Schottky-barrier and interface formation of Cs/GaSb(110) and Rb/GaSb(110) at room temperature

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The Schottky-barrier and interface formation of Cs/GaSb(110) and Rb/GaSb(110) at room temperature are investigated by soft-x-ray core level photoemission spectroscopy using synchrotron radiation. A large splitting (0.9 eV) is found at the Cs $4d$ core level and indicates two different adsorption sites (having a large difference in ionicity) for the alkali-metal atoms on the GaSb(110) surface with bonding to both cation and anion. The large Fermi-level overshootings observed at very low alkali-metal coverages [0.03 monolayer (ML) Cs or Rb] for the p-type GaSb(110) samples are directly related to the specific donor character of alkali-metal atoms with charge transfer into the empty Ga dangling bond. The unique room-temperature growth properties of alkali metals are also likely to be of relevance. Further Cs or Rb deposition is found to be highly disruptive with large reactive components at Sb $4d$ but also Ga $3d$ core levels and a higher reactivity for the smaller alkali metal (Rb). Interestingly, this interface reactivity, which results from surface defects, is also significantly higher for p-type than for n-type samples, suggesting that the nature of the doping might play some role in the interface chemistry. The final Fermi-level pinning position for both p- and n-type GaSb(110) is already achieved at an alkali-metal coverage of about 0.3 ML, corresponding to significant changes in the mode of growth and to the threshold of surface disruption. This pinning position is located at about 0.1 eV above the valence-band maximum, in agreement with a defect acceptor state model.

I. INTRODUCTION

The formation of metal-semiconductor interfaces has been a subject of intense research work for several decades.[1–5] However, despite a widespread field of applications for Schottky diodes, the basic mechanisms of Schottky-barrier formation are still not fully understood.[4] Several experimental investigations using ultrahigh-vacuum techniques have been performed to characterize the structural and electronic properties of those interfaces. This has resulted in the development of different models in order to explain the pinning of the Fermi level during the metal-semiconductor interface formation including defects, surface structural changes, and metal-induced-gap states.[1–3] In general, the (110) surfaces and interfaces of III-V compound semiconductors have been widely investigated in combination with many different metals, especially in the case of GaAs.[4] Alkali metals are interesting test-case candidates for metal-semiconductor interface studies, both experimentally and theoretically.[6,7] Their simple electron configuration and their tendency to act as donors have motivated growing interest into the understanding of their basic properties including the adsorption sites, mode of growth, nature of the bond, and band bending.[6,7] Furthermore, the drastic decrease of the surface work function under alkali-metal

deposition is of importance in many technological applications such as negative-electron-affinity electrodes.[8] In addition, the specific properties of thin alkali-metal layers as promoters of passivating reactions[6,9] were further centers of interest. In the case of III-V semiconductors, the presence of an alkali-metal overlayer was found to promote the oxidation rate up to 13 orders of magnitude.[10] However, unlike alkali-metal-promoted oxidation (nitridation) of elemental semiconductors such as silicon,[11–16] the formation of defects at the underlying metal/III-V semiconductor interfaces was found to play a crucial role in the oxide (nitride) layer growth,[17,18] since in many cases, a successful promoted nitridation or oxidation could be achieved for reactive interfaces only. Furthermore, we observed that the reactivity during the interface formation also depends on the dopant nature.[17] Therefore, it is challenging to systematically investigate the initial interface formation, the reactivity, and the electronic properties of alkali metals on n- and p-type GaSb(110), a III-V semiconductor having a low heat of formation (10 kcal/mol). Also, GaSb is a small band-gap semiconductor potentially promising for optoelectronical technological applications. Unlike the corresponding Cs/GaAs(110) or Rb/GaAs(110) interfaces, the Rb/GaSb(110) interface was found to be very reactive,[17] even at liquid-nitrogen temperature.[19] So far, there have

been only a few investigations on the interface formation of metals on GaSb(110) (Refs. 20–22) including some early works on the band bending under Cs and oxygen adsorption limited only to the n-type GaSb(110) surface.[23–25]

In this paper, we investigate the room-temperature band bending and interface formation of the Cs/GaSb(110) and Rb/GaSb(110) systems. The two interfaces are found to be strongly reactive. At low coverages, we show that the alkali-metal atoms are adsorbed on two inequivalent sites having a significant difference in the ionicity with bonding to both Ga and Sb. In both cases, we find an overshooting of the Fermi level by 0.25 and 0.35 eV for the p-type GaSb. This overshoot is shown to result from the donor character of the alkali adsorbate which is associated with the ionic bonding site of the alkali-metal atom and specific room-temperature growth properties. The Fermi level is already stabilized at low alkali-metal coverage near the valence-band maximum.

II. EXPERIMENTAL DETAILS

The photoemission experiments have been performed with grasshopper Mark II and 6 m toroidal grating (TGM 6) monochromator beam lines using the light emitted by the "Aladdin" 1 GeV storage ring of the University of Wisconsin-Madison. The data were collected at a working pressure better than 4×10^{-11} Torr in an ultrahigh-vacuum chamber equipped with an angle integrating double-pass cylindrical mirror analyzer. Using a gold sample, the overall resolution was determined to be better than 0.35 eV. Measurements were performed on (110) cleaved surfaces of n- and p-type GaSb single crystals, doped with Te and Zn, respectively. Although surface photovoltage effects are very unlikely in such a small band-gap semiconductor as GaSb, only degenerated samples were used (Te, $E_{Fn} - E_C = 24$ meV; Zn, $E_V - E_{Fp} = 38$ meV; E_C is the minimum of the conduction band; E_V is the maximum of the valence band; $E_{Fn,p}$ is the bulk Fermi level for n- and p-type). Ohmic contacts along the side of the whole bars have been made by evaporating under vacuum conditions Au on p-type GaSb and Au and Sn on n-type samples followed by a thermal annealing at 260 °C in a mixed hydrogen-nitrogen ambient. Only mirrorlike cleaved surfaces have been used for data collection. The investigation of the Schottky-barrier formation on alkali-metal–semiconductor systems has been conducted with extreme care concerning surface preparation and alkali-metal depositing in order to avoid the effects of contamination due to the high sticking coefficient of organic and inorganic molecules on surfaces modified by alkali-metal overlayers.[9] In fact, we have recently shown that traces of foreign atoms could drastically change the properties of alkali-metal–semiconductor systems.[26] Typically, low metal doses were evaporated successively on the surface, followed by immediate data acquisition. The deposition of alkali-metal atoms on the surface was performed under a maximum pressure rise of 2×10^{-11} Torr during metal deposition using extremely well outgassed SAES Getters chromate sources. No

traces of contamination have been observed under these conditions during data collection. All the other experimental details can be found elsewhere.[17]

III. RESULTS

A. Cs/p-type and n-type GaSb(110)

We first look at the Sb $4d$ core-level spectra for Cs deposition on p-type GaSb(110), shown in Fig. 1(a). In order to highlight band bending and reactive changes, we have scaled all the spectra to a constant maximum height. The deposition of 0.03 monolayer (ML) of Cs is shifting the Sb $4d$ spectrum towards lower kinetic energy by about 0.25 eV as a result of band bending during the interface formation. This shift is reversed at higher Cs coverages with Sb $4d$ spectra moving back to their initial
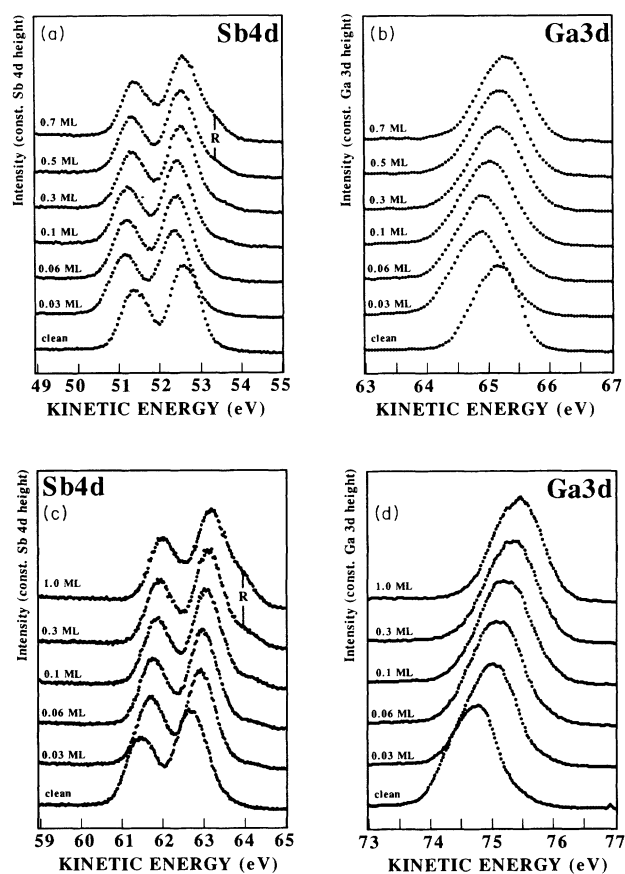

FIG. 1. (a) Cs/p-type GaSb(110): Sb $4d$ core-level spectra for increasing Cs coverages on the p- (Zn) doped GaSb(110) surface at room temperature. The photon energy was 90 eV. (b) Cs/p-type GaSb(110): Ga $3d$ core-level spectra for increasing Cs coverages on the p- (Zn) doped GaSb(110) surface at room temperature. The photon energy was 90 eV. (c) Cs/n-type GaSb(110): Sb $4d$ core-level spectra for increasing Cs coverages on the n- (Te) doped GaSb(110) surface at room temperature. The photon energy was 100 eV. (d) Cs/n-type GaSb(110): Ga $3d$ core-level spectra for increasing Cs coverages on the n- (Te) doped GaSb(110) surface at room temperature. The photon energy was 100 eV.

energy position of the clean surface. Furthermore, for a Cs coverage above 0.5 ML, one can clearly see by simple visual inspection the growth of a new shifted component (peak R) on the high kinetic-energy side of the Sb $4d$, indicating an interface reaction. Figure 1(b) displays a similar sequence for the corresponding Ga $3d$ core level, which exhibits the same rigid shifts due to the band bending as observed above for Sb $4d$.

We now turn to the n-type GaSb(110) interface. We can follow the formation of the Cs/n-type GaSb(110) interface for similar Cs coverages in Figs. 1(c) and 1(d). In this case, the Sb $4d$ and Ga $3d$ core-level energy shifts are moving towards the valence-band maximum on the higher kinetic-energy side with no overshoot as previously observed for other alkali-metal atoms on n-type III-V semiconductors except in the case of low-temperature Cs and Rb on n-type InP(110).[27] One can also notice that the lowest deposit of 0.03-ML Cs already results in core-level shifts of about 0.3 eV to higher kinetic energies for both Sb $4d$ and Ga $3d$.

B. Rb/p-type and n-type GaSb(110)

We now proceed with the Rb on p-type and n-type GaSb(110) interface formation using the same Sb $4d$ and Ga $3d$ core levels. Qualitatively, the changes in the spectra during interface formation are the same in this case as under the Cs deposition shown above. Upon the deposition of 0.03 ML of Rb, we can see initial shifts by 0.35 eV towards lower kinetic energy in Fig. 2(a) at the Sb $4d$ core level for the p-type GaSb(110). The Ga $3d$ core levels show the same behavior and, therefore, are not displayed. An overshoot takes place at lowest coverages (0.03-ML Rb), similarly to the case of the Cs/p-type GaSb(110). A reactive spectral feature (peak R) is clearly visible in the Sb $4d$ spectrum already at 0.1-ML coverage. This reactive component is rapidly growing at additional Rb deposition and becomes the dominant feature at 0.9- and 1-ML Rb coverages. As far as we know, such dominating
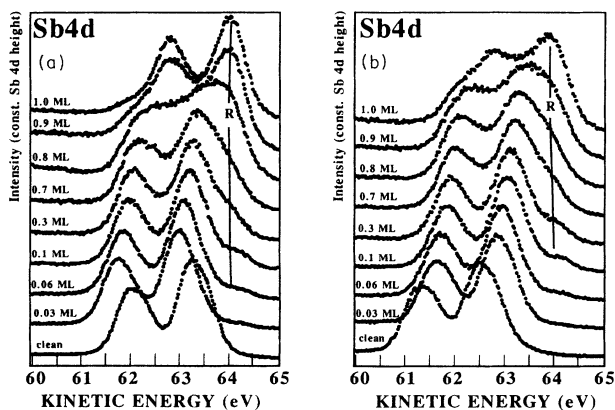

FIG. 2. (a) Rb/p-type GaSb(110): Sb $4d$ core-level spectra for increasing Rb coverages on the p- (Zn) doped GaSb(110) surface at room temperature. The photon energy was 100 eV. (b) Rb/n-type GaSb(110): Sb $4d$ core-level spectra for increasing Rb coverages on the n- (Te) doped GaSb(110) surface at room temperature. The photon energy was 100 eV.

reactive components have never been observed for other alkali-metal/III-V semiconductor interfaces.[27-31] This behavior is likely due to the fact that GaSb has a lower heat of formation than GaAs or InP.[32] A rather similar reaction is also observed on the n-doped surface, as shown at the Sb $4d$ in Fig. 2(b), although the reactivity is somewhat lower in this case than for the p-type doping. The n-type GaSb(110) substrate core-level spectra are shifting unidirectional towards higher kinetic energy under the alkali-metal deposition.

C. Sb $4d$ and Ga $3d$ peak decomposition

All spectra for the clean and alkali-metal-covered surfaces and interfaces have been analyzed using a least-squares fitting of the experimental data by a comparison of peaks, convoluted from a Gaussian with the theoretical Lorentzian line shape. The only open parameters were the peak intensities and the energy positions. The experimental and theoretical linewidths have been kept fixed (see Table I). The reactive components (R) were treated with the same line shapes as bulk (B) and surface (S) components while a linear background was subtracted during the fit. As an example, we show the decomposition of Sb $4d$ [Fig. 3(a)] and Ga $3d$ [Fig. 3(b)] spectra for the 0.5-ML Cs coverage on p-type GaSb(110). The reacted components are chemically shifted by 1.0 eV in the Sb $4d$ spectrum and by 0.3 eV for Ga $3d$. We have performed the complete Sb $4d$ and Ga $3d$ spectral peak decomposition at different Rb coverages for both n- and p-type GaSb(110) and have published it already elsewhere.[17]

D. Band bending

We have used the bulk peak positions obtained by peak decomposition to plot the Fermi-level movement for the p- and n-type GaSb(110) surfaces at various Cs or Rb coverages. The typical band-bending diagrams are shown in Figs. 4(a) and 4(b) for the Rb/p-type and n-type GaSb(110) and Cs/p-type and n-type GaSb(110) interfaces. The deposition of 0.03 ML of Rb already induces a dramatic Fermi-level movement towards midgap by 0.35 eV on p-type and 0.33 eV on the n-type samples [Fig. 4(a)]. Then, further Fermi-level motion upon increasing Rb coverages is about the same for both p- and n-type samples with a final pinning position near the valence-band maximum already reached at 0.2-ML Rb. We now examine a similar sequence for the corresponding Cs/GaSb(110) interface. The deposition of Cs on p- and n-type GaSb(110) shows a very similar behavior with

TABLE I. Parameters used for curve fitting of Cs $4d$, Ga $3d$, and Sb $4d$ core levels (all the energies are in eV).

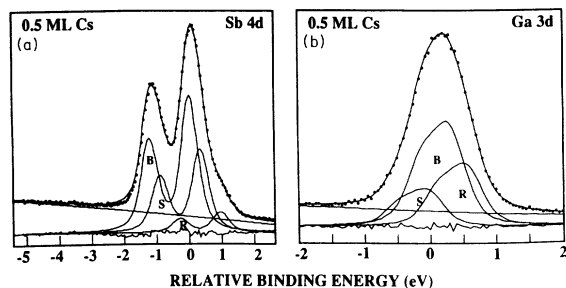|	Cs $4d$	Ga $3d$	Sb $4d$
Spin-orbit splittings	2.3	0.48	1.24
Branching ratio	1.5	1.5	1.5
d spectral width (full width at half maximum)	0.35	0.24	0.34
Instrumental linewidth	0.35	0.35	0.35

FIG. 3. (a) Peak decomposition of the Sb $4d$ core-level spectrum for 0.5-ML Cs coverage on p-type GaSb(110) into bulk (B), surface (S), and reacted (R) component. The photon energy was 90 eV. (b) Peak decomposition of the Ga $3d$ core-level spectrum for 0.5-ML Cs coverage on p-type GaSb(110) into bulk (B), surface (S), and reacted (R) component. The photon energy was 90 eV.

FIG. 5. (a) Ga $3d$ and Sb $4d$ integrated peak intensity for the interface formation of Rb on p-type GaSb(110) at room temperature. (b) Ga $3d$ and Sb $4d$ integrated peak intensity for the interface formation of Cs on n-type GaSb(110) at room temperature.

similar band-bending curves [Fig. 4(b)] as for Rb, with an overshoot level that seems to be lower in this case by 0.1 eV. However, it is rather difficult to estimate the exact overshoot energy value, since the overshoot position strongly depends on very small variations in the alkali-metal coverage. The final pinning position for p and n type is found to be near the valence-band maximum and is already achieved at a Cs coverage around 0.3 ML, as observed also above for Rb at room temperature. However, it is interesting to notice that, while the final Fermi-level pinning position is the same at both room and low temperatures, it is significantly delayed to higher Rb coverages in the case of the low-temperature interface.[19]

E. Mode of growth

In order to relate the band-bending behavior more specifically to the interface formation, we have also investigated the Cs and Rb mode of growth on the studied GaSb(110) surfaces. The alkali mode of growth is monitored using Sb $4d$ and Ga $3d$ substrate core-level total-integrated-intensity analysis as a function of the alkali-metal (Rb, Cs) coverage [Figs. 5(a) and 5(b)]. We look at the Rb/p-type GaSb interface [Fig. 5(a)] as the most reactive and at the Cs/n-type GaSb(110) interface [Fig. 5(b)]
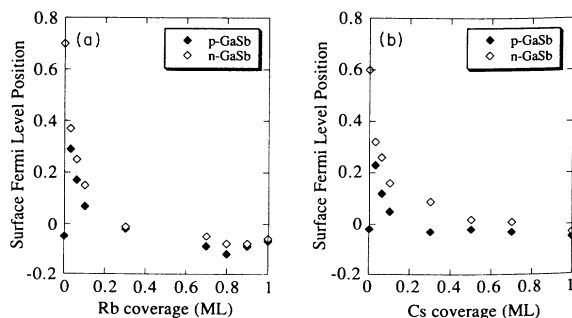
that is the less reactive one of all the systems investigated here or previously.[17] A linear decrease of Ga $3d$ and Sb $4d$ core-level total spectral intensities is found for both interfaces at the very beginning of the adsorption range until about 0.1-ML coverage. When the reaction between the alkali adsorbate and the surface takes place, we can see a clear change in the slope of the intensity decrease in both cases. In fact, the lowered bulk and surface component intensities are compensated by the growth of the reacted spectral part. However, further adsorption of Rb over 0.3-ML Rb does not induce additional significant changes in the Sb $4d$ or Ga $3d$ substrate core-level shapes and intensities [Fig. 5(a)], in contrast to the behavior of the less reactive Cs/n-type interface for which the intensity lowering continues with a decreased slope.

F. Cs $4d$ core levels

Additional very valuable information on the interface formation can be found by looking at the Cs $4d$ core level at various Cs coverages. In Fig. 6(a), we show a set of Cs

FIG. 4. (a) Band bending for the interface formation of Rb on p-type and n-type GaSb(110) at room temperature. (b) Band bending for the interface formation of Cs on p- and n-type GaSb(110) at room temperature.
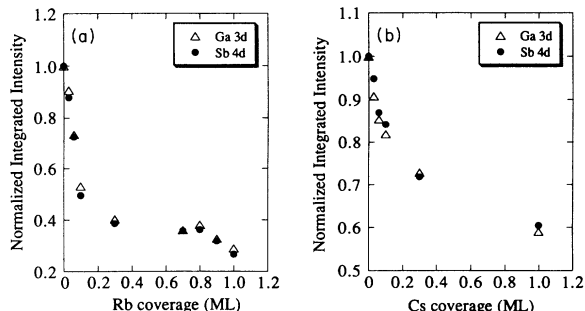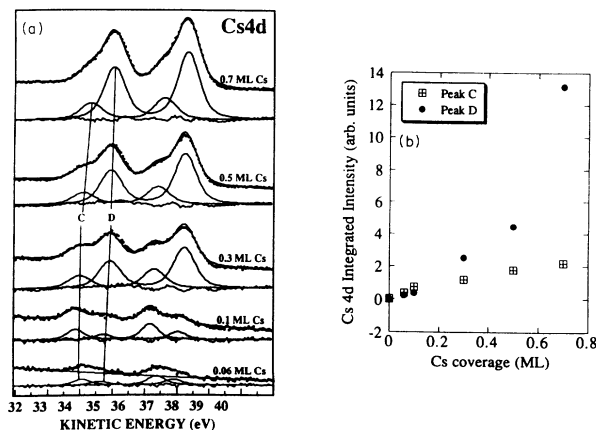

FIG. 6. (a) Peak decomposition series of the Cs $4d$ core levels for the interface formation on GaSb(110) for increasing Cs coverage. The spectra have been taken at 120-eV photon energy. (b) Cs $4d$ integrated peak intensity for the spectral components C and D in the interface spectra of Cs on p-type GaSb(110) [(a)].

4d spectra for different Cs coverages on a p-type GaSb(110) surface. It is obvious from a direct visual inspection of the experimental data that the spectra consist of two doublet components separated in energy by about 0.9 eV. A similar large splitting (∂E) of the adsorbate core-level spectra in the submonolayer coverage of alkali metals has already been reported for several other III-V compound semiconductor surfaces (room temperature) including Cs/GaAs(110), Cs/InP(110), and Na/InP(110), with ∂E values of 0.7 eV (Cs 4d), 1.0 eV (Cs 4d), and 1.3 eV (Na 2p), respectively.[28-30,33] Although a similar splitting should also be expected on the corresponding Rb 3d core level, we were not able to observe it. This is likely to result from the fact that this phenomenon for the case of the Rb/GaSb(110) surface, is overshadowed by the Rb 3d core-level spin-orbit splitting (1.2 eV), which has about the same energy value as the expected "structural" split. In fact, we have observed a clear broadening of the Rb 3d core level for the low Rb coverages.

The existence of this large splitting ($\partial E = 0.9$ eV) at the Cs 4d core level indicates that the Cs atoms are adsorbed on two different inequivalent adsorption sites having a significant difference in ionicity. Based on the same alkali-metal core-level splittings, but also on inverse photoemission spectroscopy experiments, double adsorption sites have already been proposed for other III-V compound semiconductor surfaces covered with alkali metals such as Cs and/or Na/GaAs(110) and/or InP(110) interfaces.[7,28-30,34] The difference in ionicity between these two Cs adsorption sites on the GaSb(110) surface is larger than for the GaAs(110) one[28] but slightly below the value obtained for the corresponding Cs/InP(110) interface.[29] Both sites are already partially occupied at low Cs coverages as can be seen for Cs/GaSb(110) in the 0.06-ML Cs spectrum [Fig. 6(a)]. We have used the same peak-separation method as for the substrate core-level spectra in order to evaluate the intensities (doublets C and D) corresponding for each site [Fig. 6(b)] at increasing Cs coverages. At low coverages, between 0.06–0.1-ML Cs, peak C on the low kinetic-energy side is the more intense feature. But, this relation is changing at a Cs coverage of 0.3 ML since peak D, on the Cs 4d high-kinetic-energy (low-binding-energy) side, is growing further at higher Cs doses, while peak C intensity remains basically constant [Fig. 6(b)]. At a Cs coverage of 0.7 ML, peak D is clearly the dominant spectral feature of the Cs 4d core level.

IV. DISCUSSION

Comparing our experimental results on the initial adsorption and the interface formation of alkali-metal atoms on GaSb(110) with studies of alkali-metal atoms on other III-V semiconductors, we get some common features but also interesting major differences concerning the adsorbate-substrate chemistry. As already indicated above, a similar double-adsorption site of alkali metal (Cs, Na) has been observed previously on GaAs(110) (Ref. 28) and InP(110) (Refs. 29 and 30) as shown by a splitting of the corresponding Cs 4d (Na 2p) core-level doublets in the submonolayer Cs (Na) coverage regime. The large

energy difference ($\partial E = 0.9$ eV) between the two components C and D indicates that the Cs atoms have a very different ionicity depending on the site. Peak C located on the higher binding-energy (lower kinetic-energy) side corresponds to a rather ionic type of bonding. However, in the low coverage regime (< 0.3-ML Cs), this "ionic" component (peak C at lower kinetic energy) is clearly more intense than peak D. In fact, at the earliest stage of adsorption, this interesting feature indicates that Cs atoms preferentially bond to the Ga atoms (which have an empty dangling bond) in a rather ionic type of bonding. In that case and in agreement with their well-known donor character, the Cs atom would transfer its valence electron (at least in part) to the Ga empty dangling bond, which would result in a reduced Cs-atom radius. In contrast, the Cs 4d component D (separated by about 0.9 eV from component C) is very likely to indicate that the corresponding emission is coming from Cs atoms bonded to Sb. Further support for our interpretation could be found by looking at the coverage dependence of peak-D intensity that increases with the Cs coverage. In fact, it is known that, when a reaction between a metal (including alkali) and GaSb(110) surface takes place, Sb stays on the surface.[20-22] This behavior will in turn, facilitate the bonding between the alkali-atom adsorbate and Sb, especially in the monolayer regime, when the reaction becomes the dominant feature.[17]

In these views, it is also interesting to notice the gradual increase of the Sb reactive component (R) when compared to the growing intensity of the Cs 4d component D versus the alkali-metal coverage, with both peaks becoming dominant spectral features at higher coverages. This would support our above interpretation that associates peak D to Cs atoms bonding primarily to Sb atoms. Similar doublet components observed at the Cs 4d core level have been interpreted for the low-temperature Cs/GaAs(110) interface to correspond to single-atom adsorption and to dimers, trimers, or island coordination, respectively.[33] It is definitively not the case here since the linear decrease of the integrated substrate core-level peak intensities clearly indicates a uniform growth mode in the low-coverage regime. Furthermore, in contrast to other metals such as Ag or In where a Volmer-Weber growth mode was observed,[20-22] alkali-metal adsorption on III-V compound semiconductor surfaces is, in general, characterized by a slightly stronger adsorbate-substrate interplay (as compared to the adsorbate-adsorbate interaction) avoiding clustering at low coverages even at room temperature.[35] At higher coverages above 0.3-ML Cs, the D component of the Cs 4d core level becomes the dominant feature (Fig. 6). Initially, this behavior might result from depolarization effects taking place when the distance between two Cs atoms decreases with the increasing coverages. However, it is likely that, at a coverage of 0.7-ML Cs, the emission coming from the D component results primarily from the reaction between Cs and the GaSb(110) surface as stressed above and evidenced by looking at the substrate core levels.

The existence of two alkali-atom adsorption sites on the GaSb(110) in the low-coverage regime as observed before for other III-V semiconductor surfaces[28-30] is also

likely to imply some significant changes of the substrate surface structure. These structural changes are likely to be driven by an electronic redistribution resulting from establishment of the bonding between the alkali atoms with both Ga (primarily ionic bond) and Sb (mainly covalent bond) atoms. In fact, even at very low coverages, it is well established that alkali metals induce important substrate surface structural changes (establishment or removal of reconstruction or relaxation). This has been shown for many substrates having very different surface properties such as full (or almost full) d-band metals such as Ag(110), Cu(110), Au(110), or Pd(110),[36-38] transition metals such as Mo(100) (Ref. 39) and W(100),[40] as well as elemental and compound semiconductors.[7,26,41] In the case of III-V semiconductors, the Na atoms, which also have two adsorption sites (cation, anion) on the InP(110) surface in the low-coverage regime,[30] also modify dramatically the structure of the substrate surface. It includes reconstruction and removal of the clean InP(110) surface relaxation as demonstrated by very surface sensitive photoemission extended x-ray-absorption fine structure experiments.[7,41] Similar structural changes are very likely to take place also here on the GaSb(110) surface when covered by Cs, Rb, or other alkali metals.

We now discuss the band bending and Schottky-barrier formation of the Cs/GaSb(110) and Rb/GaSb(110) interfaces. We observe a clear overshoot in the Fermi-level position for both alkali metals as previously reported also at low temperature for the Rb/GaSb(110) system.[19] It is interesting to notice that such a Fermi-level overshooting at room temperature is rather unique to alkali-metal-covered III-V semiconductor surfaces[28-31] and is not observed for other metal/GaSb and many other III-V semiconductor interfaces,[1-3,20-22] except in the case of alkali-earth metals.[42] At this point, one should also remark that, for the Cs/p-type GaSb(110) interface, this Fermi-level overshooting takes place already at the very low Cs coverages [Fig. 5(b)], corresponding precisely to a regime where the Cs atoms present on the surface are predominately ionic as already discussed above. Evidently, there is a direct correlation between charge transfer from Cs atoms to the surface and the GaSb(110) Fermi-level overshoot. This view is also valid for the other alkali-metal/III-V semiconductor interfaces for which similar double adsorption sites have been reported.[28-30] An adsorbate-induced donor level at 0.3 eV above the valence-band maximum proposed for GaSb(110) surfaces[43] would correspond to the experimentally observed overshoot levels.

Nonequilibrium effects as previously proposed for other systems[44] are not likely to play a role in the present case. In fact, photovoltaic band-flattening effects are very unlikely in a small band-gap semiconductor, especially at room temperature and also when have sufficiently high doping levels ($p = 6.7 \times 10^{+18}$ cm^{-3}). Furthermore, the same overshoot on a GaSb(110) surface covered by Ag has been observed at low temperature by both Kelvin probe measurements, avoiding radiation-induced effects, and core-level photoemission spectroscopy.[21,22] This further indicates that Fermi-level overshooting on these GaSb(110) surfaces does not result from surface photo-

voltage effects. It stresses our interpretation that the observed Fermi-level overshoot for alkali-metal/GaSb(110) interfaces results from the donor character of the alkali adsorbate. Also of interest, one can notice that the mode of growth at low alkali-metal coverages is similar at room and liquid-nitrogen temperatures, in contrast to many other metals such as Ag or In where a Volmer-Weber mode of growth is taking place at room temperature instead of a laminar growth mode at low temperatures.[21] Having the same growth mode in the low-coverage regime is also likely to be of relevance in the observed similar behavior of alkali-metal/GaSb(110) band bending at both room temperature (here) and low temperatures.[19]

We now turn to the interface formation in the higher alkali-metal coverages regime, where adsorbate-substrate reactions are predominant and to its correlation to the Fermi-level pinning. We have seen above in Fig. 5 that the Fermi-level pinning is achieved at the earlier stages of the reaction between the alkali adsorbate and the GaSb(110) substrate. The observed Fermi-level pinning position near the valence-band maximum is, therefore, in agreement with a model of a defect-acceptor state located around 0.1 eV above the valence-band maximum. Reactions between metal adsorbate and a semiconductor surface are generally driven by the presence of surface defects. In fact, the heat of adsorption of alkali metals on III-V semiconductor surfaces is considerable, since, e.g., the heat of adsorption of Cs and GaAs(110) at low coverages is about 60 kcal/mol (Ref. 45) as compared to the low heat of formation of GaSb of 10 kcal/mol.[32] It is, therefore, evident that, at a certain alkali-metal coverage, a breaking of the substrate bonds begins, leading to major structural changes as can be seen by the broadening of the substrate core-level spectra with growing reacted components (R) and slope changes in the core-level intensity curves, see Figs. 5(a) and 5(b) and Ref. 17. In this context, it is also interesting to notice that, unlike the Rb/GaSb(110),[19] the Cs/GaAs(110) and Cs/InP(110) interfaces have been found to be nonreactive at room temperature.[28-31] Differences in the degree of surface disruption of p-type (Zn doped) and n-type (Te doped) samples at higher coverages, that we have observed systematically under Cs and/or Rb deposition, seem to stem from different mechanisms of defect creation and possibly, different cleavage properties between n- and p-type samples.[46] We have recently shown that these differences between n- and p-type GaSb(110) are also very important in the surface-interface reactivity of these systems.[17] Most interestingly, the Fermi level is found to be pinned at Cs or Rb coverages corresponding to significant changes in the growth mode [Figs. 5(a) and 5(b)] and to the subsequent appearance of surface disruption, giving rise to important reactions between the alkali adsorbate and the GaSb(110) surface. These reactions have been shown to result from surface defects in the case of other alkali-metal–III-V semiconductor systems[28-31] and are, therefore, very likely to explain the Fermi-level pinning observed here for both interfaces.

The common Fermi-level pinning position near the valence-band maximum for the p- and n-type GaSb(110) samples is in agreement with previous experimental stud-

ies for Cs on n-type GaSb(110).[20,23−25] In this context it is interesting to remark that a defect-related acceptor level, due to missing Sb and located at 0.1 eV above the valence-band maximum, has been proposed[43] to explain the Fermi-level pinning at adsorbate coverages where overlayer metallization is not yet reached. This situation is very likely to be similar here in the case of alkali-metal-covered GaSb(110) surfaces. Finally, it should be stressed that the room-temperature Fermi-level overshooting observed here on p-type GaSb(110) as well as on other III-V compound semiconductors[28−31] for very low coverages, appears to be a rather unique feature of alkali- and alkali-earth metal-covered III-V compound semiconductor surfaces. As far as we know, a similar behavior has not been observed at room temperature for other metal/III-V semiconductor interfaces.

V. CONCLUSIONS

In conclusion, we have investigated the room-temperature Schottky-barrier and interface formation of Cs and Rb/p-type and n-type GaSb(110) systems. We have shown that, unlike the case of GaAs(110) and InP(110) surfaces, the interface formation of Cs (Rb) on GaSb(110) is strongly reactive at room temperature with a larger reactivity for the small alkali metal. The interface reactivity has also been found to be significantly higher for the p-type than for n-type GaSb(110) suggesting that the nature of the dopant might play some role in the interface chemistry. The alkali atoms are found to occupy two different adsorption sites having a large difference in ionicity with bonding to both cation and anion. The ionic site is associated with a significant charge transfer into the Ga empty dangling bond taking place already at the very initial stage of alkali-metal deposition. The large Fermi-level overshoot observed for the p-type GaSb(110) surfaces at very low alkali-metal coverages clearly results from this alkali-atom adsorbate donor character. Due to rather similar growth properties, the room-temperature Schottky-barrier formation for both Rb and Cs on p- and n-type GaSb(110) is found to present common features with the corresponding low-temperature one. The final Fermi-level pinning position on p- and n-type samples, which is already achieved at low alkali-metal coverages (0.3 ML), is located at about 0.1 eV above the valence-band maximum in agreement with a defect acceptor state model.

Note added in proof. A theoretical study on alkali metals/GaAs(110) by Pankratov and Scheffler (PS) appeared in Phys. Rev. Lett. **71**, 2797 (1993). The authors predicted removal of surface relaxation by alkali metals that, as mentioned above, we have already evidenced experimentally some time ago for the Na/InP(110) system.[41] This unrelaxation could appear as being a rather general mechanism valid also for other III-V semiconductor surfaces including GaSb(110) as addressed in the present work. In addition, PS have verified another very interesting feature, namely, a negative-U behavior for Na and K atoms on the GaAs(110) surface—see also Allan and Lannoo (AL), Phys. Rev. Lett. **66**, 1209 (1991) and J. Vac. Sci. Technol. B **9**, 2135 (1991). In their work, PS have assigned this negative-U behavior to double adsorption sites for the alkali atoms. From the negative-U trend when going from Na to the larger K atom, PS have estimated a positive U for the Cs atom which, according to their view, would imply a single adsorption site on GaAs(110) and perhaps also on other (110) III-V semiconductor surfaces. However, the suggestion of PS is not consistent with clear experimental evidence of two Cs adsorption sites on GaAs(110),[7,28,34] InP(110),[7,29] and GaSb(110) (present work) surfaces. It suggests that all alkali metals should exhibit a similar negative-U behavior, in agreement with AL's general arguments.

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