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Evidence of a bipolaronic, insulating state of Na submonolayer on GaAs(110)

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We present electron-energy-loss-spectroscopy results for the Na/GaAs(110) ultrathin interface. The data do not show the loss features commonly found for Cs, K, and Rb overlayers, which are considered to be the fingerprints of a Mott-Hubbard insulating state of the interface. In photoemission we observe a distinct Na-induced surface state, appearing at a coverage of about 0.25 ML, which disappears approaching the complete monolayer. We interpret our results on the basis of the bipolaron model which suggests that insulating character of the interface originates from the "negative-U" behavior of the surface state.

It has become evident, recently, that two important assumptions abut the interaction of alkali metals (AM) with surfaces of III-V semiconductors are wrong. The first one, based on the "simple nature" of alkali metals and on the lack of surface states in the fundamental energy gap at (110) surfaces of the most III-V compounds, treats AM/III-V interfaces as the "ideal" system to study formation of the Schottky barrier. The second one is a commonly assumed similarity of different AM adsorbates, which implies similar electronic structure of all AM/III-V interfaces.

The illusion of simplicity was broken when it was experimentally found that AM/III-V interfaces persist to be nonmetallic at submonolayer coverages,[1-6] in conflict with one-electron energy spectrum derived from the electronic structure calculations.[7,8] The calculations predict that AM valence electrons partially fill the Ga-originated surface band, which is located slightly above the conduction-band edge for a clean GaAs/(110) surface and is gradually shifted into the energy gap upon the increase of the AM coverage.[8] Therefore the surface is expected to be metallic with the Fermi level being pinned in the surface band. However, photoemission (PE) and inverse photoemission[1,9,10] show that a totally occupied adsorbate-induced state appears close to the top of the valence band and another unoccupied state appears at the conduction-band edge. The Fermi level stays in the gap so that the interface remains insulating. Also the scanning tunneling microscopy (STM) experiments[5,6] confirm the nonmetallic character of the surface. Further evidence of nonmetallicity emerges in the electron-energy-loss spectroscopy (EELS) results,[2-4] which do not show a metallic excitation continuum at low energies. At the same time, two well-defined subband loss features were found for Cs,[2] at room temperature (RT) and low temperature (LT), and then for K (Ref. 3) and Rb,[4] at LT, on GaAs(110). Analyzing these loss features DiNardo, Wong, and Plummer[2] concluded that the Cs/GaAs(110) interface is a two-dimensional Mott-Hubbard insulator. They attribute the new losses to localized subband excitations arising from the Hubbard splitting of the surface state.[11,12]

Assuming "similarity" of all AM, one would expect that a Na submonolayer on GaAs(110), which is also nonmetallic,[6] should show a similar excitation spectrum. In this paper, we present the high-resolution EELS and PE data for Na/GaAs(110). We found that interfaces, which were formed both at RT and at low temperature ($LT \approx 130$ K), *do not show subband losses* at any Na coverage. We interpret these results using the bipolaron model for nonmetallic Na/GaAs(110) interface;[13] this model also accounts for a difference between STM images for Na (Ref. 6) and Cs (Ref. 5) submonolayers.

The measuring apparatus was a two chambers system (preparation and analysis), with a base pressure of 7×10^{-9} Pa (7×10^{-11} mbar), in which different kinds of electron spectroscopies can be performed [high-resolution electron-energy-loss spectroscopy (HREELS), ultraviolet photoemission spectroscopy (UPS), and x-ray photoemission spectroscopy]. The HREEL spectrometer was a tandem double pass 127° cylindrical sector analyzer (Leybold ELS22), working with a primary beam energy $E_0=15$ eV, an incidence angle of 67°, in the reflection geometry. The energy resolution was degraded to 30 meV to gain signal intensity in the electronic loss region. The photoemission spectra, excited by He-I and He-II UV radiation, were measured collecting the photoelectrons with a cylindrical mirror analyzer (CMA). The light beam impinged on the sample at grazing incidence along the [001] direction, while the analyzer axis was $\approx 35°$, with respect to the sample normal. The Fermi level was determined from the valence-band spectrum of a freshly evaporated gold spot on the sample holder, which also indicated an energy resolution of about 150 meV. Sodium was evaporated from well outgassed SAES Getters dispensers, on n-GaAs samples (Si doped, 3×10^{18} cm^{-3}) in a vacuum that never exceeded 3×10^{-8} Pa, at both RT and ≈ 130 K (LT), as measured by a thermocouple in contact with the copper sample holder. At $T\approx130$ K, it is possible to deposit more than one Na monolayer (ML), while at RT, the sat-

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uration coverage seems to be $\theta_S < 1$ ML. We indicate by 1 ML the coverage of two Na atoms per unit cell. At LT, the coverage (θ) was deduced from the plot of the work function of the Na/GaAs interface vs deposition time assuming that, as reported by many authors,[14] this curve shows a well-defined minimum at 0.5 ML (Fig. 1 inset). At RT, this attribution is more difficult as no clear minimum, but only a decrease in slope is recognized at 0.5 ML.[14]

Figure 1 shows the evolution of the valence-band spectra of the Na/GaAs interface, starting from the clean surface and at increasing Na coverages. Though the CMA is not an angle-resolved analyzer, the spectra are very similar to those obtained with angle-resolved analyzers and are sensitive to sample orientation.[15] The actual orientation was chosen to maximize the intensity of the surface peak A_5, at a binding energy (BE) of ~ -2.5 eV. The intensity of this peak is clearly quenched by the progressive Na deposition, but the peak is still visible at the highest coverages obtained in the present investigations. For $\theta > 0.1-0.2$ ML, a Na-induced state with a BE ≈ -1 eV appears in the gap. For $\theta \approx 2.5$ ML, a weak but clear Fermi edge is seen in the spectrum, indicating that the interface is metallic. We also note that the "sample" Fermi level coincides with that of the spectrometer, confirming that no surface photovoltage (SPV) occurred.[16] To put into better evidence the features induced by Na deposition, in Fig. 2, we magnify the region of the valence-band top. Syncrotron UPS measurements of Na on GaAs(110) were already reported by Evans, Lapeyre, and Horn,[10] who have been working with a photon energy of 61 eV, in normal emission, and did not distinctly see gap states. Different angular resolution could be at the origin of the disagreement.

From the shift of the features of the valence band not modified by the deposition and from the shift of the Ga 3*d* core levels (BE = 19 eV), measured with the He-II radiation, the band bending associated with the formation of the metal-semiconductor interface was measured. The final value is reached at $\theta \approx 0.5$ ML and amounts to 0.55–0.6 eV, in agreement with previous investigations.[14]

The HREEL spectra of the Na/GaAs(110) interface in the 0.6–7 eV loss region, at LT, are plotted in Fig. 3 for increasing Na coverages. As already found for other AM/GaAs interfaces,[2–4] the lowest deposition induces an overall increase in the intensity of the loss spectrum, in particular, between 2 and 5 eV. Above $\theta = 0.15$ ML, the losses start to fill the gap region, which gradually narrows. At $\theta = 0.3$ ML, a clear edge appears with an onset at about 0.8 eV. A sudden change occurs between $\theta = 0.6$ and 0.9 ML, as at this last coverage the gap is completely filled by a continuum of losses starting from the tail of the elastic peak. This behavior can be taken as an indication of an incipient interface metallicity. In photoemission the Fermi edge can be detected only for $\theta \approx 1.5$ ML,

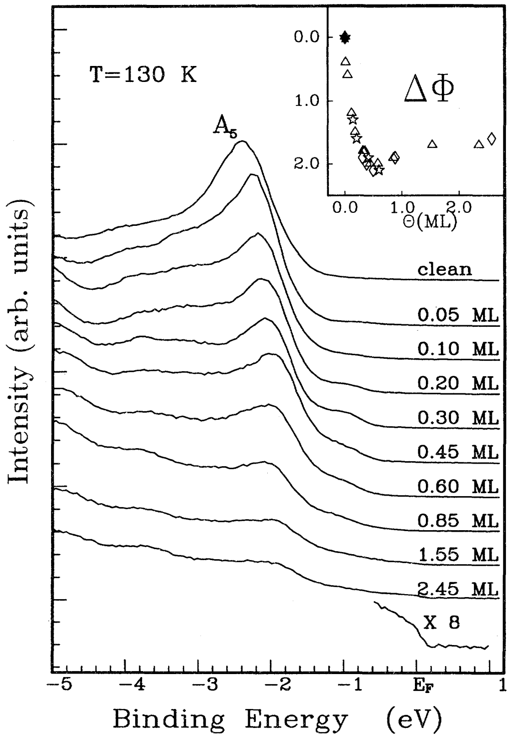

FIG. 1. Evolution of the He-I photoemission spectra from the valence band of the clean GaAs(110) surface and of the Na/GaAs(110) interface, with Na coverage. Inset: Work-function change with Na coverage, as deduced from the shift of the secondary cutoff in the UP spectra.

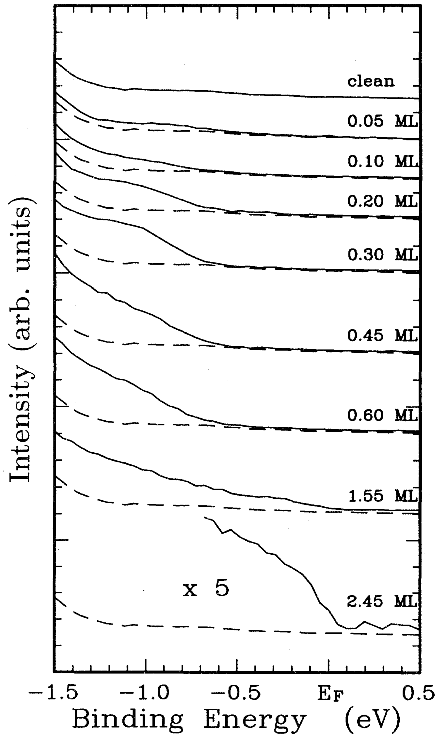

FIG. 2. Expanded plot of the UP spectra of Fig. 1 in the region −1.5–0 eV, emphasizing the Na-induced gap state.

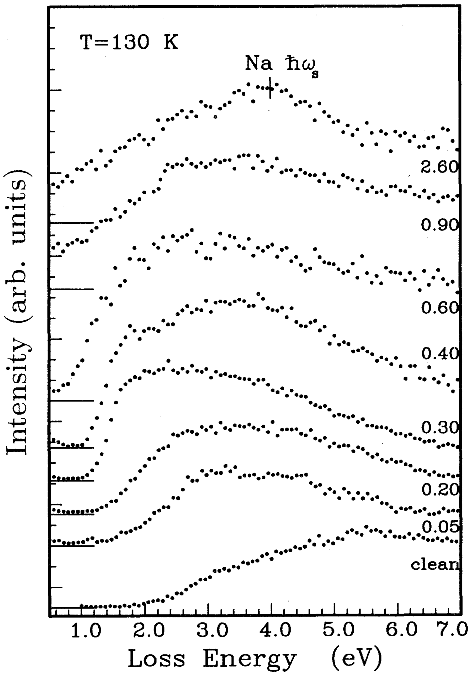

FIG. 3. High-resolution electron-energy-loss spectra of the Na-GaAs(110) interface, as a function of coverage. $\hbar\omega_s$ is the surface-plasmon energy of metallic sodium.

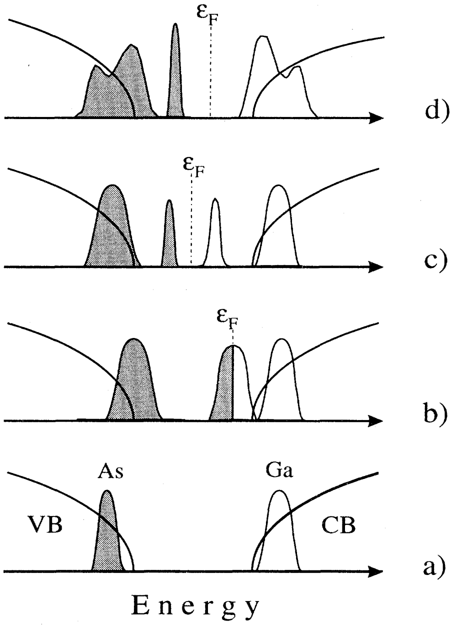

FIG. 4. Density of states (DOS) in the gap region (schematically) for the clean (a) GaAs(110) surface and for $\theta=0.25$ Na ML (b)–(d). The labels CB and VB denote the bulk conduction and valence bands; the labels Ga and As stand for Ga- and As-derived surface bands. (b) One-particle DOS for AM/III-V interface without taking into account the Hubbard correlations or polaronic interaction. (c) Mott-Hubbard insulating state. (d) Bipolaronic insulating state. The narrow peak is formed by the doubly occupied Ga-Na bonds.

this confirms once more the higher surface sensitivity of the HREELS technique. At the largest coverage attained the whole loss spectrum consists of a wide background peaked at the metallic Na surface-plasmon energy (4 eV),[12] analogously to that found for the other AM/GaAs interfaces.[2–4]

The fundamental difference between the HREELS results shown above (and also the results at RT, which are not reported here) and data for other AM adsorbates[2–4] is the complete absence of the two low-energy features that motivated the correlation model.[2,11] Qualitative difference between Na/GaAs(110) and Cs/GaAs(110) was already found in STM experiments that show that Cs adatoms form zig-zag chains,[5] whereas Na appears as much sparser linear chains.[6] Since the ionic radius of Na is almost twice as small as that of Cs, it is very unlikely that Na indeed forms a sparser structure. In Ref. 13, it was suggested that Na adatoms are arranged in the same zig-zag structure as Cs adatoms, but the STM images are different, due to different nature of the nonmetallic state. The density-functional theory calculations[13] revealed that the surface unrelaxation around the occupied dangling bonds induces a strong electron-electron attraction. It was found that in the case of Na/GaAs(110), this attraction overwhelms the Hubbard repulsion so that the "effective" Hubbard U becomes negative[17] and electrons make pairs (bipolarons) occupying only half of the Ga-Na bonds. Since the empty bonds are invisible in the occupied-state STM image, half of adatoms are missing and a zig-zag structure looks like a linear chain (assuming an ordered arrangement of the occupied bonds).

Figure 4 schematically shows the density of states (DOS) at the interface. There are two surface bands on a clean GaAs(110) surface [Fig. 4(a)]–the empty Ga-derived and the occupied As-derived state. Figure 4(b) shows the one-particle DOS for AM/III-V interface as predicted by electronic structure calculations without taking into account neither the Hubbard correlations nor the polaronic interaction. From now on, the AM coverage of one adatom per two surface elementary cell ($\theta=0.25$ ML) is assumed, which corresponds to an ordered layer of closely packed zig-zag AM chains.[5,13] The adsorbate overlayer makes the two neighboring Ga atoms nonequivalent, which results in a splitting of the Ga surface band into two subbands. The lower subband is half-filled, since there is one AM valence electron per two Ga dangling bonds. Apparently, the picture predicts that the surface should be metallic, with the Fermi level ε_F being pinned in the surface band. The Mott-Hubbard insulating state arising from the splitting of the lower Ga subband by the Hubbard gap $2U$ (Ref. 11) is shown in Fig. 4(c). Finally, Fig. 4(d) shows DOS in the bipolaronic insulating state,[13] which corresponds to the case $U<0$. The narrow peak is formed by the doubly occupied Ga dangling bonds. It is obvious that this model leads to an insulating ground state, because the doubly occupied orbitals form a completely filled surface state. Its small width indicates that this state is highly localized.[13] Since there is no Hubbard splitting, there should be no subband loss features in the EELS in this case. We attribute the adsorbate-induced peak in the PE spectrum (Fig. 1) to the doubly occupied Ga-Na bond. The calculations[18] predict that this level is located about 0.4 eV above the valence-band edge. The most important result is that the bipolaronic mechanism is consistent with the fact that this state does not gradually pass through the energy gap as the coverage increases. Although this state split from the Ga surface band, which is located above the conduction-band edge [Fig. 4(a)], the strong lattice deformation pushes the electron energy level down almost to the valence band. In addition, trapping the electron pair induces a potential that splits the occupied As-derived surface state[18] and hence broadens the valence-band edge, as is observed experimentally.

A particularly strong polaron effect for Na/GaAs (110) is likely related to the small ionic radius of Na;[13] a Na adatom is closer to the surface and polarizes the Ga dangling bond stronger than other AM. The polaron effect and Hubbard correlation seem to be complementary mechanisms of the metal-insulator transition on AM/III-V interfaces. The calculations[12] show that the value of the Coulomb repulsion $U \approx 0.5$ eV does not exceed the width of the Ga surface band at the clean relaxed surface. Therefore, even when the polaronic interaction is not able to provide the negative U (e.g., for Cs adsorbate), the polaron effect is important since it substantially narrows the bandwidth[18] and thus promotes the Mott-Hubbard transition. In this case, similar to the case of negative U, the polaronic energy shift lowers the position of the occupied Ga state, pushing it towards the valence band.[18] It is noteworthy that in both PE and HREEL spectra, additional features appear at coverages ≥ 0.25 ML.

In conclusion, we have shown that for Na/GaAs(110), there are no subband losses in the HREEL spectrum, which have been found for Cs, K, and Rb adsorbates, but only a sharp edge appears at coverages $\theta \geq 0.25$ ML. From the same coverage, we observe in the PE spectra an additional state in the gap, which disappears before metallization occurs. Both results can be explained assuming that Na/GaAs (110) is a bipolaronic insulator,[13] with electron pairs localized on the surface Ga-Na bonds. The Ga-derived surface state thus shows a "negative-U" behavior. Our results show that the surface polaron effect, along with Hubbard correlations, plays an important role for AM/GaAs(110) interfaces.

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