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Photoemission observation of Na-induced states in the band gap and evidence for charge transfer in Na/GaP(110)

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Na adsorption on GaP(110) is shown to induce a photoemission peak in the region of the band gap above the valence-band maximum. This peak is interpreted as arising from the formerly empty Ga dangling-bond surface state, which is occupied and lowered in energy by interaction with the Na 3*s* level. The interaction between Ga and the Na substrate atoms is reflected in the appearance of a shoulder on the Ga 3*d* core-level line and two separate Na 2*p* emission lines. These data, which are interpreted by recourse to recent self-consistent electronic-structure calculations, provide strong evidence for charge transfer in the bonding of Na to GaP.

Investigations of alkali-metal adsorption on semiconductor surfaces have played a key role in the long-standing debate about the mechanism of Schottky barrier formation because of the simple electronic structure of the alkali-metal atom.[1,2] In an intuitive picture, bonding between the alkali-metal atom and the substrate proceeds by charge transfer from the alkali-metal *s* level into the unoccupied surface state of the substrate, thus forming a dipole layer which gives rise to the large decrease in work function found experimentally. Among the theoretical studies for alkali-metal adsorption on semiconductors,[3-6] this picture is generally supported, but with some groups suggesting almost total charge transfer,[7] while others find very little.[8] Direct experimental evidence for the charge-transfer process through photoemission and electron-energy-loss (EELS) studies has been lacking so far for clean elemental or compound semiconductor surfaces in spite of considerable experimental effort.[8-13] However, in a recent study of the boron-passivated Si(111) surface, large shifts in the substrate core levels upon alkali-metal adsorption[14] were found. Here we report high-resolution photoemission experiments for the Na/GaP(110) system which clearly demonstrate charge transfer through the occurrence of symmetric peak shifts on the Na and Ga core-level lines. This interpretation is supported by the observation that Na adsorption on GaP(110) induces a new peak in the region of the fundamental band gap, which is identified with the formerly empty Ga-derived surface state which is filled by charge transfer from the Na *s* level.

The experiments were performed in an ultrahigh vacuum photoemission chamber, with a base pressure of 8×10^{-11} mbar, equipped with low-energy electron-diffraction (LEED) optics, cleaving tools for substrate surface preparation, and a crystal holder which allowed sample cooling to 100 K. Photoelectron spectra were recorded using light from the BESSY (Berliner-Elektronen-Speicherrings-Gesellschaft für Synchrotron-strahlung) electron storage ring, using toroidal grating monochromator 4 with a photon energy range from about 10 to 120 eV, such that the phosphorus 2*p* line was not accessible in this experiment. Photoelectrons were energy analyzed and detected using a spherical deflector energy analyzer (HA 50 from VSW Ltd., Great Britain). The overall resolution was about 90 meV as measured *in situ* by gas-phase photoemission from the argon 3*p* level.[15] The substrates were prenotched bars of *n*- and *p*-type GaP with carrier concentrations of about 6×10^{17} (*n*) and 2×10^{18} cm^{-3} (*p*) (MCP Ltd., U.K.), which were cleaved *in vacuo* and showed mirrorlike surfaces with only a few large-scale steps. Temperatures were measured with a thermocouple attached to the samples. Na overlayers were deposited from well outgased getters (SAES Getters, Torino, Italy), and their cleanliness was monitored through valence-level photoemission, where even the slightest [less than $\frac{1}{20}$ of a monolayer (ML)] contamination through oxygen or water can be detected. The pressure increase during Na overlayer preparation was less than 1×10^{-10} mbar, consisting mainly of hydrogen as determined with a quadrupole mass spectrometer. Experiments reported here were carried out at 100 K since scanning tunneling microscopy (STM) data[16] have shown that badly ordered layers with a tendency for clustering are grown at room temperature. Our LEED results, reported elsewhere,[17] show a hexagonal superstructure at coverages above one monolayer, demonstrating epitaxial growth at low temperature. A parallel photoemission study of the room-temperature growth revealed the absence of uniform growth at 300 K, as for the related Na/GaAs(110) interface.[18]

Evidence for Na-substrate charge transfer is deduced from the Ga 3*d* substrate core-level spectra shown in Fig. 1. The clean surface spectrum (bottom) clearly shows the presence of the bulk Ga line as well as the surface core level (SCL), shifted by 0.31 eV towards higher binding energies as derived from a line-shape analysis.[19] This uses Lorentzian lines convoluted by Gaussians, where parameters are optimized by the Marquardt algorithm.[20] Adsorption of small amounts of Na leads to a suppression of the surface core level, and causes an extra feature to appear, initially shifted about 1.13 eV towards higher kinetic energies with respect to the bulk Ga line (second spectrum from bottom). The coverage series of the Ga 3*d* emission spectra could be fitted using three components (surface, bulk, and a third, high-kinetic-energy component) by varying only the relative intensities and energies of each peak. A typical curve-resolved spectrum, showing all three components and the difference between

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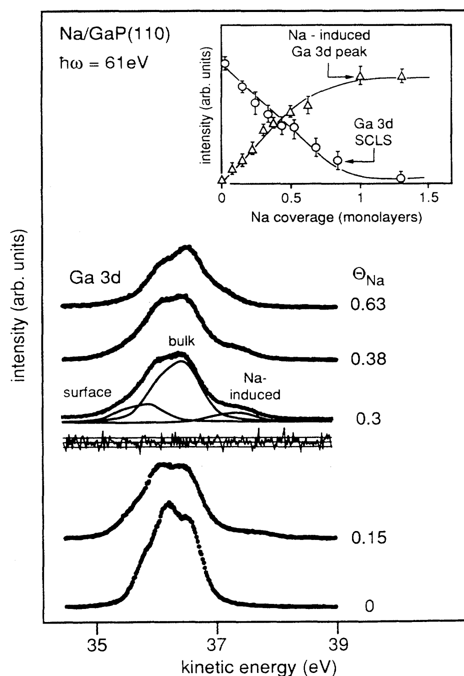

FIG. 1. Set of spectra from the Ga 3*d* core level as a function of Na coverage in monolayers. Note the clear shoulder due to the surface core level in the clean surface spectrum and the emergence of a feature at higher kinetic energy upon Na exposure. The spectrum for 0.3 ML includes a line-shape analysis in terms of bulk, surface, and Na-induced components. The trace below the line-shape analysis indicates the residual; upper and lower lines indicate the limits of random noise. Inset: Intensity of Ga 3*d* surface core level, and Na-induced component, as a function of Na deposition.

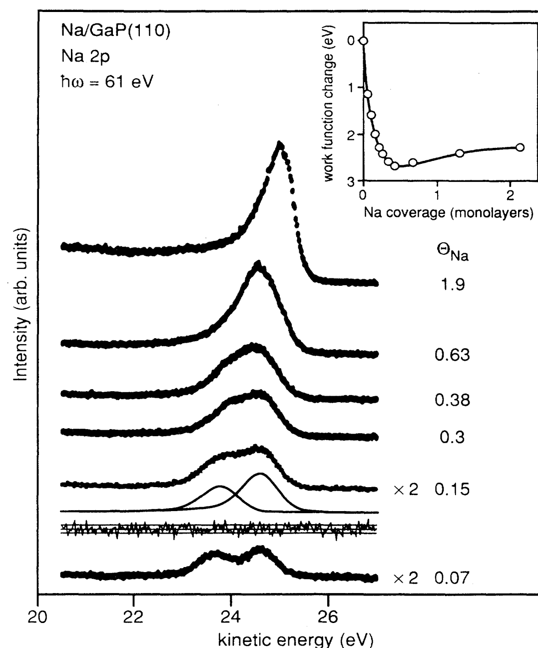

FIG. 2. Set of Na 2*p* spectra with increasing Na coverage. Initially, two separate peaks appear, which merge with increasing coverage. The first two spectra are enlarged by a factor 2. The spectrum at 0.15-ML coverage is analyzed in terms of two Na 2*p* lines. Inset: Work function change as a function of Na exposure.

data and fit, normalized for the counting rate, is shown in Fig. 1 for a coverage of 0.15 ML. The high-kinetic-energy feature intensifies with Na deposition and shifts towards the bulk Ga line as evident from the series of spectra in Fig. 1. The Na-induced component and the SCL have the same dependence on surface sensitivity, i.e., both are due to surface processes.[17] The increase of the Na-related feature coincides with the decrease of the SCL up to 1-ML coverage (see inset of Fig. 1), showing that the high-kinetic-energy peak is indeed related to increasing Na coverage and to the occupation of Ga sites on the surface. Here monolayer coverage is defined as follows:[17] from the relative intensities of Ga 3*d* bulk and surface emission, a mean free path $\lambda=4.5$ Å for a kinetic energy of 37 eV is derived.[21] The exponential decay of the Ga 3*d* line with Na deposition then permits a calibration of deposition times in terms of monolayer coverage, assuming that λ is similar in GaAs and Na. On the basis of this calibration, the minimum in the work-function change $\Phi_{\min}$, recorded from the low-energy cutoff in the spectra, and shown in the inset of Fig. 2, occurs at $\frac{1}{2}$-ML coverage, where 1 ML corresponds to 8.8×10^{14} atoms/cm^2. Coverages in excess of 1 ML lead to the occurrence of a metallic Fermi edge (see Fig. 3) and the occurrence of loss features on the Na 2*p* peak.[17]

Shifts in semiconductor core-level lines have been successfully related to charge transfer between overlayer and substrate atoms, and their magnitude may in fact be correlated with the electronegativity of the atoms involved.[22] On the basis of this model, we interpret the large shift of the Na-induced component on the Ga 3*d* peak towards higher kinetic (lower binding) energy as due to charge transfer from the Na adatoms towards the Ga substrate atoms. This charge transfer should then also be reflected in the appearance of the Na core-level peak, shown in Fig. 2. Here two peaks are initially observed, separated by 0.95 eV. With increasing deposition, the peak at higher binding energy moves towards the other, stationary one, their separation decreasing to about 0.35 eV at $\frac{1}{2}$-ML coverage. The ratio of intensities of both peaks remains constant up to this coverage,[17] beyond which a distinction is difficult since changes in peak shape occur as the layer moves into a regime of increasing metallicity (top spectrum). Similar splittings of alkali-metal core-level peaks for Cs/GaAs(110),[8] Na/InP(110),[23] and Na/GaAs(110) (Ref. 18) have been previously observed. However, relative shifts in these components have not been linked to the change in alkali-metal–semiconductor charge transfer. In line with this assignment, we assign the Na 2*p* low-kinetic-energy component in Fig. 2 to Na atoms bonded to a gallium substrate atom, and the stationary component to Na atoms bonded to anion (phosphorus) atoms. The observation of chainlike structures in STM images of Cs/GaAs(110) (Ref. 24) and InSb(110) suggests that such bonding sites are occupied. It is also possible that this peak may have another origin such as Na clusters as suggested for

Na/GaAs(110).[18] However, even for the latter interface a more recent study[25] shows that a degree of Na-anion interaction is detected in the As 3*d* core level. A precise assignment of the stationary peak will have to await more structural information for Na/GaP(110). The shift of the Na-Ga component is thus in opposite direction to that on the Ga 3*d* level, in agreement with the proposed direction of charge transfer,[22] and of about equal magnitude at low coverages. The shift Na 2*p* and Ga 3*d* lines is reduced in a symmetric fashion with increasing coverage. This is expected, since mutual depolarization of neighboring adatoms, reduces the charge imbalance that would otherwise occur at higher coverages.

The evidence for Na-Ga charge transfer outlined above is derived from a straightforward initial-state interpretation. One might argue that other effects, such as a change in final-state screening, or structural changes might be responsible for the observed core-level shifts. However, there has been a lack of evidence in favor of a final state induced by the buildup of a metallic overlayer. Karlsson *et al.*[26] have calculated such effects and have concluded that shifts on the order of about 0.2–0.3 eV may result, much smaller than those found here. Structural changes are more difficult to assess; however, changes other than a partial derelaxation of the surface, as derived from the self-consistent total energy calculations,[5] are unlikely in these low-temperature experiments. For SCL emission on the clean surface, it has been found that the relaxation contributes about $\frac{1}{3}$ to the total observed shift as compared with the unrelaxed surface, rendering unlikely such structural changes as a source for the large shifts shown in Figs. 1 and 2.[28]

Direct evidence for the charge-transfer process indicated by the core-level spectra is derived from the valence level data shown in Fig. 3. The clean surface spectrum (bottom left) is characterized by direct transitions and density-of-states emission from the GaP bulk bands, and the phosphorus-derived dangling bond surface state near the top of the valence-band maximum (VBM).[29] Depositions of Na gives rise to a peak located initially about 0.5 eV above the VBM, well inside the fundamental band gap of gallium phosphide (see close-up spectra on the right-hand side). The intensity of the gap emission peak increases until it saturates at a coverage somewhat less than half a monolayer. This increase is accompanied by a movement towards the valence-band maximum. At its maximum intensity, the peak is located only about 0.2 eV above the VBM, merging with it around monolayer coverage. Above 1 ML, another peak emerges, which forms part of the Fermi edge. Deposition of Na leads to a decrease of the anion-derived surface state emission, suggesting also a degree of Na-anion interaction; this effects has been noted before by Magnusson and Reihl in their study of K and Cs on GaAs(110).[10]

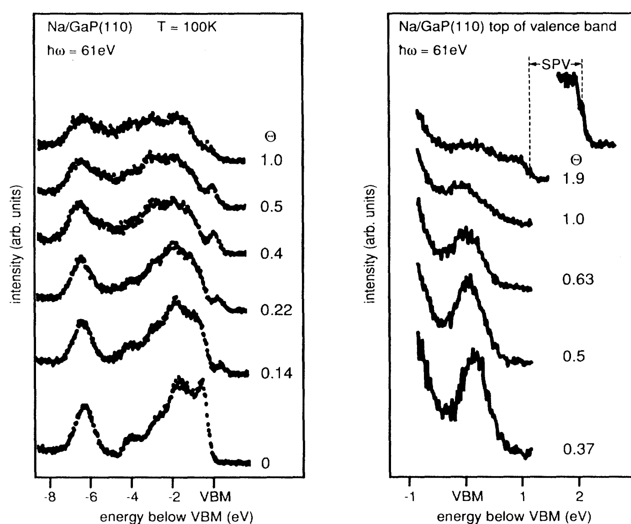

FIG. 3. Valence-level spectrum of GaP(110), recorded at normal emission at a photon energy of 61 eV, for different coverages of Na as indicated. Left: Spectrum including the region of the main valence bands. Right: Close-up spectrum featuring the Na-induced state in the band gap, as a function of Na deposition. Note the emergence of a clear Fermi edge in the 1.9-ML spectrum, shifted with respect to the reference Fermi level (top) because of the occurrence of a surface photovoltage.

The picture of alkali-metal bonding to semiconductor surfaces outlined above, and supported by recent calculations, gives a straightforward interpretation for the Na-induced peak within the fundamental band gap. The level directly involved in adsorbate-substrate charge transfer is the unoccupied Ga-derived dangling-bond surface state. This level, initially at about 1.8 eV above the VBM,[29] is pulled down in energy upon being filled by the Na 2*s* electrons. This is precisely what is reflected in the valence-level photoemission spectra in Fig. 3. This picture is in agreement with simple models of charge transfer and the electronic structure of the (110) surface, and it agrees with the recent self-consistent local-density approximation calculations for Na/GaAs(110).[5] These predict that previously empty surface state consists of highly localized states, which are not adequately described in a Bloch picture.[5] While this prediction is based on a specific adsorption geometry, its consequences, i.e., a lack of dispersion with the parallel component of electron momentum $E(\mathbf{k}_{\parallel})$, can be readily tested in angle-resolved photoemission. Valence-level spectra were recorded along both high-symmetry directions in the surface Brillouin zone (SBZ) for Na coverages close to the maximum intensity of the state in the gap. By analyzing the peak position using Gaussians, dispersion was found to be below 150 meV over the entire SBZ.[17] Thus the predicted localized nature of the gap state seems to be supported by the angle-resolved photoemission data.

The filling of surface states in the band gap by the metal overlayer has obvious consequences for the determination of the Fermi level in this interface. The location of the Fermi level was determined by photoemission, and its value for thicker films[17] agreed well with transport measurements from thick films ($\Phi_b^p = 1.1$ eV).[30] As evident from the close-up spectra in Fig. 3 (top), the present data are affected by a surface photovoltage (SPV) at low coverages, such that a determination of the Fermi level from substrate core-level data at low coverages, where corrections cannot be applied from photoemission data alone,[31]

is subject to uncertainty. However, values for E_F may be extrapolated to low coverages for data from n-type substrates as suggested by the Kelvin probe data of Mao *et al.* for Ag/GaAs(110).[32] At low coverages, the VBM of the substrate can still be discerned and the edge of the filled interface state peak can be determined with respect to the VBM. Its edge then defines E_F and thus the low-coverage barrier height can be determined, even in the presence of a SPV. For Na/GaP(110), the high-energy tail is at VBM + 0.9 eV, which is close to the position of the Fermi level determined from high-coverage band-bending data.[17] This indicates a link between the position of the gap state and the Fermi-level pinning position, although the influence of the localized nature of the band on the appearance of the spectra cannot be ruled out at present.

While the electronic structure of alkali-metal–semiconductor interfaces has been extensively studied by means of various techniques, the nature of the bond between alkali-metal and substrate is still debated. A Mott insulator picture, i.e., highly localized states of the alkali-metal atoms, has been invoked in order to explain photoemission and EELS findings, in particular the lack of peaks due to states within the band gap in photoemission spectra.[11,12] However, such states had indeed previously been observed by Magnusson and Reihl[10] in photoemission from K and Cs on GaAs(110) surfaces, but their presence had not been related to the processes of charge transfer in these systems. The data presented here for Na/GaP(110) provide a consistent picture of the alkali-metal–semiconductor bond, through an analysis of core-level shifts in terms of charge transfer, and the observation of the Ga-derived surface-state occupancy and energy lowering as a consequence of this process. Preliminary data for the Na/GaAs(110) system indicate that a picture similar to that presented here for Na/GaP(110) may also apply in this case.[27]

The absence of alkali-metal-induced core-level shifts on silicon surfaces has been taken as evidence in support of a predominantly covalent bond. However, recent high-resolution photoemission data for K on the Si(111) $\sqrt{3}\times\sqrt{3}R-30°$-boron surface by Ma *et al.*[14] have shown large (~ 1 eV) core-level shifts, indicative of charge transfer in this system. The authors argue that the *occupied* surface states on Si(111)-7×7 and other clean Si surfaces greatly reduce charge transfer from the alkali-metal atom, leading to a mainly covalent bond. This is important for the present Na/GaP(110) system, since the boron-induced $\sqrt{3}\times\sqrt{3}R\,30°$ reconstruction induces an electronic structure very similar to that of the (110) surfaces of the III-V semiconductors, with a large energy splitting between the filled and empty surface states. The observations by Ma *et al.* thus give strong support to our interpretation of the observed core-level shifts and valence-band features in terms of alkali-metal–semiconductor charge transfer.

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