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Observation of a Cs-induced state in the band gap of GaP(110): Alkali-metal bonding and Fermi-level pinning

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The deposition of submonolayer quantities of Cs onto GaP(110) causes strong photoemission features in the region of the semiconductor fundamental band gap. This observation is interpreted in terms of emission from a hybrid state caused by the interaction of the Cs 6*s* level with the unoccupied dangling-bond state. This hybrid state has long been postulated in descriptions of the metal-semiconductor surface bond, and is responsible for the pinning of the Fermi level. The absence of dispersion in the state suggests that Cs/GaP(110) represents a realization of a Mott-Hubbard insulator, by comparison with results from other alkali-metal/compound-semiconductor systems. [S0163-1829(96)03936-7]

Alkali-metal overlayers have been extensively used for the investigation of barrier formation in metal-semiconductor junctions because of their simple electronic structure.[1–3] A large body of experimental and theoretical work has been performed on the (110) surface of III-V semiconductors, since these, with the notable exception of GaP(110),[4] do not have surface states in the band gap. The model for the determination of the Fermi-level position in the fundamental band gap upon alkali-metal overlayer formation rests on the interaction between metal states and the unoccupied surface state of the III-V surface.[3,5,6] Here we present a study of Cs overlayer formation on GaP(110) where the formation of a hybrid state within the fundamental band gap, made up of the Cs 6*s* state and the Ga dangling-bond surface state is *directly observed* in photoemission. Moreover, we are able to follow the evolution of this state and its movement within the gap as a function of metal coverage. Our data show that the present system must be regarded as a Mott-Hubbard insulator, by comparison with similar systems and extensive calculations for alkali metals on III-V semiconductors.

The evolution of changes in the clean surface GaP(110) spectrum with cesium deposition is shown in Fig. 1, recorded at an emission angle of 14° along the [$\bar{1}$10] azimuth. The clean surface spectrum (bottom) is characterized by strong structures in the valence bands, most notably emission from the phosphorus-derived dangling-bond surface state at about 1 eV below the valence-band maximum (VBM), and a flat region up to 2.5 eV above the VBM, except for a very small structure at about 1.9 eV above the VBM, possibly due to residual Cs in the chamber. Deposition of Cs leads to the appearance of a sharp peak (*A*), and a second, broader peak (*B*) which develops at higher binding energies. With increasing coverage, both peaks shift to higher binding energies, and peak *B* gains relative intensity while peak *A* ultimately disappears, concomitant with the rise of intensity just above the VBM.[7,8] The P-derived dangling-bond surface state (intense leading peak in the valence band) is strongly suppressed upon Cs deposition; its observation about 1 eV below the VBM stems from the fact that the spectra in Fig. 1 were recorded at the $\bar{X}$ point of the surface Brillouin zone.

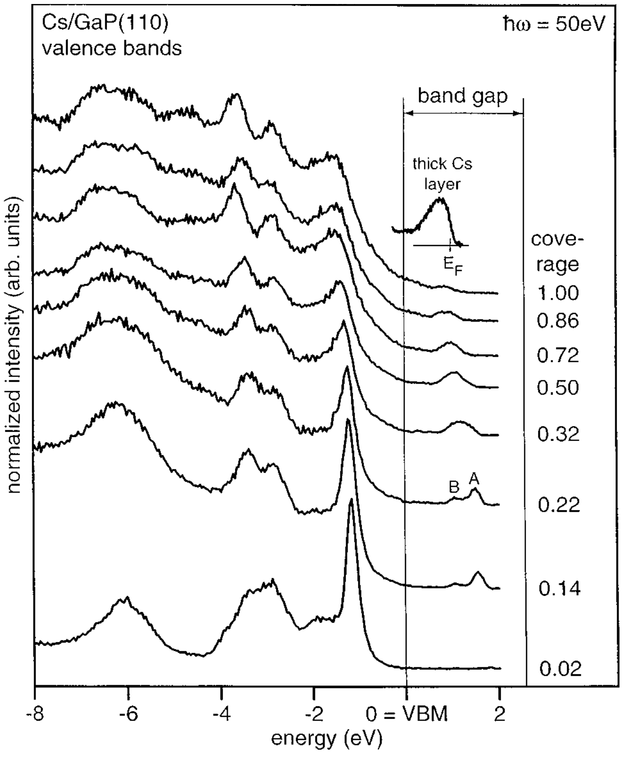

FIG. 1. Photoelectron spectra of the valence-band and band-gap region, for increasing coverages of Cs on GaP(110). Band-gap emission induced by Cs is clearly evident. The topmost spectrum shows the Cs valence-band from a multilayer coverage. All spectra are aligned at the VBM as deduced from Ga 3*d* core-level line-shape analysis.

Coverages are given here in fractions of the coverage necessary to reach the work function minimum (set at 1 ML).

Experiments were performed in two different chambers, with base pressures of 4–8$\times10^{-11}$ mbar, equipped with commercial angle-resolved photoelectron spectrometers (HA 50 from VSW Ltd, and ADES 400 from VG Scientific, GB). Cs was evaporated from well outgassed getter sources (SAES SpA, Italy). Electrons were excited by photons from the BESSY storage ring, using toroidal-grating monochromators, giving an overall resolution of 120 meV, at an angular resolution of 1.5° half angle. GaP(110) surfaces were prepared by cleaving *n*-type (sulfur doped) material with a carrier density of 2×10^{17} cm^{-3} (MCP, England). Swift experimenting (less than about 2 h for one particular layer) was found to be most important, contamination being easily recognized by a suppression of band-gap emission and the formation of a sharp cesium suboxide peak at 2.7 eV below VBM. All experiments were carried out at 120–140 K. Work-function changes induced by Cs exposure were measured from the low-energy cutoff in the spectra under conditions where surface photovoltage does not play a role.

Important evidence concerning the nature of the peaks in the band gap is derived from their intensity as a function of emission angle. Spectra from a 0.27 ML Cs layer are shown in Fig. 2, for different angles along the Γ-X direction of the surface Brillouin zone (SBZ) (top of Fig. 2). The peaks are most intense at angles of ±14° with respect to the surface normal, corresponding to the X point. They are very weak in normal emission and at all angles along the Γ-X' azimuth (not shown). Their binding energy is independent of photon energy, demonstrating their surface state nature. Their intensity is found to be strongly peaked at a photon energy of 50 eV where, with an angular setting at the X point of the SBZ, direct transitions occur into the primary cone-free electron final state at the X point of the bulk Brillouin zone. Since surface states exhibit their maximum intensity at photon energies where direct transitions from their corresponding bulk states occur,[9] this strengthens our interpretation of these peaks as arising from surface states with wave functions of X symmetry.

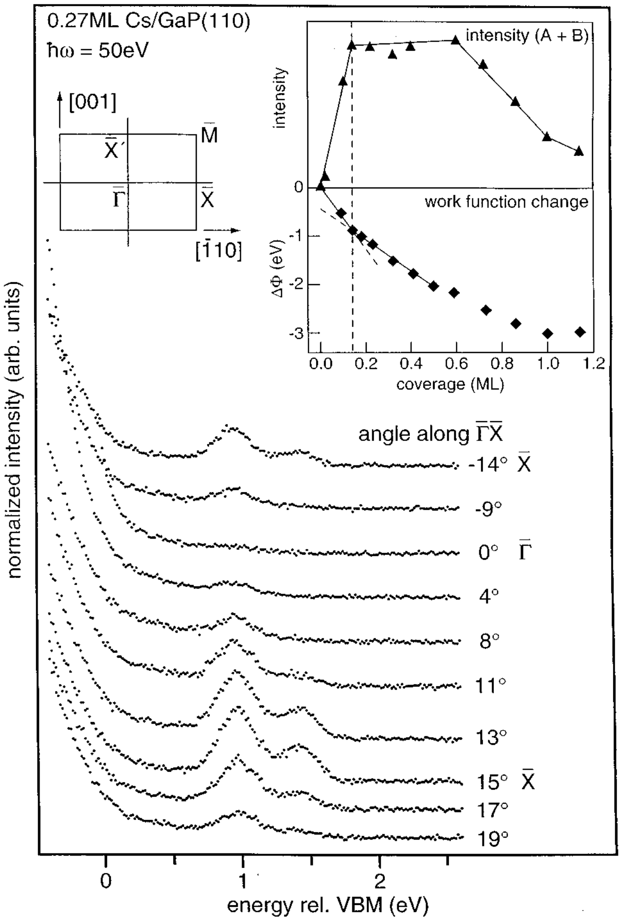

FIG. 2. Spectra of band-gap peaks, for a Cs coverage of 0.27 ML for different angles of emission as indicated. Note the lack of emission around the surface-normal. The maximum of intensity corresponds to the X point of the surface Brillouin zone which is also shown. Inset: Intensity of emission in the gap (peak A plus B) as a function of Cs coverage (top), and Cs-induced work-function change (bottom trace). Note the break in the work-function curve as the peak intensity saturates.

Structural differences rather than the electronic structure of the adatom layer itself are thought to be responsible for the observation of two distinct peaks (A and B), since their relative intensities at a given coverage differ between preparations. In scanning tunneling microscopy work on the similar Cs/GaAs(110) system, different morphologies were found in the course of overlayer growth. At coverages corresponding to 0.1 ML in our definition, the formation of sparsely distributed, very long zigzag double- and triple-row chains along the [110] azimuth is observed, which at higher coverages turn into more densely packed islands.[10,11] Since core-level spectra from Cs layers or GaP(110) exhibit two separate Cs 4*d* and 5*p* peaks,[7] the Cs atoms are present within these structures in two inequivalent environments. Concentrating on the low-coverage situation, the leading peak A is tentatively assigned to Cs atoms in the zigzag chains, while peak B is ascribed to two-dimensional islands of Cs.

We interpret the peaks in the band gap within a molecular model of the bonding interaction,[3] in which the alkali-metal *s* orbital essentially couples with the cation-(Ga)-derived dangling-bond orbital. The energy of the bonding state is determined by the energies of the 6*s* level and the cation dangling bond. The anion dangling-bond level is doubly occupied, such that it does not take part in the bonding. This model, which describes the energies of the bonding states for different alkali metals on GaAs(110),[5] also accounts for our experimental observations in Cs/GaP(110): first, emission from the gap state being concentrated around the $\bar{X}$ point is readily explained by the fact that the Ga-derived, unoccupied surface state has its minimum in energy at this point,[12] and consequently electrons donated into this level by its interaction with the Cs 6*s* level will occupy states at $\bar{X}$ in the SBZ. Second, the intensity of emission from the state in the band gap increases with Cs coverage up to a certain maximum, as shown in the inset in Fig. 2. The intensity maximum coincides with a break in the work-function change curve (lower trace), indicative of a change in dipole moment per additional adatom. Such behavior is interpreted as the onset of depolarization, where the amount of charge transfer per adatom starts to decrease. Third, the strong intensity of the gap-state emission arises from its concentration in a small part of the SBZ, causing intensity enhancement where the peak is

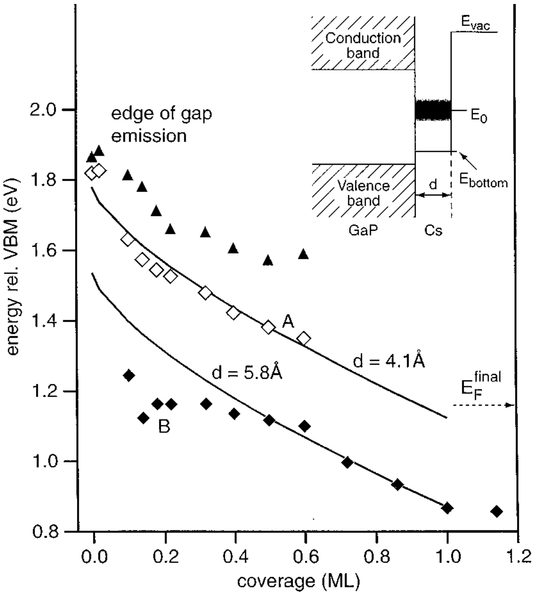

FIG. 3. Energy of peaks *A* and *B* and the location of the high-energy edge of emission in the gap, as a function of Cs coverage. Also given are the positions of the Cs state in the different quantum-well geometries (''chain'' and ''island'') used for modeling the data (see text). Inset: Schematic energy diagram of the model used to calculate the coverage-dependent energy of the Cs 6*s* state.

actually observed. A rough guess puts this enhancement at a factor 12; a peak-spread out over the entire SBZ would be barely detectable.

The state giving rise to the peaks in the gap is directly involved in determining the position of the Fermi level E_F at the surface. On the clean surface a position of E_F at 1.9 eV above the VBM is observed. This coincides with the upper edge of the emission in the gap at low coverages of Cs (Fig. 1). For the entire range of submonolayer coverages the edge of emission puts a lower limit on the position of E_F. The shift of the edge of the gap emission points towards the final pinning position of E_F (arrow in Fig. 3) as determined from a spectrum of a thick Cs layer (Fig. 1, top). The peaks in the gap can well be modeled by single Gaussians. The results of such an analysis are shown in Fig. 3, combined with an estimate of the low-energy limit for E_F as deduced from the emission edge where possible. A gradual decrease similar to the one of the edge was also seen in the position of the Fermi level in Cs/GaAs(110),[2] and is in accordance with the trend predicted by Mönch, and broadly similar to the results from work-function change measurements by Linz, Clemens, and Mönch.[13]

The coverage dependence of the gap-state energy demonstrates that a model of isolated molecular orbitals cannot fully account for the observations; instead, a Cs-Cs interaction must be considered. In the absence of *ab initio* calculations, the energy of the electronic state resulting from Cs adsorption and its movement in the gap as a function of Cs coverage was therefore calculated[14] within a quantum-well model employed successfully in the description of Na-induced states on Cu(111).[15] Here the well depth is determined from the surface Cs density, and the well width is the only free parameter. Two different quantum wells with individual widths were assumed for the different Cs species. The width of the ''island'' peak was adjusted at a coverage of 1 ML to match the observed energy, while the well of the ''chain'' peak *A* was adjusted at 0.5 ML just before it strongly decreases in intensity. The calculated energies of the stationary state for the two different geometries are shown in Fig. 3. There is good agreement between the experimental results and the calculated peak positions for well widths of 4.1 Å for the ''chain'' peak *A* and 5.8 Å for the ''island'' peak *B* with a discrepancy at low coverages for the latter which probably indicates that in this region only the number of islands change, but not their local Cs density. While the agreement of the data points with the calculated curves at 0.5 for *A* and 1 ML for *B* is forced by the adjustment, the energy shift as a function of coverage is evidence for the validity of the model.

GaP is so far the only example among the III-V semiconductor (110) surfaces where photoemission peaks deep in the gap have been found upon metal deposition. Two factors may account for this. First, the atomic ionization potential of 3.9 eV for Cs puts this state above the energy of the unoccupied surface state, located about 4.3 eV below the vacuum level. For Na, with an ionization energy of 5.1 eV, the difference in energy renders interaction less likely, and similar peaks were not reported in a study of Na/GaP(110) by Evans, Lapeyre, and Horn;[16] a comparison with data from Na/GaAs(110) (Ref. 17) and calculations[18] also suggests that there are qualitative differences in the electronic structure as discussed below. Second, *n*-type GaP(110) is the only one among these surfaces where the Fermi level is pinned by a surface state.[4] However, interaction between Cs atoms and the unoccupied surface state is thought to take place in other systems also. For Cs/GaAs(110), a splitting of this state was found in inverse photoemission, with a subsequent lowering of energy with increasing coverage.[19] In Cs/InAs(110), where the surface state lies considerably *above* the conduction-band minimum (CBM),[20] emission from two states has been found in the conduction band close to E_F. These have been explained by Aristov *et al.*[20] in terms of a two-dimensional electron gas (2DEG) in the downward-bent conduction-band. Our present interpretation suggests a different explanation of their results, i.e., that the corresponding peaks arise from a residual charge in Cs-related states; this is particularly likely since the charge in the 2DEG was calculated by Aristov *et al.* to be located several tens of Å away from the surface, rendering its detection in photoemission implausible. Even in InP(110), where the surface-state band is located only slightly higher than the CBM, the adsorption of small quantities of Cs places the Fermi level about 0.2 eV into the conduction band,[21] giving further support to our view that interaction between the Cs 6*s* level and the unoccupied surface state is central to Fermi-level pinning in such systems.

From the interaction of cesium with its single 6*s* electron with the surface state, a partly filled band and thus a metallic surface should result. However, a symmetric line shape of the Cs core levels, and the absence of specific loss features on the core levels[7] demonstrate that the surface is not metallic. This is in agreement with the findings from electron-energy-loss[22] and scanning tunneling spectroscopy in the similar Cs/GaAs(110) system.[11] However, charge transfer from the alkali metal *s* level into the Ga dangling-bond band means that a half-filled, metallic band exists. This apparent conflict has been interpreted for Cs/GaAs(110) by DiNardo, Wong, and Plummer[22] in terms of the Mott-Hubbard model, where an energy U has to be spent for metallic charge transport in order to add a second electron to a particular lattice site, such that the Bloch band picture is not appropriate. Density-functional calculations by Pankratov and Scheffler[18] have shown an alternative way to explain the absence of metallicity in such alkali-metal layers: a lattice distortion which causes two electrons to pair up in one lattice site (''bipolaron''). It was recently suggested by del Pennino *et al.*[17] that, depending on the nature of the adsorbed alkali-metal, either the Mott-Hubbard or the bipolaron scenario may be realized; in both cases, a singly (Mott-Hubbard) or doubly (bipolaron) occupied state will act as the highest occupied state which determines the energy of E_F, but the surface remains nonmetallic; these seem to be complementary mechanisms in determining the nonmetallic nature of the metal-semiconductor interface. The calculations also suggest that, even for a situation where the Mott-Hubbard correlation dominates, such as expected for the case of adsorbed Cs,[22] the polaronic interaction still is effective in substantially narrowing the bandwidth, thus promoting the Mott-Hubbard correlation.

This is important in the present context, where we are faced with two apparently conflicting observations: the surface is not metallic, but emission from the gap state occurs near the edge of the surface Brillouin zone only. These observations can be reconciled on the basis of the following reasoning: the surface unit cell extends over two unit cells of the clean surface along [1$\bar{1}$0] and includes two inequivalent Cs atoms found in the chains.[7,10] Thus the SBZ is folded back by the new periodicity, and a small gap opens up at the newly formed zone boundaries, splitting the surface band into two branches. Consequently, the bandwidth of the clean surface-state band of 0.6 eV (Ref. 4) is divided among the branches, reduced by the width of the small gap. Since the main intensity of the hybrid state is still observed at the original $\bar{X}$ point (Fig. 2), the character of the wave function is not strongly affected by the imposition of the new periodicity.[23] The interaction with the adsorbed Cs further reduces the bandwidth, through the bipolaron influence. Our measurements show no detectable dispersion in the gap state, suggesting a very flat band. This proves that the resulting gap state bandwidth is well below the on-site Coulomb repulsive energy U, which is estimated to be about 0.5 eV;[18] thus the system is a Mott insulator. A changeover from bipolaronic to Mott-Hubbard behavior in going from Na to Cs as suggested by Pankratov and Scheffler[18] and del Pennino *et al.*[17] then readily explains the fact that strong emission from states deep in the gap was not found for Na/GaP(110);[16] instead, a feature close to but slightly above the VBM was found, in agreement with expectations for the energy of a bipolaronic state.[17]

In summary, we have observed photoemission from a state in the semiconductor band gap, which is instrumental in determining the Fermi level and causes its shift towards the final position upon metallization. This state can be thought of as a combination of the Cs 6*s* level and the unoccupied surface state, and the dependence of its energy is well described by a one-dimensional quantum-well model. We interpret the absence of dispersion in this state as evidence that Cs/GaP(110) is a realization of a Mott-Hubbard insulator, by comparison with results from other alkali-metal/compound-semiconductor systems.

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