

Surface electronic structure of submonolayer to full-monolayer coverages of alkali metals on GaAs(110): K and Cs

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The development of the electronic structure of two interfaces of alkali metals with semiconductors, K/GaAs(110) and Cs/GaAs(110), has been studied experimentally. Changes in the occupied states have been monitored with ultraviolet photoelectron spectroscopy while the unoccupied states have been investigated using angle-resolved inverse photoemission. It is found that K and Cs behave quite differently on GaAs(110). Potassium induces two surface states, one filled and one empty. The dispersion of the empty state is presented and shows the nonmetallic state of this surface. Cesium, on the other hand, yields an empty state, which beyond saturation exposure moves down to the Fermi level, thus rendering the surface metallic.

INTRODUCTION

Metal-semiconductor interfaces are an issue of both scientific and technological interest.¹ Due to the forced alignment of the semiconductor Fermi level, which necessarily lies within the fundamental bulk band gap, with that of the metal overlayer, the creation of the interface will, in general, be accompanied by a semiconductor band bending. The important role is played by the semiconductor surface states, since these are the states with the largest overlap with the metal states close to the Fermi level. A delicate balance between charge transfer into or out of the semiconductor surface states and the possible reconstructions of the interface will determine the properties of the contact, making it Ohmic or of Schottky type.

The case of alkali metals on semiconductor surfaces has for some time generated considerable interest.² A major motivation is the anticipated simple description of the possible charge transfer, since alkali metals are monovalent. This should lead to a theoretical description which, assuming no induced reconstruction, is rather straightforward. The drastic changes in the macroscopic property, the work function, is experimentally well known, e.g., in the production of negative electron affinity cathodes. As a consequence these systems are attractive as model examples of metal-semiconductor interfaces.

With the GaAs(110) surface as substrate earlier studies have dealt with the formation of the interface with Cs.³⁻⁵ Later investigations have widened this to the entire group of alkali metals.^{6,7} These studies have focused on the core-level binding energies as a means to determine band bending and possible Fermi-level pinning mechanisms. Information on the valence-band structure of Cs/GaAs(110) has been given by Gregory and Spicer⁵ and more recently by Maeda Wong *et al.*⁸ In the latter study⁸ careful photoelectron spectroscopy work showed the nonmetallic behavior of the saturated surface formed at room temperature.

We have experimentally studied the changes in the sur-

face electronic structure in the energy region around the band gap which appear upon evaporation of K and Cs on a room-temperature GaAs(110) cleaved surface. Combining ultraviolet photoelectron spectroscopy (UPS) and angle-resolved inverse photoemission both filled and empty surface states have been observed. In the K case we have shown that the surface stays semiconducting while in the case of Cs the surface ultimately becomes metallic, the latter in contrast to the results of Maeda Wong *et al.*⁸

EXPERIMENTAL DETAILS

The experiment was performed in a two-chamber vacuum system where preparation of the surface and subsequent characterization and measurements were done in separate, interconnected chambers. (110) surfaces of *n*-type GaAs (Te doped, $1 \times 10^{17} \text{ cm}^{-3}$) were prepared by *in situ* cleavage and all showed nice 1×1 low-energy electron diffraction (LEED) patterns. Evaporations of K and Cs were done from resistively heated, well-outgassed dispensers (SAES Getters) with the GaAs crystal held at room temperature. Base pressure in the entire system was below 5×10^{-11} mbar and never rose above 1×10^{-10} in the preparation chamber during evaporation. Calibration of the alkali-metal sources was done by noting the change in secondary-electron cutoff energy in UPS which has a characteristic dependence on coverage. The UPS utilized an angle-integrating hemispherical electron-energy analyzer and a He resonance lamp. The He II line was suppressed in order to avoid radiation-induced band bending.⁹ Angle-resolved inverse photoemission spectra were recorded using an electron gun with a beam divergence of less than 3° and a Geiger-Müller type detector working at photon energy 9.5 eV. The *k*-space resolution was better than 0.1 \AA^{-1} and the total-energy resolution was 0.35 eV, the latter derived from the width of the Fermi-level onset for a tantalum foil. This was periodically interchanged with the GaAs crystal and the position of the onset E_F was used as reference energy.¹⁰

RESULTS

Potassium on GaAs(110)

Figure 1 shows the change in the secondary-electron cutoff energy in UPS as a function of K evaporation time. After a rapid initial decrease a minimum value of -3.25 eV is found for 5 min of evaporation, followed by a slow increase. We interpret the minimum as indicating the formation of the saturated, monolayer coverage. At this coverage an ordered 1×1 LEED pattern is observed. Studies of the Ga $3d$ level using HeII radiation showed an upward band bending of 0.3 ± 0.1 eV at saturation coverage, whereas no band bending was observed after 1 min of K evaporation.

The changes in surface electronic structure are presented in Fig. 2. Note the different energy scales for UPS (left) and inverse photoemission (right) spectra. In the angle-integrated UPS spectrum from the clean, cleaved GaAs(110) surface the valence-band maximum (VBM) is found 1.2 eV below E_F , showing the nearly flat-band condition. After just 1 min of K, corresponding to approximately 0.2 monolayers, a new K-induced state labeled S_1 appears. This, the top of a surface-state band, lies 0.85 eV below E_F , i.e., 0.35 eV above the VBM and thus within the fundamental band gap. Upon further evaporation of K the S_1 state relaxes and is found at saturation 1.10 eV below E_F . Due to the band bending induced by K the final energy position of S_1 is 0.2 eV below the VBM. The structure labeled S_2 is the B_2 internal gap surface state according to Huijser *et al.*¹¹ and is found to merely reflect the observed band bending, shifting to

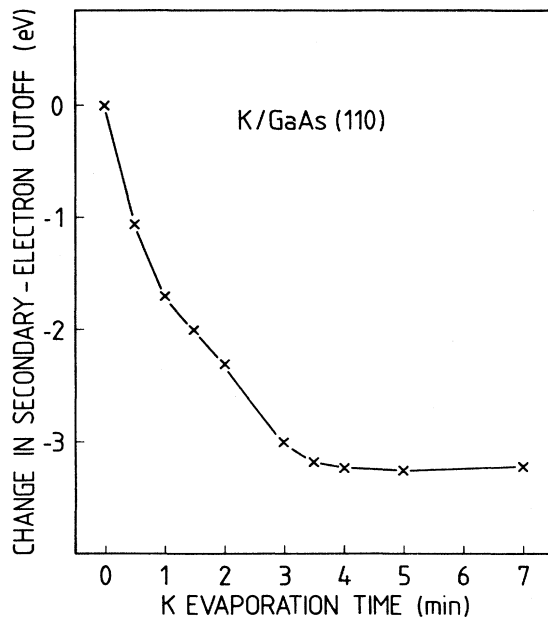


FIG. 1. The change in the cutoff energy for secondary electrons in UPS from the K/GaAs(110) surface as a function of K evaporation time. The maximum change is -3.25 eV and saturates at 5 min of evaporation time. We use this value as the definition for the saturated monolayer evaporation.

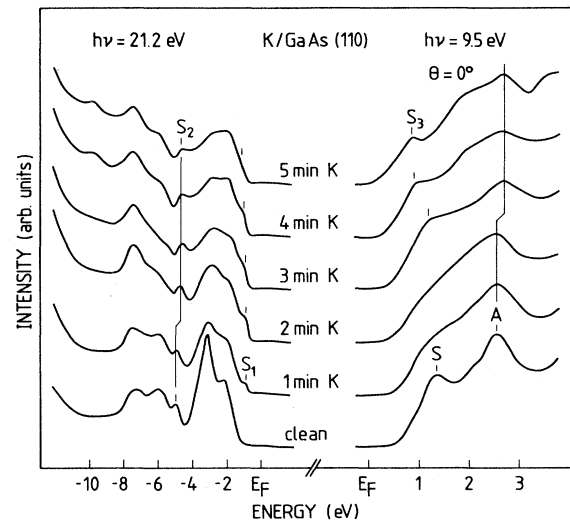


FIG. 2. Angle-integrated photoelectron spectra at $h\nu=21.2$ eV recorded in normal emission (left) and angle-resolved inverse photoemission spectra at $h\nu=9.5$ eV recorded at normal incidence (right) after various K evaporation times on the GaAs(110) surface. The 5-min spectra correspond to the saturated monolayer coverage according to our definition.

lower binding energy by 0.25 eV at the monolayer coverage. The two structures observed between 2 and 4 eV below E_F are due to the upper surface states on clean GaAs(110).¹¹ We note an early weakening and their continued change upon K evaporation. The full exploration of the effects of K on the occupied surface states found on clean GaAs(110), angle-resolved UPS is needed and this work is in progress.

Angle-resolved inverse photoemission spectra recorded at normal incidence for successive evaporations of K are also shown in Fig. 2. In the clean spectrum the Ga-derived surface state S and bulk conduction-band state A are clearly observed.^{12,13} The movement of state A to higher energies with increasing K coverage is due to band bending. After 1 min of K evaporation the surface state S is strongly damped and after 2 min it has disappeared. Upon further evaporation of K a new state labeled S_3 appears. This state moves down in energy and becomes sharper as the surface approaches saturation. The final energy position of S_3 at $\bar{\Gamma}$ in the surface Brillouin zone (BZ) is 0.9 eV above E_F , i.e., 0.4 eV above the conduction-band minimum. An increase in intensity on the low-energy side of A is also observed, developing a strong shoulder at saturation.

The energy dispersion of S_3 along the high-symmetry directions of the surface BZ has been measured. Figures 3(a) and 3(b) show angle-resolved inverse photoemission spectra for various incidence angles θ along $\bar{\Gamma}-\bar{X}$ and $\bar{\Gamma}-\bar{X}'$, respectively. The structure S_3 is strongest in normal incidence but can be clearly observed throughout the surface BZ. We note the appearance of a second, unidentified structure in the $\theta=30^\circ$ spectrum in Fig. 3(b). The $E(k_{\parallel})$ dispersion of S_3 is presented in Fig. 4. Included within parentheses is the second structure discussed

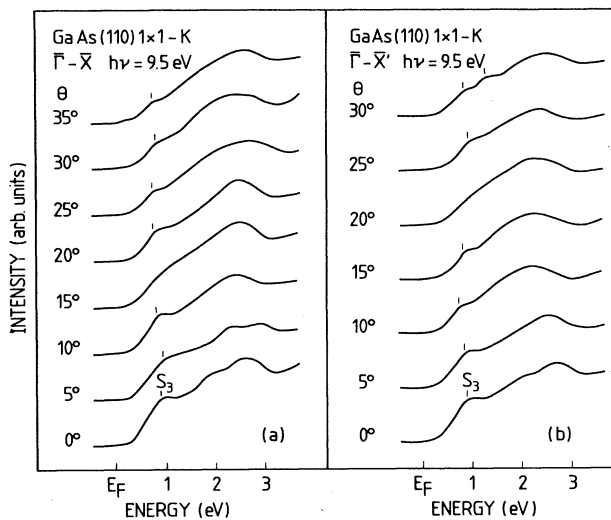


FIG. 3. Angle-resolved inverse photoemission spectra at $h\nu=9.5$ eV probing various angles of incidence θ along the (a) $\bar{\Gamma}-\bar{X}$ and (b) $\bar{\Gamma}-\bar{X}'$ directions of the surface Brillouin zone of GaAs(110)(1×1)-K, i.e., of the monolayer coverage (5 min of K evaporation).

above. The crosses represent the tickmarks in Fig. 3 while the line is drawn to guide the eye. The dispersion is rather weak in both directions, bandwidth approximately 0.2 eV; with one minimum at \bar{X} and a second roughly midway between $\bar{\Gamma}$ and \bar{X}' .

Combining the results of UPS and inverse photoemission presented in Figs. 2–4 we get a picture of the development of the K/GaAs(110) interface up to a monolayer coverage. The filled surface state S_1 moves down in energy with increasing K coverage and definitely does not cross the Fermi level. The empty surface state S_3 has been mapped along the main symmetry directions of the surface BZ and from this it is clear that the dispersion is weak, never coming closer than 0.6 eV to E_F . The conse-

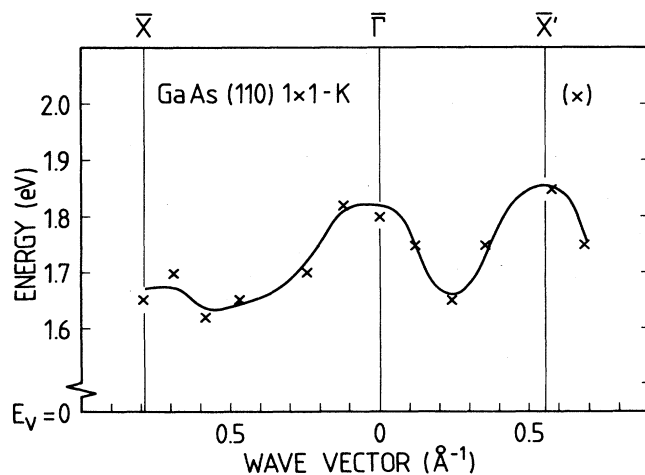


FIG. 4. Derived $E(k_{||})$ dispersion for the results in Fig. 3. Crosses represent observed transitions while the line is drawn to guide the eye.

quence of these findings is that the GaAs(110)(1×1)-K surface formed at room-temperature saturation is semi-conducting.

Cesium on GaAs(110)

The investigation of the interface between GaAs(110) and Cs has been done in analogy with the K study. Figure 5 shows the change in secondary-electron cutoff energy in UPS as a function of Cs evaporation time. A minimum of -3.35 eV is observed after 2-min evaporation which we interpret as the completion of the saturated monolayer. Further evaporation increases the value of the work function only slightly and the integrated Cs $5p$ emission does not increase. We find these two effects to roughly coincide, in contrast to the results of Ref. 8. Studies of the Ga $3d$ level show an upward band bending, fully developed after 1 min of Cs evaporation. LEED studies show a somewhat disturbed 1×1 pattern which we interpret that Cs does not go into a well-ordered structure at room-temperature evaporation.

In Fig. 6 we show the development of the surface electronic structure for successive evaporations of Cs on the GaAs(110) surface. Note the different energy scales for UPS (left) and inverse photoemission (right). The VBM is found 1.2 eV below E_F , yielding a nearly flat-band condition. The different appearance of the UPS spectrum from the clean surface in Fig. 6 compared to that in Fig. 2 is due to the effect of turning the azimuth 90° relative to the incident light vector, as noted already by Huijser *et al.*¹¹ After just 15 sec of Cs evaporation a filled surface state labeled S'_1 appears 0.95 eV below E_F , i.e., 0.25 eV above the VBM and clearly within the fundamental band gap. Upon further evaporation S'_1 stays almost constant in en-

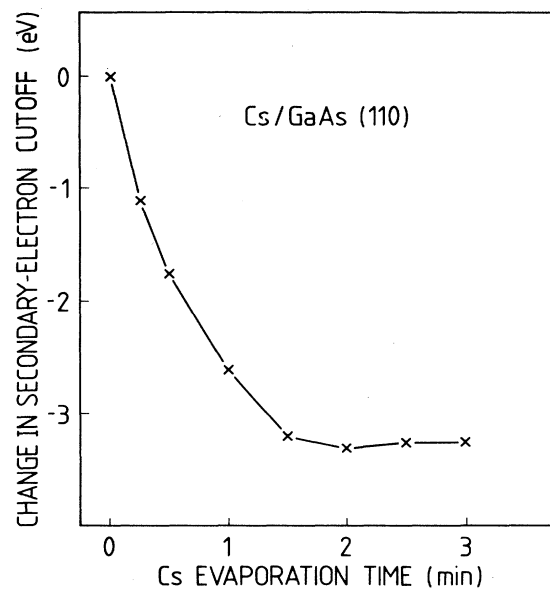


FIG. 5. The change in the cutoff energy for secondary electrons in UPS from the Cs/GaAs(110) surface as a function of Cs evaporation time. The maximum change is -3.35 eV and saturates at 2 min of evaporation time. We use this value as the definition for the saturated monolayer coverage.

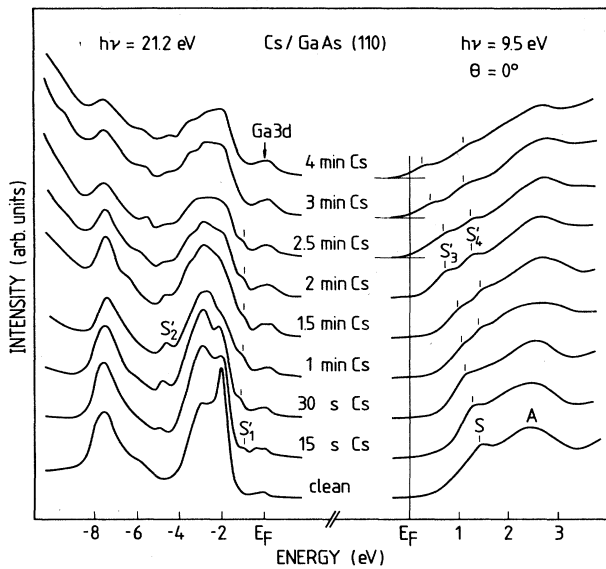


FIG. 6. Angle-integrated photoelectron spectra at $h\nu=21.2$ eV recorded in normal emission (left) and angle-resolved inverse photoemission spectra at $h\nu=9.5$ eV recorded at normal incidence (right) after various Cs evaporation times on the GaAs(110) surface. The saturated monolayer is defined for 2 min of Cs evaporation.

ergy and its position at saturation coverage after 2 min is equal to the energy of the VBM. Interestingly, evaporation beyond the saturation of the work function removes the S'_1 state. We also note large changes in the energy region between 2 and 6 eV below E_F for the full range of evaporation times, e.g., the appearance of a possible internal gap state S'_2 , which need to be investigated with angle-resolved UPS.

Angle-resolved inverse photoemission spectra are shown in the right part of Fig. 6. In the clean spectrum we again find the two structures S and A . In contrast to the K case the surface state S never disappears but merely changes continuously into the two surface states S'_3 and S'_4 . These two new states are found 0.7 and 1.2 eV above E_F at saturation coverage after 2 min. At this coverage the conduction-band minimum lies 0.5 eV above E_F . Extensive studies in off-normal incidence gave further indications that the saturated Cs/GaAs(110) surface is not well ordered.

As noted above, further evaporation of Cs does not increase the integrated Cs $5p$ intensity. In the inverse photoemission spectra for evaporation times beyond 2 min we note, however, a continued change in the surface electronic structure. The state S'_4 broadens slightly and moves down 0.2 eV while S'_3 moves down by 0.5 eV, clearly into the fundamental band gap, and broadens slightly. In the spectrum recorded after 4 min of Cs evaporation, S'_3 has thus moved all the way down to 0.25 eV above E_F yielding quite a high intensity at the Fermi level. To elucidate the development of the intensity close to E_F , Fig. 7 shows the difference between the inverse photoemission spectra for 2 min of Cs evaporation and the clean surface (bottom) and for 4 min of Cs evapora-

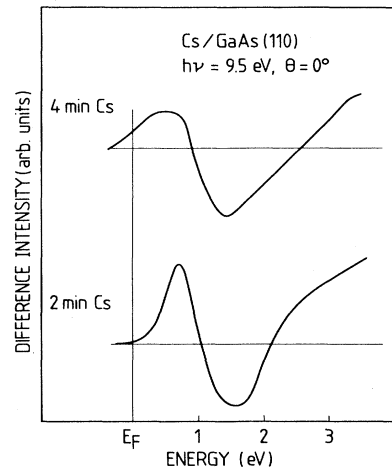


FIG. 7. The difference between the inverse photoemission spectrum recorded after 2 min of Cs evaporation and the clean GaAs(110) spectrum (bottom) and that recorded after 4 min of Cs evaporation and the clean GaAs(110) spectrum (top) from Fig. 6. The lines of zero difference are included.

tion and the clean surface (top). The lines of zero difference are included. In the 2-min spectrum in Fig. 7 the positive peak at 0.7 eV above E_F is the S'_3 state while the negative peak is the difference between the S'_4 state and the clean surface S state, since these are closely located in energy. For the 4-min spectrum the description of the peaks is unchanged but of utmost importance is the appearance of a Fermi-level cutoff with a width close to that found for a clean Ta foil. We can thus clearly state that upon Cs evaporation on a room-temperature GaAs(110) surface beyond the minimum of the work function, the empty surface state S'_3 moves down to E_F and renders the surface metallic.

DISCUSSION

By combining UPS and inverse photoemission we have demonstrated how the electronic structure of GaAs(110) changes during the growth of submonolayer to full-monolayer K and Cs overlayers. UPS shows the appearance of alkali-metal-induced surface states within the fundamental band gap for submonolayer coverages, states which relax into the projected valence bands at the saturation coverage. The filled surface states on the clean GaAs(110) surface are removed or at least drastically altered, although the internal gap states (which we label S_2, S'_2) seem to remain. In the unoccupied part of the electronic structure we have concentrated on the examination of the $\bar{\Gamma}$ point. Here the surface state S is removed and the subsequent appearance of a new state S_3 upon K evaporation is observed. In the case of Cs overlayer growth, the S state does not disappear but merely changes continuously into two new surface states S'_3 and S'_4 . We note that the major differences between the two investigated systems are thus observed in inverse photoemission, clearly indicating that these originate from different mechanisms of empty states generation in the adsorption process. LEED results and the off-normal in-

idence inverse photoemission studies show a lack of long-range order in the Cs/GaAs(110) surface as prepared. Kendelewicz *et al.*⁶ have proposed a two-site adsorption model for Cs on GaAs(110) from the observation of doublet formation in the Cs 4*d* levels. Our observation of two new empty surface states is qualitatively in accordance with this model. Information from scanning tunneling microscopy work by Stroscio¹⁴ is rather limited but indicates the early growth of one-dimensional chains of Cs on GaAs(110).

Preliminary results from Kendelewicz *et al.*⁶ showed the K/GaAs(110) system to be chemically reactive, the consequence of which would be the creation of a non-abrupt interface. We note that saturation of K produces an ordered GaAs(110)(1×1)-K surface with an empty surface-state band which has been mapped along the surface BZ high-symmetry directions. Our UPS results show no major difference between K and Cs adsorption which could indicate differences in chemical reactivity.

In both investigated systems the monolayer coverage found at the minimum of the work function is shown to give a nonmetallic, semiconducting state of the surface. In the case of Cs, however, our result shows that so-called over-cesiation, i.e., evaporation beyond the minimum of the work function, yields a negligible increase in the Cs 5*p* intensity but a change in the surface electronic structure which finally makes the surface metallic. We suggest this behavior to be due to the Cs-Cs interaction which, driven by the nonequilibrium Cs pressure at the already saturated surface, changes the ordering on the surface and subsequently the direction of charge transfer. By this we mean that from an initial growth where the Cs-Ga interaction dominates⁴ the system enters a regime where the Cs-Cs interaction makes it energetically favorable to reorganize the Cs atoms with respect to the Ga atoms. Derrien and Arnaud d'Avitaya⁴ have suggested a similar behavior which is also discussed in Ref. 6. This reorganization is accompanied by a reversed charge transfer in which the Cs valence electron is partially recaptured by the Cs overlayer producing a me-

tallic overlayer. Note that if this recapture is only partial the resulting Cs overlayer and the GaAs(110) surface (if discussed separately) may both be metallic. We stress that this is a nonequilibrium process with possible energy transfer to the surface and that the size of the Cs atom compared to the K atom in relation to the distance between adsorption sites becomes important in making the alkali-alkali interaction the driving force of interface metallization.

To our knowledge theoretical work on these surfaces is limited to the treatment of the alkali-metal overlayer as a jellium slab.¹⁵ This results in a metallic surface. Interestingly, this is in contradiction to our experiment and to that performed by Maeda Wong *et al.*⁸ for the just-saturated surface. The fact that the over-cesiated surface becomes metallic is, however, within our proposed model of nonequilibrium alkali-alkali interaction, in good agreement with the prediction¹⁵ that a jelliumlike overlayer renders the surface metallic.

SUMMARY

Adsorption of K and Cs on GaAs(110) has been shown to produce substantial differences in the surface electronic structure of the saturated monolayers formed at room temperature. Filled and empty surface states, precursors of interface states, have been observed which, taking band bending into account, all lie outside the fundamental band gap yielding semiconducting surfaces at saturation. Inverse photoemission results indicate the possibility of two inequivalent adsorption sites for Cs on GaAs(110) in agreement with the proposition by Kendelewicz *et al.*⁶ and further directly show the metallization of the Cs/GaAs(110) surface upon continued exposure to the flow of Cs atoms.

ACKNOWLEDGMENTS

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