Interface states and Schottky barrier formation at metal/GaAs junctions

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We report results of x-ray photoemission and cathodoluminescence spectroscopies studies of interface formation at metal–GaAs junctions. The results are interpreted by using a microscopic model of metal–semiconductor interfaces. Our low-temperature measurements and analyses show the validity of Schottky's phenomenological description, thereby suggesting that metal-induced gap states and native defect mechanisms are not major factors in determining the Fermi-level energy at the low-temperature formed interface. Our room-temperature results show that a broad range of Fermi-level stabilization and the formation of two reaction-induced interface states are obtained upon metallization of GaAs(100) surfaces. These results strongly imply that the insensitivity of rectifying barrier height on metal work function results from metallization-induced atomic relaxations at the interface.

I. INTRODUCTION

Over the last years our research group has reported several systematic studies on a variety of metal/III–V compound semiconductor interfaces which reveal Fermi-level (E_f) stabilizations energies distributed over a range of values of the order of the semiconductor band gap. These studies of room-temperature formation of metal interfaces with molecular-beam epitaxy (MBE) grown InGaAs ($0 < x < 1$, Ref 1) and GaAs,[2] and melt-grown InP,[3,4] GaP,[5] and InAs[1] showed a strong dependence of Schottky barrier heights (SBH's) on metal work function (ϕ_m) and metal reactivity. On the other hand, early studies of SBH formation of the cleaved (110) surface of GaAs have shown interface E_f positions nearly independent of the metal work function.[6] This insensitivity is referred to as Fermi-level "pinning" and has been assumed to be a general characteristic of rectifying contacts on covalently bonded semiconductors. This result stimulated several theoretical models aimed at assessing the pinning behavior of metal/GaAs(110). Two phenomena are repeatedy invoked within these models: Fermi-level pinning is either attributed to atomic rearrangements near the metal–semiconductor (M/SC) interface (i.e., creation of defects,[6] chemical reactivity,[7] effective work function[8]) or to redistribution of the valence electron charge density at the interface (i.e., surface states,[9] metal-induced gap states[10]). Evidently, models which predict pinning cannot account for the observed unpinned behavior of a large variety of metal/III–V semiconductor junctions.[1–5]

In this paper we present an internally consistent set of experimental observations and theoretical analysis which indicate that atomic rearrangements near the junction are responsible for observed deviations from the linear proportionality between the barrier height and metal work function. In addition, by performing low-temperature (LT) experiments which inhibit the extent of these atomic rearrangements, we observe that the rectifying barrier is indeed proportional to ϕ_m in accordance with Schottky's original description.[11] Room-temperature (RT) interface formation, including a variety of metals having dissimilar electronic and chemical properties, indicate that a continuous set of values covering a wide range of SBH are observed at metal/MBE-grown GaAs(100) interfaces. The measured SBH values and interface optical emissions are used to extract the energy and effective concentration of reaction-induced interface states from the analysis of SBH dependence on ϕ_m.

II. EXPERIMENTAL

Soft x-ray photoemission spectroscopy (SXPS) experiments were performed at the Aladdin ring of the SRC, University of Wisconsin-Madison. The sample temperature was maintained at 300 K (RT) or 80 K (LT) during evaporation and measurements. We measure bulk (surface) sensitive spectra of As 3*d* and Ga 3*d* core levels using $h\nu = 55$–60 eV (100 eV) and 35–40 eV (80 eV), respectively. These energy sets produce photoelectrons with identical escape lengths for As and Ga at energies about 9–14 eV (54 eV). Thus, the core level SXPS spectra show similar depth resolution for both elements. The bulk/surface sensitive spectroscopy allows us to monitor core level shifts due to rigid energy-band movements upon metal deposition, and separate out contributions due to chemical shifts. Details of the cathodoluminescence (CLS) and photoluminescence (PLS) measurements can be found elsewhere.[12]

The As-coated MBE specimens have an unstrained, epitaxial overlayer, Ohmic contact layer structure consisting of a 7500-Å-thick GaAs ($n = 2\times10^{16}$–5×10^{17} Si/cm^3, and $p = 1\times10^{18}$ Mg/cm^3) grown over a 2000-Å layer of MBE GaAs ($n = 2\times10^{18}$ Si/cm^3, $p = 6\times10^{18}$ Mg/cm^3) on top of an $n+$ ($p+$) GaAs(100) substrate. Clean ordered MBE-grown GaAs(100) surfaces were obtained by thermal desorption of the As protective cap in UHV.[13] The thermal desorption spectroscopy (TDS) experiments were per-

formed by raising the specimen temperature linearly in time and following the evolution of As with a UTI 100C mass spectrometer. Typical heating rates were in the range 1–7 °C/s. Additional pumping speed during the TDS experiments was provided by a 1000 l/s cryopump. Metals were evaporated from outgassed W baskets on the clean surfaces held at RT or LT and film thicknesses were monitored by means of a quartz-crystal oscillator positioned next to the specimen surface. Monochromator scan energies, signal acquisition, rate of heating, and mass spectrometer were controlled by a PC AT microcomputer.

III. RESULTS

A. Surface preparation

Clean ordered GaAs surfaces of GaAs present a variety of relaxations and reconstructions depending upon the particular crystal plane and surface stoichiometry.[14] Surface relaxations cause the shift of intrinsic surface states out of the band gap for the GaAs(110) surface. Thus, no band bending is to be found at these GaAs surfaces. Experimentally, the cleaved nonpolar (110) surface of GaAs has been shown to be unpinned.[15] The polar GaAs(100) surfaces present a broad range of surface stoichiometries which determines the surface reconstructions. Minute deviations in the particular surface concentration ratio between Ga and As, $R = [\mathrm{Ga/As}]$, causes the formation of unsaturated surface bonds with energies in the semiconductor band gap. These surface states are responsible for moving the surface E_f towards midgap. Calculations showed that the minimum number of surface defects needed to pin the bare semiconductor surface at the defect level energy is of the order of 10^{12} cm^{-2}.[16] For metal/semiconductor interfaces the concentration of interface states needed to pin the E_f is of the order of 10^{14} cm^{-2}.[16]

A well-established criterion of a good-quality clean ordered semiconductor surface is given by the photoemission spectrum of the semiconductor valence-band. Two observations are used to demonstrate the quality of the surfaces: first, the energy between the valence-band (VB) edge and the Fermi level of the system, which indicates the amount of band bending at the bare surface. For n-type semiconductors, the VB photoemission spectrum of high-quality surfaces should show an energy comparable to the SC band gap. For p-type semiconductors, this energy should be nearly zero and E_f at VBM. Second, sharp features in the shape of the VB spectrum indicate the absence of disorder and contamination on the semiconductor surface.

Figure 1 shows the VB photoemission spectra of UHV cleaved n-type GaAs(110)[17] and of UHV thermally cleaned n-type MBE-grown GaAs(100). The photon energies used are similar for both spectra so that a comparison of the VB spectral features between the (110) cleaved surface and the (100) cleaned surfaces is straightforward. Figure 1 indicates the spectral shape of the UHV cleaned MBE GaAs(100); Curves 1(b)–1(c) are identical to that of the cleaved GaAs(110) [curve 1(a)]. The valence-band spectrum [curve 1(b)] was obtained after thermal desorbing the As cap at heating rates of ~3 °C/s. Curve 1(b) shows that the

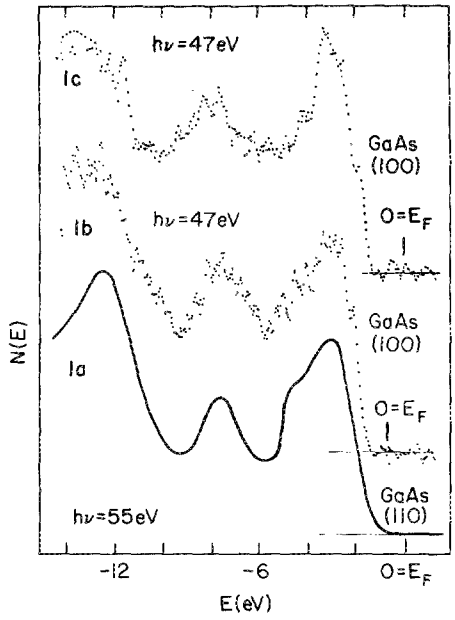

FIG. 1. Soft x-ray photoemission spectra of (a) (110) cleaved melt-grown n-type GaAs, (b) UHV cleaned ordered MBE-grown n-type GaAs(100) with surface E_f at 0.8 eV above VBM, and (c) UHV cleaned ordered unpinned n-type GaAs(100).

surface E_f is at 0.8 eV above the VBM. This E_f position indicates that surface states within the band gap are still present after the As desorption. For a large number of UHV-cleaned GaAs(100) surfaces, we measured Ga:As ratios corresponding to reconstructions from (4×6) through (2×8).[18] These GaAs surfaces showed sharp spectral features similar to that of curve 1(b) and a spread on initial E_f is ~0.3 eV. Metallization of these surfaces causes E_f movements over a relatively broad energy range (see below).

Unpinned GaAs(100) surfaces were obtained by thermal desorbing the As cap at low heating rates, of ~1 °C/s. One of the VB photoemission spectra of these unpinned surfaces appears in curve 1(c). The VB spectrum shows an initial clean surface $E_f - E_v \simeq 1.3$ eV, which indicates the absence of band bending at this surface. The normalized intensity ratio of the surface sensitive core level photoemission spectra of the clean GaAs(100) surface $R = [\mathrm{Ga}\ 3d(80\ \mathrm{eV})/\mathrm{As}\ 3d(100\ \mathrm{eV})]$ is $\sim 1.2 \pm 0.03$. This value closely corresponds to the 4×6 reconstruction of the GaAs(100) surface.[18] Most experimental evidence to date shows the Fermi level of the GaAs(100) surfaces pinned at midgap energies. To the best of our knowledge, this is the first report of clean ordered unpinned GaAs(100) surfaces. The results depicted in Fig. 1 indicate the high quality of the UHV-cleaned semiconductor surfaces and demonstrate the thermal desorption procedure provides an effective technique for obtaining clean ordered GaAs(100) surfaces from As-capped GaAs(100) systems. The difference in Fermi-level stabilization between the two GaAs (100) surfaces shown here may be due to residual As present in curve 1(b). Indeed, an additional shoulder in curve 1(b) at ~5.7 eV belowthe Fermi level may be due to As, consistent with the recent As-state assignment of Chiang and Spicer.[19]

B. Low-temperature interface formation

Interfacial reactions (clustering, interdiffusion, and chemical reactions) are inhibited when the M/SC junction is formed at low temperature.[20] Consequently, metal–semiconductor contacts formed at LT represent a unique opportunity to test theoretical models of "ideal" metal–semiconductor junctions and their predictions. Figure 2(a) shows Fermi-level movement as a function of Al and Au coverages on MBE-grown GaAs(100). No indication of chemical reaction or interdiffusion was observed in these experiments.[21] The results indicate that the difference in final interface E_f values between Al and Au contacts is ~ 1.0 eV, and that E_f movements are delayed up to above monolayer coverages. The difference in final E_f positions between Au and Al closely corresponds to the difference in the work functions of the deposited metals, and the SBH equals the absolute difference $\phi_m - \chi_{sc}$ as expressed by the single Schottky model. The results shown in Fig. 2 clearly indicate that the E_f is not pinned and, consequently, suggest that models based on pinning mechanisms are of little relevance in determining the position of the interface Fermi level at metal/GaAs(100) contacts formed at low temperature.

C. Room temperature interface formation

Figure 3 indicates Fermi-level movements as a function of metal coverage for Ag, Al, Au, Cu, In, Sm, and Yb deposited on n- and p-type MBE-grown GaAs(100) at RT. Inspection of Fig. 3 reveals that deposition of various metals on MBE-grown GaAs at room temperature produces rectifying barrier heights covering a continuous and wide range of values, over 0.7 eV. This range of E_f stabilization energies indicates a relatively strong dependence of SBH on metal work function. The measured final E_f values for Ag, Al, and Au interfaces to both n- and p-type MBE-grown GaAs(100) are similar. The results of Fig. 3 also indicate that Fermi-level movements evolve over multilayer metal coverage. For reactive low work function metals like Sm and Yb deposited on GaAs (100) surfaces, the E_f final stabilization energies are 0.75 and 0.85 eV, respectively. Al metallization seems to produce the lowest (highest) barrier for n-(p-) type MBE-grown GaAs(100). Overall, the results shown in Fig. 3 demonstrate that band bending and SBH's for metals on GaAs are in fact spread over a large range.

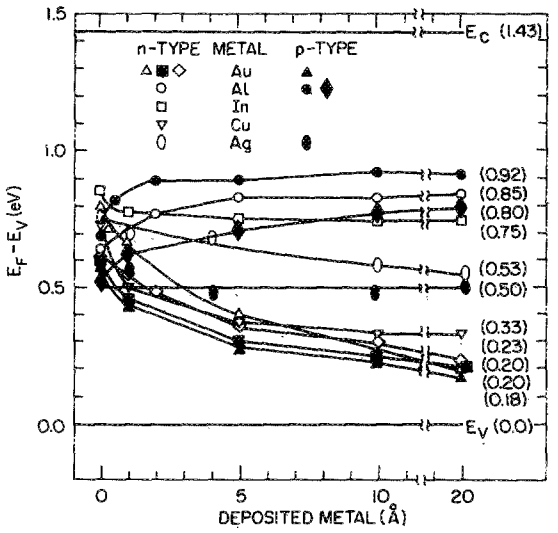

FIG. 3. E_f movements as a function of metal coverage for Ag, Al, Au, Cu, and In deposited on n- and p-type MBE-grown GaAs(100) at room temperature. E_f stabilization energies for Sm and Yb GaAs interfaces (not shown) are 0.75 and 0.85 eV, respectively.

D. Interface state formation

Experimental evidence of the existence of reaction-induced interface states and some of their properties is provided by cathodoluminescence experiments.[4,12] These CL measurements at metal/SC interfaces have shown the formation and evolution of discrete interface states with energies within the semiconductor band gap which correlate with the interface Fermi level. Figure 4 shows CL spectra of As-capped, UHV-cleaned GaAs(100), and with deposited Au and Al. These results have been reported previously.[13] Figure 4 indicates that cathodoluminescence transitions at about 0.8 and 1.25 eV are observed upon metallization of MBE-grown GaAs(100). Differences in the relative intensity of each emission are evident for Al and Au interfaces to MBE-grown GaAs (Fig. 4). These differences are caused by distinct concentration of reaction-induced interface states. The determination of these concentrations requires the knowledge of the cross sections for radiative recombination.

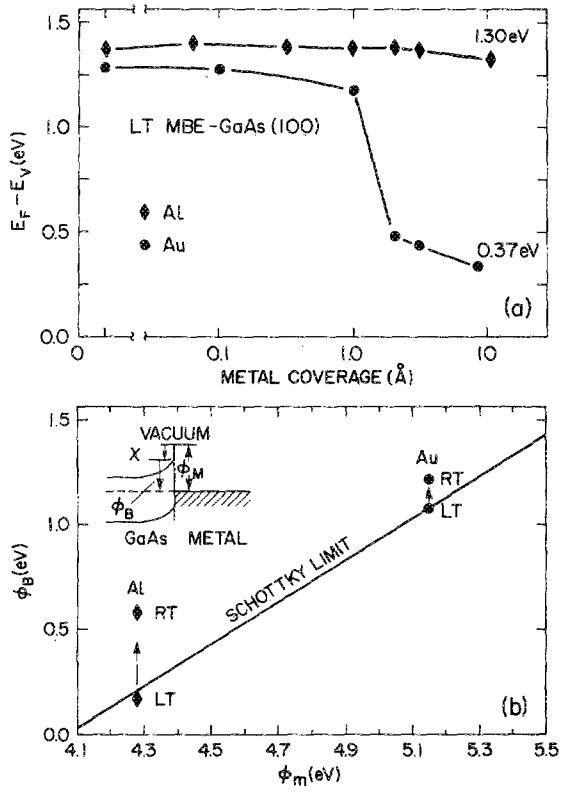

FIG. 2. (a) E_f movements as a function of metal coverage for Al and Au deposited at LT MBE-grown GaAs. (b) Predictions of basic model: rectifying barrier heights as a function of metal work function for contacts on GaAs. LT and RT measurements of SBH for Al and Au on GaAs are indicated. The calculation is performed by assuming the semiconductor photoelectric threshold constant (see, for example, *Photoemission in Solids*, edited by M. Cardona (Springer, 1980), Vol. 1, p. 40.

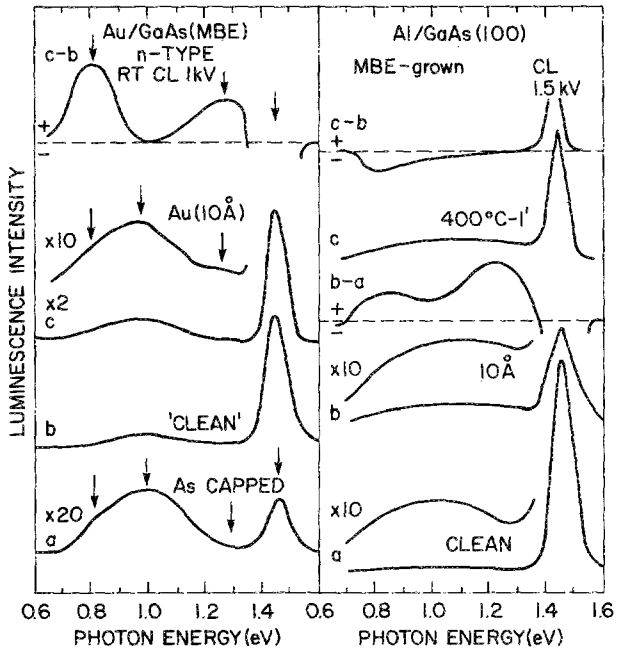

FIG. 4. CL spectra of As-capped, UHV-cleaned, Au and Al deposited on MBE GaAs(100).

Beyond this determination, the CL experiments demonstrate that the concentration of interface states at a given energy depends upon the particular metal. The observed CL optical emissions involve transitions between semiconductor bands and deep levels. For *n*-type SC, hole accumulation at the interface favors transitions which involve the semiconductor valence band or deep levels close in energy to the VBM.[12] This consideration together with the analyses of the dependence of SBH on metal work function (see below) suggest that the emission at $\sim$0.8 eV corresponds to a transition between a level at 0.8 eV and the VBM. The emission at $\sim$1.25 eV is assigned to a transition between the CB and a level at $\sim$0.2 eV above the VBM. An independent measurement of formation of interface states at metal/GaAs(110) surfaces using scanning tunneling microscopy (STM) was recently reported.[22] These STM measurements showed that two states are formed upon Sb deposition on GaAs at energies about 0.8 eV and (to a lower degree of certainty) 0.1–0.2 eV above VBM. This result agrees with our CLS results and confirms the existence of two reaction-induced interface states at metal/GaAs interfaces.

IV. DISCUSSION

The E_f movements at metal/MBE-grown GaAs(100) indicate an absence of pinning behavior, which most proponents of the various Schottky models have not dealt with until now. The theoretical models of metal–semiconductor interfaces aim to explain the observed pinning behavior of metal/melt-grown GaAs(110) interfaces.[6–10] The SBH result of metal/melt-grown GaAs(110) junctions typically show a narrow range of E_f stabilization energies, of $\sim$0.2 eV, with E_f movements occurring upon submonolayer metal deposition.[6] Both observations support models that invoke no role for the particular metal and the associated work function in the formation of the Schottky barrier. On the other hand, our results on metal/III–V semiconductor interfaces and the recent results on (110) cleaved melt-grown GaAs[22] indicate that theoretical models aimed at explaining the obtained broad range of SBH are more appropriate. Recent measurements of SBH formation at the cleaved (110) surface of GaAs suggest that even this surface can exhibit a broader range of E_f stabilization, albeit only on an atomic scale. In addition, Kaiser used a novel method for measuring SBH, based on the STM technique, to determine a mix of local barrier heights at Au/melt-grown GaAs(110) interfaces, including a value as large as 1.2 eV.[23] This value is identical to our result for the Au/MBE-grown GaAs(100) interface.

The theoretical model which serves as the basis for the description of unpinned M/SC junctions has been described in detail elsewhere.[24,25] This model affords a complete description of the energetics and electrostatics of the M/SC contact. A unique feature is the simultaneous description of both the short-range valence-electron charge density at the interface and the ionized dopants in the semiconductor. This model is utilized to calculate the self-consistent one-electron potential throughout the junction. The total potential drop across the contact is mandated by thermodynamic equilibrium boundary conditions. This evaluation indicates the near cancellation of short-range valence-electron dipoles (metal–vacuum surface dipole, semiconductor–vacuum surface dipole, and metal–semiconductor interface dipole). This near cancellation makes the rectifying barrier on the semiconductor directly proportional to the work function of the metal. Consequently, this self-consistent electrostatic model provides a microscopic derivation of Schottky's phenomenological description of M/SC junctions.

Low-temperature interface formation present an experimental situation for which our model is applicable, i.e., junctions for which chemical reaction and interdiffusion are minimized. Inspection of Fig. 2(b) reveals that the rectifying barrier height agrees on an absolute scale with the Schottky model predictions. The results shown in Fig. 2(b) clearly indicate that the E_f is not pinned and, consequently, suggest that metal-induced gap states[10] (electronic relaxations) are of little relevance in determining the position of the interface E_f at ideal metal–semiconductor interfaces. The absence of atomic rearrangements and interface states at the low-temperature interfaces strongly suggest the presence of an activation energy barrier for interface state formation, and precludes the role of the detailed chemistry in determining their concentration.[7] The significance of the results presented in Fig. 2 is remarkable: they provide a theory of the rectifying potential at metal–semiconductor contacts together with the experimental verification of its predictions, and these results demonstrate the validity of Schottky's phenomenological description of metal–semiconductor interfaces.

For metal–semiconductor junctions formed at room temperature, the observation of interface chemical reactivity[7] and formation of interface states[4,22] indicates the presence of atomic rearrangements at the interface. As a consequence of the presence of these atomic rearrangements, the behavior of

SBH deviates from that predicted by our model (Schottky limit). We adopt a phenomenological approach to the description of the consequences of the atomic rearrangements by postulating that the created interface states are the main cause of deviation from the Schottky limit behavior.[25,26] Within this approximation, estimates of the nature of the interface states, their energies, and effective concentrations can be extracted from the dependence of the measured SBH on the metal work function and the energies of the optical emission from reaction-induced interface states. The following discussion demonstrates the usefulness of such analyses of experimental Schottky barrier height data.

Figure 5 shows the variation of measured SBH's as a function of ϕ_m for various metals deposited on n- and p-type MBE-grown GaAs(100) at RT and our model calculations of SBH for metal/GaAs interfaces with two acceptor states. It has been shown that the dependence of SBH on ϕ_m can be used to identify the nature (donor, acceptor, etc.) of the reaction-induced charge centers.[25] Our model calculations indicate that the observed metal/GaAs CL transitions involve interface acceptor states at about 0.8 and 0.2 eV with respect to the GaAs valence-band maximum. Our calculations reveal that metallization of GaAs creates interface charged centers whose maximum total effective concentrations are in the low-10^{14} cm^{-2} range. The same interface state energies and concentrations are used to calculate the SBH for metal interfaces to n- and p-type GaAs, as shown in Figs. 5(a) and 5(b). Alternatively, the ϕ_m vs ϕ_B dependence can be well fit for a constant density (3×10^{13} cm^{-2}) at 0.2 eV and a metal-dependent density ranging into the low-10^{14} cm^{-2} range at 0.8 eV, consistent with CLS observations. These numerical results also indicate that the concentration of the interface acceptor state at $\sim$0.8 eV controls the barrier heights for low work function (reactive) metals. Therefore, these results are consistent with our model predictions that the energy and effective concentration of the reaction-induced interface states determines the SBH dependence on ϕ_m. The RT results also suggest that metal-induced gap states plays no role in determining the rectifying barrier height at metal–semiconductor junctions.

The evolution of interface E_f level with metal coverage at LT and RT unambiguously demonstrate the role of the development of metallic character in the formation of SB at M/SC interfaces.[27,28] At submonolayer metal coverages and in the absence of reaction-induced charge centers (cf. low-temperature results in Fig. 2), charge transfer between the SC and the adsorbed metal depends upon the difference of relative ionization potentials. This value is, in general, smaller for metals than for SC. Thus, the E_f is determined by the semiconductor bulk doping: it remains approximately constant upon metal deposition for n-type material and moves upwards for p-type material.[27] At high coverages, when the band structure and density of states of the metal are established, charge transfer occurs to or from the SC to equalize the bulk chemical potentials on each side of the contact. Thus, the metal work function determines the position of the E_f for the LT interface. On the other hand, for the room-temperature SBH formation, submonolayer metal deposition produces reaction-induced charge centers. The density of these centers is, in principle, a function of the interface reactivity and of the amount of deposited metal. Charge transfer from(into) the SC to(from) the charge center occurs. At low metal coverage the charge state of the centers is determined by the semiconductor bulk doping, and the evolution of the E_f with metal deposition is a function of the amount of reaction-induced charge centers. At high coverages (metallic state) the charge state of the centers is deter-

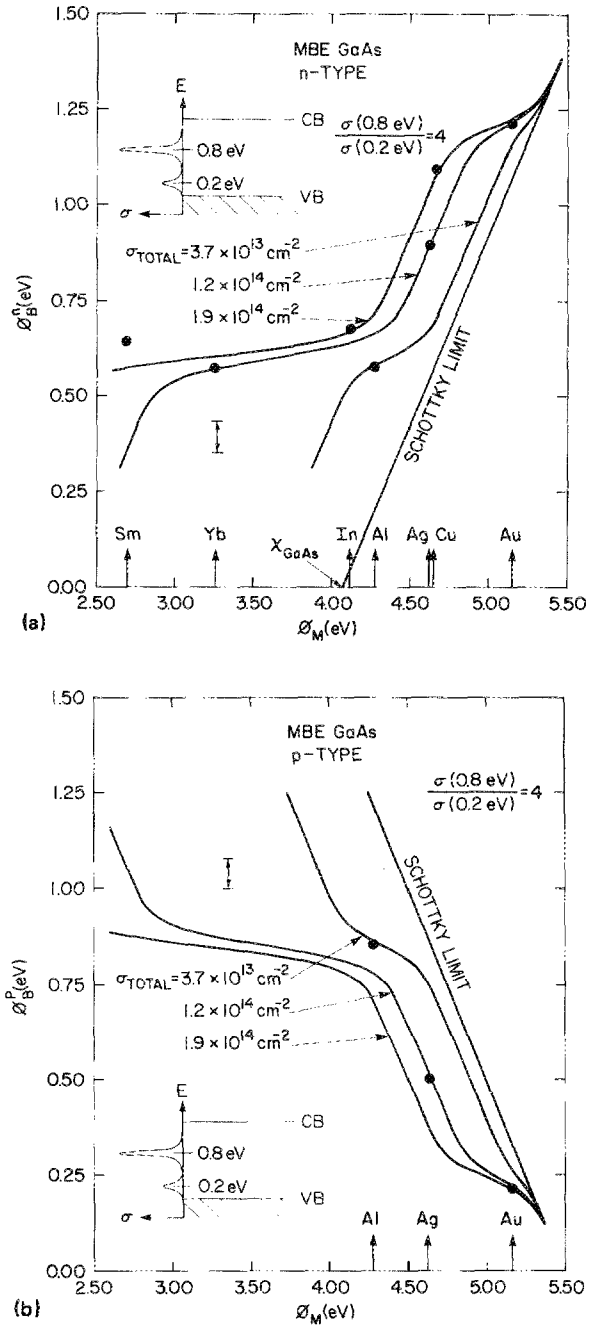

FIG. 5. (a) Experimental SBH for Ag, Al, Au, Cu, In, Sm, and Yb contacts to MBE-grown n-type GaAs(100) at RT. (b) Experimental SBH for Ag, Al, and Au contacts to MBE-grown p-type GaAs(100) at RT. Model predictions incorporating charge centers to simulate atomic rearrangements occurring at RT interface formation: SBH as a function of metal work function including two interface acceptor states with energies at 0.8 and 0.2 eV, and concentration ratio (0.8 eV/0.2 eV) equal to four for (a) n-type, and (b) p-type GaAs.

mined by ϕ_m. The position of the E_f at the RT interface is then dependent on ϕ_m, and on the energies and concentrations of metal-induced interface states. As a consequence of the presence of these reaction-induced interface states the evolution of E_f with metal coverage at n-type semiconductors does not exhibit the abrupt change due to the onset of metallic character observed at low temperatures.[27]

Our experimental results indicate that a much broader range of SBH are obtained for metal/MBE-grown GaAs(100) interfaces than for metal/melt-grown GaAs(110) interfaces at low[27,29,30] and room[6] temperature. Our measurements challenge the concept of pinning as an general property of metal/III–V semiconductor interfaces. More significant is the fact that our results are also at variance with a whole class of models (metal-induced gap states,[10] native defects models,[6,30] etc.) predicting that the rectifying Schottky barrier is an insensitive function of the metal work function, and is only determined by the properties of the semiconductor. Our results are significant and indicate that SBH's are correlated to specific physical characteristics of the metal–semiconductor interface. Our methodology provides a useful tool for analyzing electronic properties at M/SC interfaces and finding energies and effective concentration of interface states.

V. CONCLUSIONS

In conclusion, we have observed a broad range of SBH's at metal/MBE-grown GaAs(100) interfaces. We observe optical emission from two interface states. The dependence of measured SBH at metal–GaAs interfaces on metal work function is interpreted in terms of a microscopic model of metal–semiconductor contacts. In the absence of interfacial reaction-induced charge centers, our basic model predicts that the SBH scales linearly with the metal work function. Interfacial atomic rearrangements and chemical reactions are modeled by the presence of charge centers near the interface. These predictions are experimentally verified by LT and RT measurements of SBH and interface states at metal/GaAs contacts. These experimental observations demonstrate that the insensitivity of rectifying barrier height on metal work function has its origin in atomic, rather than electronic, relaxations at the interface.

ACKNOWLEDGMENT

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