface states responsible for the band bending are donor states. This becomes more evident at the LT interfaces. Since there is one type of dominant states, a quantitative study is possible. To preserve the charge neutrality, for a certain amount of charge on the semiconductor surface, there

should be an equal amount of charge with opposite sign in the depletion region. Then the band bending of the semiconductor can be calculated with the depletion approximation. For a p-type semiconductor one has

$$\Delta\phi = \frac{qQ^2}{2\epsilon_r \epsilon_0 N_A} , \quad (1)$$

where $\Delta\phi$ is the band bending of the p-type semiconductor, Q is the surface charge density, ϵ_r is the dielectric constant (10.9 for GaAs), and N_A is the doping concentration.

In this work, p-type GaAs with $N_A = 1.4 \times 10^{19}$ atoms/cm^3 was used. We assume that the density of the surface states is equal to that of the deposited Cs atoms. The parabolic curve from Eq. (1) and the low coverage p-type GaAs band bending at both RT and LT versus number of the deposited Cs atoms are plotted in Fig. 7. Excellent agreement between the model calculation and the LT data before the band bending reaches the maximum assures a one-to-one correlation between the amount of the deposited Cs atoms and surface donor states. The RT data show a deviation from the depletion approximation. One explanation is the presence of other states, such as defects, which compensate the existing donor states. Other possibilities are not excluded, such as stronger interaction due to formation of a Cs chain at RT, which may result in less charge transfer from Cs to GaAs and in turn less substrate band bending.

The same analysis has been applied to other LT metal/GaAs systems also. We found that in general, the less reactive interfaces show the better agreement with the depletion model. Large deviation is found for the systems where interfacial reaction takes place even at LT. In other words, other states may be involved.[19]

Another interesting aspect of the low coverage band bending study is the correlation between the p-type GaAs maximum band bending and the electronic properties of metal atoms, which was first reported by Cao *et al.*[9] This correlation is illustrated in Fig. 8, in which the maximum p-type GaAs band bendings induced by a variety of metal atoms are presented as a function of first ionization potential of metal atoms. It is clearly seen that the larger the ionization potential, the larger the maximum band bending. These findings provide strong evidence that the surface donor states are metal atom dependent. In other words, the energy levels of the surface donor states are closely associated with electronic properties of metal atoms. In the low metal coverage regime the deposited materials will behave as individual atoms at reduced temperature due to slow surface mobility. This determines that the band bending in this coverage regime should be approached from the atomic point of view. An electron-positive metal atom chemisorbed on the GaAs surface leads to surface donor states, and charge transfer from metal atoms to GaAs will cause band bending of p-type GaAs but not n-type GaAs. Recently, Mönch reported a tight-binding calculation, which ascribes the surface donor states in the low coverage range to the metal atom derived states.[20] The detailed relationship is not clear yet, and more studies are certainly needed.

The same idea can be applied to electronegative

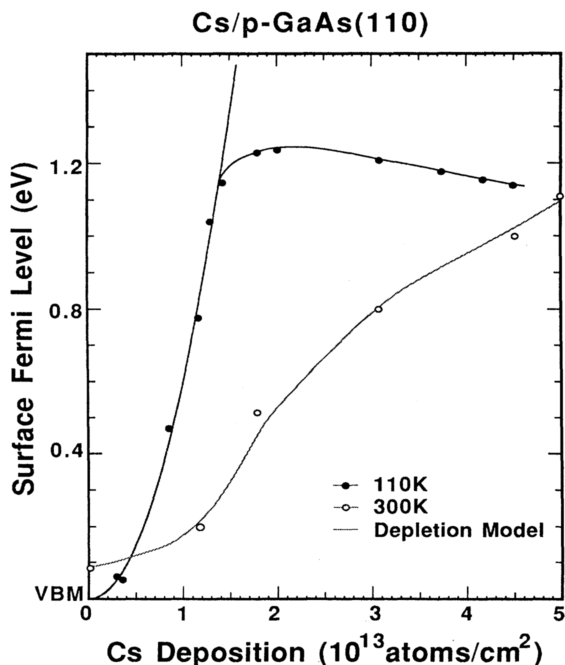

FIG. 7. The band bending of the RT and LT p-type GaAs in low coverage regime. A parabolic curve is obtained from the depletion approximation. Excellent agreement between the LT data but large deviation of the RT data with the depletion model is observed.

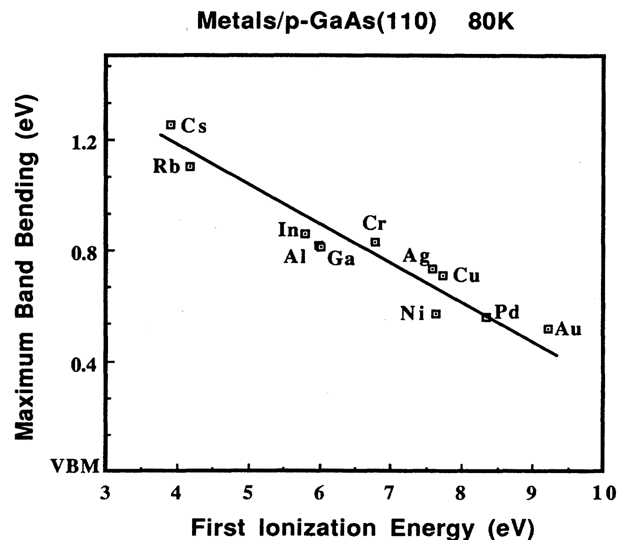

FIG. 8. The maximum band bending of LT p-type GaAs as a function of first ionization potential of metal atoms. All the data points fall close to a straight line, suggesting a correlation between the surface donor state and the electronic properties of a metal atom.

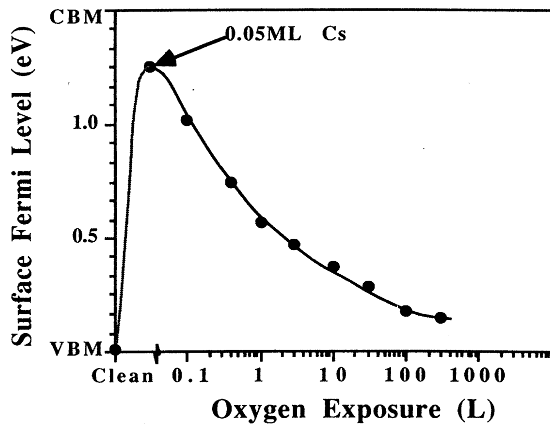

FIG. 9. Surface Fermi-level movement of the LT 0.05 ML, Cs/(*p*-type GaAs) as a function of oxygen exposure in langmuirs. It moves from 1.25 eV above the VBM (corresponding to maximum band bending of *p*-type GaAs at LT) to 0.15 eV above the VBM with less than 1000 L (1 L$=10^{-6}$ Torr sec) oxygen exposure.

species. They are expected to induce surface acceptor states. Charge flowing from GaAs back to these species will lead to large band bending of *n*-type GaAs. Recent studies for Cl_2,[21] O_2,[22] and S_2 (Ref. 23) on GaAs(110) surfaces have proven that it is the case. In this work, to further test this idea we also exposed the *p*-type GaAs surfaces with maximum band bending to oxygen. This treatment was found to result in large reduction of the band bending of *p*-type GaAs shown in Fig. 9. The band bending drops from its original high value of 1.25 eV to around 0.15 eV above the VBM. The explanation appears to be straightforward. Since oxygen atoms are electronegative they provide surface acceptor states, which compensate the existing surface donor states created by metal atoms and cause a reduction of band bending. It is also possible for an O atom to form a chemical bond with a Cs atom. This process reduces the charge flowing from Cs atoms to GaAs, and in turn the *p*-type GaAs band bending.

C. Fermi-level stabilization

Although the Fermi-level movement shows some similarities at both RT and LT in the low coverage regime, significant temperature dependence is observed on the Fermi-level stabilization at high coverages (>0.5 ML). The Fermi levels of different doping are stabilized at two positions (0.75 and 0.5 eV above the VBM for *n*- and *p*-type GaAs, respectively) up to the 1-ML saturation coverage at RT. In contrast, continuous movement of the surface Fermi level is observed at LT for *n*-type GaAs and it stabilizes only after 2 ML of coverage. At that coverage, the overlayer is metallic, and only one pinning position is observed at 0.78 eV above the VBM for both *n*- and *p*-type GaAs. The data are discussed from the perspective of various models of Schottky-barrier formation. We will focus on two prevailing models which have attracted the most attention in the past years. These are the so-called defect model[24,25] and the metal-induced gap states (MIGS) model.[26,27] Both propose that the Fermi levels are pinned by interface states but of different physical nature. The former ascribes the states to defects in the semiconductor, such as antisite defects, and the latter to the metal wave function tailing into the semiconductor. In the defect model, before the overlayer becomes metallic different energy levels of defects inside the band gap may produce different pinning positions for *n*- and *p*-type materials. The Fermi levels, however, must coincide when the semiconductor is covered by a metallic overlayer. On the contrary, the MIGS model predicts only one pinning position at about 0.5 eV above the VBM for GaAs.[28]

At the RT Cs/GaAs interfaces the largest coverage is 1 ML, and this layer, as shown before, is not metallic. This, combined with the two distinct positions, suggests that the Fermi-level stabilization cannot be due to the MIGS or any other established model except the defect model. Here we suggest a description of the Fermi-level stabilization in terms of the defect model because of the fact that the Fermi-level stabilization positions coincide with the defect levels inside the band gap.[25] The large amount of energy (60 KCal/mol) (Ref. 6) released during the Cs chemisorption most likely provides the driving force to create a relatively small amount of defects ($10^{12}-10^{13}/cm^2$) needed to pin the Fermi levels when the surface is not covered by metal. These defects may also explain the deviation of the low coverage band bending from the depletion model at RT and the initial band bending of *n*-type GaAs as well. We would like to emphasize that the RT Cs/GaAs may provide unambiguous experimental evidence that defects in the semiconductor surface region can move the Fermi level. However, further movement of the Fermi level out of its original stabilization position does occur due to the overlayer metallization. Compared with other systems, such as In, Al, and Ga on GaAs(110),[24] where the metal clustering (local metallization) and the same two pinning positions have been reported, the ideally lateral uniformity of the Cs overlayer avoids complicated argument about the lateral uniformity of the band bending. Similar results have been reported for the Sb/GaAs, another system with uniform overlayer and lack of metallicity at monolayer coverage.[29]

At the LT interfaces few defects are expected in the submonolayer regime because of higher thermal conductivity and greater rise in local temperature necessary to produce them. The Cs atoms on the top of the first monolayer are mostly physisorbed, and thus the disturbance to the substrate from these atoms is negligible. Moreover, the Fermi levels are stabilized only when the surface is covered by metallic overlayer. Through their classic analysis on the basis of the defect model and jellium model for metallic overlayer, Zur *et al.*[16] conclude that much higher density of states (about 2 orders of magnitude) is required for defects to pin the Fermi levels when the surface is covered by metallic overlayer, otherwise the Fermi-level position should be governed by the original Schottky model.[30] In this case, the MIGS were

not considered. They also found that even more defects were required for lower work-function metals (2.13 eV for Cs). At RT, the Fermi level reaches a stabilization position around roughly 0.5 ML of Cs coverage. Taking the density of defect at that coverage as the density required for the Fermi-level pinning and assuming a proportionality between the Cs coverage and the amount of defects, we find that the density of defects at LT with 2 ML Cs coverage is much lower than the requirement set by the model by Zur *et al.*[16] As a result of this analysis, the Fermi level would lie at the conduction-band minimum or an Ohmic contact would be formed. Clearly it is not the case. Above all it is evident that the Fermi-level pinning at LT for 2 ML Cs coverage is not due to the defects.

The absence of the Schottky behavior of the Fermi-level position urges one to look for other interface states which pin the surface Fermi level. We notice that the Fermi-level stabilization at the LT interfaces is accompanied by full establishment of overlayer metallicity. Theoretical calculation has shown that the metal wave function tailing into the semiconductor induces continuum states across the semiconductor band gap. Part of the states (close to the conduction band) are of acceptor nature and part of them (close to the valence band) are of donor nature. The surface Fermi level should be pinned at the charge-neutrality level (CNL) which is at 0.5 eV above the VBM for GaAs.[28] This position is lower than the Fermi-level pinning position observed at the LT interfaces by 0.28 eV. For metal deposited on GaAs, a certain amount of charge is transferred from metal to GaAs. We suggest that it leads to a shift of the Fermi-level position away from the CNL of the original MIGS model, where the charge transfer was not taken into account. In Fig. 10, the Fermi-level pinning positions observed at a number of LT metal/GaAs interfaces are presented versus electronegativity (in Pauling scale) of metals. The CNL is also included in this figure. It is clear that more charge transferring (judged by larger difference of the electronegativity between metal and semiconductor) will result in a larger shift.[31] Here, the Cs/GaAs shows the largest difference between the pinning position and the CNL. This is consistent with the lowest electronegativity of Cs of all metals studied.

We have established that the Fermi-level stabilization at the RT interfaces is due to the defects. In order to see the role of the overlayer metallization on the Fermi-level movement this interface was cooled down to LT followed by further Cs deposition. As shown in Fig. 3 the additional Cs appears to be metallic, and an additional movement of the Fermi level is observed as illustrated in Fig. 5. The Fermi level of *p*-type GaAs moves from its RT stabilization value to its LT stabilization value. Here we have both defects (remaining in the surface region) and the MIGS (turned on by overlayer metallization). In this case, both mechanisms should be taken into account, and the Fermi-level pinning position is viewed as a result of the competition between the two mechanisms. Zhang *et al.*[32] performed a theoretical calculation and concluded that the key parameter is the relative density of the states. When the density of defects is lower than that of the MIGS ($4\times10^{14}/\mathrm{cm}^2\,\mathrm{eV}$) the MIGS would be responsible for the Fermi-level pinning. On the contrary, if the density of defect states is larger than that of the MIGS, defects will be dominant. In our case, although the defects remain in the surface region, they become much less effective due to the metal screening. The density of the defects appears much lower than that of the MIGS, and the Fermi levels are pinned mainly by the MIGS. We have also found that for a highly reactive interface, such as Ti/GaAs, reaction is still strong even at liquid-nitrogen temperature so that the defects still play an important role in the Fermi-level pinning.[33] These are clearly consistent with the theoretical prediction.

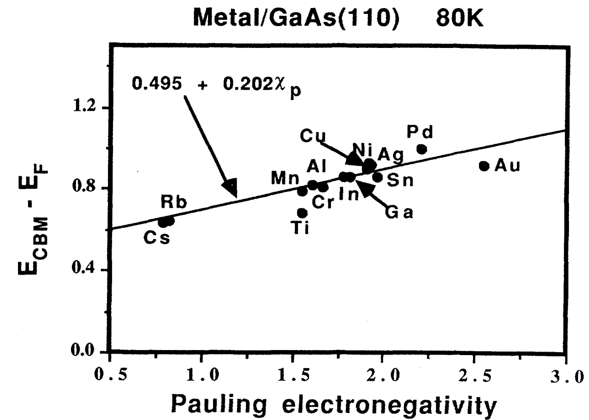

FIG. 10. Schottky-barrier height of *n*-type GaAs ($E_{\mathrm{CBM}}-E_F$) obtained at the LT metal/GaAs interfaces as a function of electronegativity (Pauling scale) of metals. The dashed line indicates the barrier height predicted by the MIGS model without taking the charge transfer between metal and GaAs into account.

Overlayer metallization and its effects on the Fermi-level pinning has been studied with another approach by Ludeke *et al.*[34] In this approach the metal wave function broadens the existing discrete levels and lowers their center of gravity. A shift of the Fermi level towards the VBM with presence of metallic overlayer is expected from the model. However, the upward movement of the Fermi level shown in Fig. 5 seriously casts doubt about such a mechanism being important in this case

V. CONCLUSION

We have studied overlayer metallization and Fermi-level movement at the RT and 110-K LT Cs/GaAs(110) interfaces. Metallization of the deposited overlayer has been investigated. Three consistent criteria (Fermi cutoff, coincidence of Fermi levels of different doping, and free-electron-plasma loss) have been proposed. We have found that 1 ML Cs is not metallic yet; whereas full metallicity is established with 2 ML Cs coverage. Study of the Fermi-level movement as a function of Cs coverage reveals a few interesting findings. The initial-stage band bending is overwhelmingly dominated by the surface donor states originated from Cs chemisorption on the GaAs surface. A one-to-one correlation is established between the number of the surface donor state and that of

the deposited Cs atoms. The energy levels of the surface donor states are suggested to be related to the electronic properties of metal atoms, such as first ionization potential. The Fermi-level stabilization shows different patterns at RT and LT. The RT Fermi-level stabilization at two distinct positions (0.75 and 0.5 eV above the VBM) and the nonmetallic feature of the saturation 1-ML coverage suggest that defects due to substrate disturbance are dominant. In contrast, defects are no longer dominant at the LT interfaces with metallic overlayer. The Fermi-level stabilization in this case is explained in terms of MIGS with the charge transfer from Cs to GaAs. This work provides strong evidence that the "conventional" approach in which a single mechanism explains everything is inappropriate. Finally, we emphasize the importance of taking the competition between the defects and the MIGS into account to determine the Fermi-level pinning position and ultimately the Schottky-barrier height.

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