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Electronic properties of ionic insulators on semiconductor surfaces: Alkali fluorides on GaAs(100)

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Photoelectron core-level spectra are measured for the interfaces RbF/GaAs(100) and LiF/GaAs(100). It is found that RbF, of which the lattice almost matches the GaAs lattice, is epitaxially grown and a F—Ga interface bonding was observed. LiF with a large mismatch to GaAs dissociates after annealing the surface and induces a reconstruction of the GaAs surface. We discuss the present results as compared with our previous investigations of NaF and KF on the same GaAs(100) surface.

I. INTRODUCTION

Recently, the field of insulators on semiconductors gave rise to interesting discussions about interface bondings.[1-4] The most popular system in this field is CaF_2 on Si(111), because CaF_2 is epitaxially grown on Si with a lattice mismatch of 0.6%. The dominant bonding is found between Ca and Si. Calcium is also valid to be the more reactive candidate at the interface for CaF_2/GaAs(100), where a Ca atom bonds with two As atoms.[5]

Very recently, alkali halides as adsorbates on metal and semiconductor surfaces are becoming more popular.[6-10] Alkali halides which can be easily vapor-deposited on the surface are insulators with a strong ionic bond. RbF on Ge(100) showed epitaxial growth and Ge—Rb bond formation above one monolayer (ML).[10] We found for NaF on GaAs (100) (Ref. 6) in the initial monolayer range a separate deposition of the constituents. F atoms are desorbed at 460 °C and only Na atoms remain on the surface. On the other hand, the multilayer deposition of NaF causes a strong charging up and a band bending of the substrate. Temperature for reducing the multilayer to the monolayer needs 610 °C, and at 650 °C the monolayer NaF is simultaneously and completely desorbed, i.e., no preferential desorption occurs. In contrast to NaF, KF seems to be unaffected by the annealing process. Neither a dissociation of K and F nor a strong charging up could be observed.

A keyword of such interface investigations is the lattice match for allowing epitaxial growth. Our aim is to study the behavior of overlayer and interface for various alkali fluorides with the different magnitude of lattice mismatch to GaAs. The mismatch range is from 0.2% for RbF to 28.8% for LiF. The values in our previous investigation of NaF (18.3%) and KF (5.7%) (Ref. 6) are intermediate.[11] We have used photoelectron core-level spectroscopy to measure the interface properties against annealing temperature and deposition thickness.

II. EXPERIMENT

Photoemission experiments were performed at the KEK Photon Factory beamline BL-1A at Tsukuba. The experimental conditions were similar to our previous studies.[6] Angle-integrated spectra were taken at a photon energy of 115.4 eV. Additionally x-ray photoelectron spectra (XPS) were observed by using a separate XPS source. A GaAs(100) wafer surface was cleaned by Ar^+ sputtering and annealing. RbF and LiF powders were evaporated from a tungsten basket. During alkali fluoride deposition the GaAs surface was at room temperature. After deposition and/or annealing the sample surface structure was monitored by low-energy electron-diffraction (LEED) observation. The clean GaAs(100) surface showed a 4×1 LEED pattern. A previously proposed structure model described the GaAs(100)-(4×1) surface as As rich.[12] Recent investigations, however, indicate this surface to be Ga rich.[13]

In order to avoid possible contamination of the analysis chamber, the sample was heated by electron bombardment in the preparation chamber. The temperature measurement, made using an optical pyrometer, was very ambiguous compared to preliminary experiments that were used for temperature calibration of this system, and the given temperatures are within errors of ±50 °C.

As in the previous case of NaF, the deposition thickness was not calibrated. The estimated amount of RbF and LiF on the surface was between 1 and 8 ML. Our main goal is, as before, to compare roughly between the depositions of the monolayer range (<4 ML) and the multilayer range (>4 ML). The important features of the results we shall discuss are independent of the exact amount of the overlayer deposition.

III. RESULTS

A. RbF/GaAs(100)

Figure 1 shows the photoemission spectra from F 2*p* and Rb 4*p* core levels of RbF on GaAs (100). The bottom

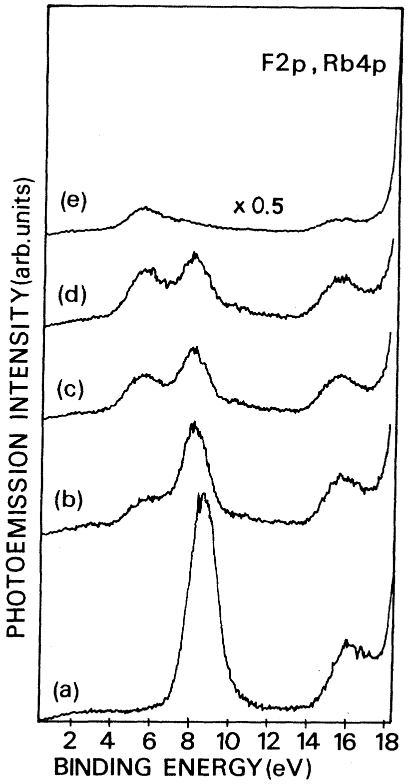

FIG. 1. Photoelectron spectra from F 2*p* and Rb 4*p* core levels of RbF on GaAs(100). (a) Monolayer deposition. (b)–(e) After annealing the initial monolayer deposition up to 200, 250, 300, and 350 °C; a second F 2*p* peak at lower BE appears and the intensity increases with increasing annealing temperatures. For all spectra a 4×1 LEED pattern was observed, which is the same for the clean GaAs(100) surface.

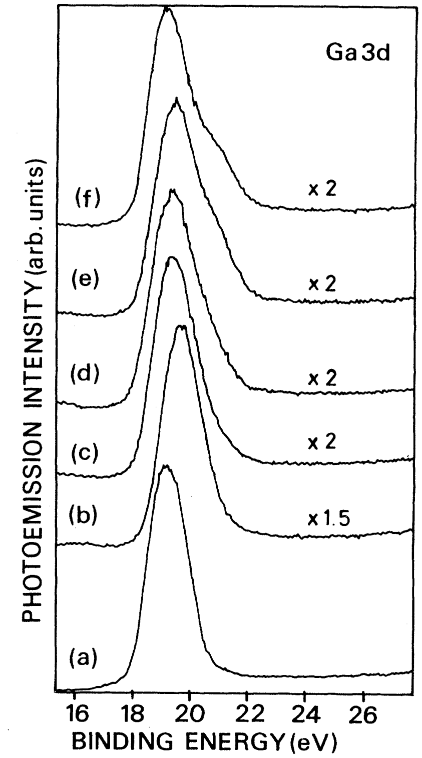

FIG. 2. Photoelectron spectra from the Ga 3*d* core level of RbF on GaAs(100). (a) Clean surface. (b) RbF monolayer deposition. (c)–(f) After annealing the initial monolayer deposition up to 200, 250, 300, and 350 °C; i.e., the same sequence as in Fig. 1.

spectrum, (a), is an initial deposition of RbF of about 2 ML. The F 2*p* peak is centered at 8.7 eV, and the Rb 4*p* peak is at 16.1 eV binding energy (BE). The LEED pattern changes at this stage from a sharp 4×1 pattern to a more diffuse 4×1 pattern with weak quarter-order spots.

Heating the sample to 200 °C [spectrum (b)], the overlayer core-level peaks are shifted by 0.6 eV to lower BE, and an additional peak appears at a BE 2.3 eV lower than that of the F 2*p* peak. The intensity of the second peak increases with increasing annealing temperatures [spectrum (c), 250 °C; (d), 300 °C]. This is correlated with sharpening of the 4×1 LEED pattern. The structure of the last overlayer [spectrum (e)], which also shows a sharp 4×1 pattern, is very stable, and Rb and F are completely and simultaneously desorbed at almost 600 °C. At low coverages we found the second-lower BE peak in some as-deposited surfaces without annealing the sample.

Figure 2 shows the Ga 3*d* photoemission peak for the same sequence as in Fig. 1. The lowest spectrum shows additionally that of the clean GaAs surface. In the as-deposited surface at a low coverage [about 2 ML, spectrum (b)], the substrate peak shifts by 0.7 eV to higher BE. For higher coverages (about 8 ML) this shift can be up to 1 eV. A backward shift occurs and a shoulder of the Ga 3*d* peak appears by annealing the sample. In spectrum (f) the separation of the shoulder is 1.4 eV from the main Ga 3*d* peak to higher BE.

For As 3*d* no additional peak could be observed. The whole spectra of more bulk-sensitive XPS are unaffected by annealing the sample. No change in any peak positions could be measured.

B. LiF/GaAs

For LiF deposited on GaAs(100) the photoelectron core-level spectra of the F 2*p* peak are shown in Fig. 3. Spectrum (a) is for a coverage of about 1 ML, and a very diffuse 4×1 LEED pattern can be observed. Contrary to RbF, the F 2*p* peak of the as-deposited surfaces is always a double peak. For monolayer coverage these peaks are centered at 9.3 and 10.9 eV. Annealing the sample to about 400 °C [spectrum (b)], the shoulder at higher BE fades away. Additionally, a second peak at 6.5 eV BE appears. The appearance of the second peak after annealing the sample is correlated with a change in the LEED pattern into a sharp 2×1 pattern. Spectra (c) and (d) are for the same sequence as (a) and (b), but for higher initial deposition (about 6 ML). In comparison with monolayer coverage, the peaks for the multilayer are shifted by 0.8

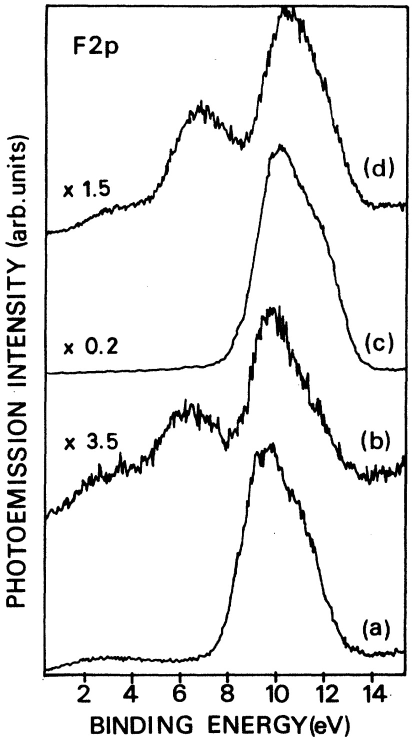

FIG. 3. Photoelectron spectra from the F 2*p* core level of LiF on GaAs(100). (a) Monolayer deposition. (b) After annealing the initial monolayer deposition up to 400 °C. (c) Multilayer deposition. (d) After annealing the initial multilayer deposition up to 400 °C.

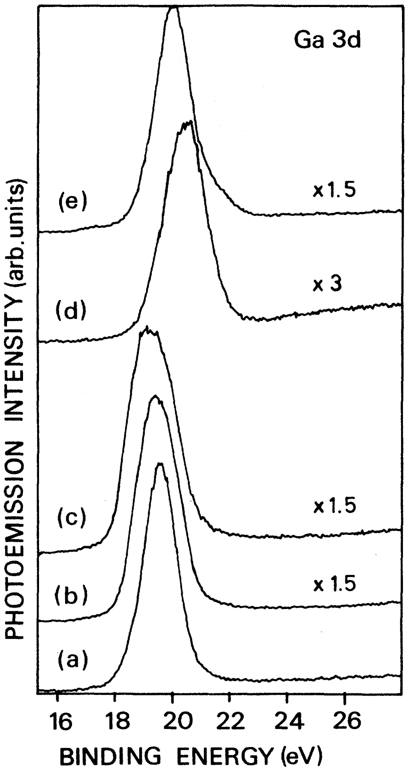

FIG. 4. Photoelectron spectra from the Ga 3*d* core level of LiF on GaAs(100). (a) Clean surface. (b) LiF monolayer deposition. (c) After annealing the initial monolayer deposition up to 400 °C. (d) LiF multilayer deposition. (e) After annealing the initial multilayer deposition up to 400 °C.

eV to higher BE, and only diffuse 1×1 spots were observed. The separation of the double peak is more pronounced. Upon annealing the sample, a second peak of the BE 3.5 eV lower than the F 2*p* peak appears, the LEED pattern changes to 2×1, and the shoulder of the double peak almost disappears.

The substrate peaks show less drastic change. Figure 4 shows the Ga 3*d* core-level peaks, where spectrum (a) gives the clean surface and spectra (b)–(e) the same sequence as in Fig. 3. Between clean and monolayer-deposited surfaces no significant shift could be observed. However, after heating the sample the Ga 3*d* peak is broadened. In the as-deposited surface of an initial multilayer, the peak is shifted by 0.8 eV to higher BE. Though the annealing procedure causes a backward shift, a shoulder at higher BE appears.

The Li 1*s* and As 3*d* peaks show a higher BE shift for the multilayer, but no additional effects could be observed. The 2×1 LEED pattern is very stable and returns to 4×1 at an annealing temperature of about 600 °C. However, the F 2*p* signal disappears at a temperature of about 500 °C. The F atoms are completely desorbed at this temperature, whereas Li atoms remain only slightly on the surface. Then, the 2×1 structure is induced by the LiF adsorption on the clean GaAs(100) surface and not by a F-adsorbed structure.

IV. DISCUSSION

Since the lattice constants of RbF and GaAs crystal are almost the same, and the RbF(100) surface is stable, we would expect the easy formation of an epitaxially grown overlayer of RbF(100) on GaAs(100) from this simple consideration. Indeed, RbF is the only one among the alkali fluorides that clearly shows additional features in the surface-sensitive region, i.e., the additional peaks at about 5.6 and 20.3 eV BE are correlated with RbF/GaAs interface formation. Of course, RbF vapor-deposited on GaAs at room temperature can hardly give a nice epitaxial film. For initial deposition the LEED pattern is a diffuse 4×1 structure. However, an annealing of the sample to 200 °C is enough to make the RbF/GaAs interface commensurate. The second F 2*p* peak at lower BE and the shoulder of the Ga 3*d* peak at higher BE are considered to be interface-induced structures, which originate in a F—Ga bonding.

At higher annealing temperature (300 °C) we found a perfectly matched interface. Further heating (350 °C) leads to RbF desorption from the surface. The intensity of the Rb 4*p* and F 2*p* peaks at higher BE decreases. The F-interface peak still remains strong. RbF at the interface is hardly removed at this annealing temperature and is desorbed at very high temperature (600 °C). Although the detailed surface structure for the 4×1 pattern of the clean GaAs(100) surface is not known, a structural model of the RbF/GaAs interface can be proposed based on our experimental results and is shown in Fig. 5.

The Ga—F bonds are formed at the interface by making the simple NaCl-type lattice, in which a F atom has two bonds coupled with the dangling bond of two Ga atoms, and the RbF(100) surface is prepared. This F atom at the interface is now bonded with two Ga atoms and five Rb atoms. Both the effective charges of the negative F ion and the slightly positive Ga atom may increase in the interface position, because the BE decreases for F and increases for Ga. The experimental result implies the ionic properties at the interface for the structure model shown in Fig. 5. The Rb atoms at the interface sit just above the As atoms of the second layer of GaAs(100). The As atoms at the interface are replaced by the F atoms, if the RbF lattice is formed. These As atoms are expected to be negatively charged. Hence, the Ga atoms at the interface are positively charged and take higher BE, since these Ga atoms are surrounded by negatively charged F and As atoms. On the other hand, the F atoms at the interface take lower BE. This implies that F atoms in the RbF lattice are stabilized by a strong ionic lattice as compared with the F atoms at the interface.

The idea for the interfacial structure comes mainly from the geometrical fit between the RbF and the GaAs lattice, and from the fact that two kinds of F and Ga atoms in different chemical environments exist. In the case of CaF_2 on Si(111),[2] the dominant Si—Ca bond at the interface causes also a second peak of Ca 3*p* about 2 eV lower than that of the lower BE, whereas the F atom shows a very weak reaction with the Si surface and is easily removed from the interface. Contrary to CaF_2, the RbF/GaAs interface shows the dominant bond to the F atom. This is not surprising, because alkali-metal atoms deposited on semiconductor surfaces usually give a very weak interaction at the interface.[14–16] In general, the detailed structure of epitaxially grown insulator-semiconductor interfaces is very sensitive to the initial surface temperature of the substrate. However, we assume a deposition of RbF at the evaluated substrate temperature will not change the fact of a strong F—Ga bond.

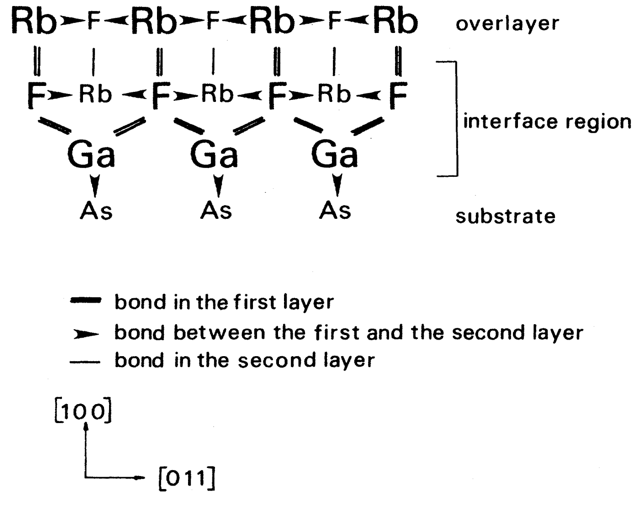

FIG. 5. Structural model for the RbF/GaAs(100) interface (side view). The larger and the smaller letters show the first-layer and second-layer atoms, respectively, in the cross section.

The F 2*p* double peak of LiF on GaAs is very different from the other alkali fluorides. It was experimentally and theoretically found that this double peak is a typical feature for the band structure of LiF due to crystal-field effects.[17,18] The splitting of 1.5 eV is in good agreement with our data. The present result is the first direct indication from the core level itself that alkali halides can be crystal-deposited on the semiconductor surface.

The LiF-crystalline film is nonepitaxial on the surface for initial monolayers and multilayers and charged up at higher depositions, as shown by the shift of the core-level peaks of the substrate and the overlayer. This behavior is similar to NaF. Both LiF and NaF crystals have a large mismatch to the GaAs crystal. Only after heating the sample did the diffuse LEED pattern change to a sharp 2×1 structure. This LEED pattern is still observable after F has been desorbed from the surface. We assume that during the annealing process LiF partially dissociates, and a reconstruction of the GaAs surface is induced. Another argument for the dissociation of LiF is the disappearance of the distinct double structure of the F 2*p* peak after heating, correlated with the increase of the intensity of the second F 2*p* peak at lower BE. Similar to RbF the appearance of the second F 2*p* peak and the broadening of the Ga 3*d* peak could be interpreted as a Ga—F bonding. In the case of LiF, however, the dissociated F atoms are bonded to Ga. One would expect that two Li 1*s* peaks could be observed, if dissociated and nondissociated LiF exists on the surface. Within our experimental resolution, we could not find such an additional peak for Li. The Li 1*s* peak shifts by 0.5 eV when the initial monolayer deposition of LiF is changed to the deposition where only Li is left on the surface.

The alkali fluorides LiF, NaF, KF, and RbF deposited on GaAs(100) show very different behavior with one another regarding their electronic properties for various coverages and after annealing the crystal. However, some general tendencies can be noted. Except for the initial monolayer of NaF, where Na and F are deposited separately on the surface, we found that the alkali fluorides are initially crystal-deposited on the surface. Of course, we could not decide, in the extreme submonolayer range, whether the alkali-metal and F atoms are separately or molecularly adsorbed, and whether at higher depositions a transition to a crystalline phase occurs or not, as reported for RbF on Ge(100).[10]

The interatomic distance between the F and alkali-metal atoms is longer in the case of the lattice than in the corresponding monomer or dimer, which can be observed in alkali fluoride vapor.[19] The lattice-constant change seems to have a strong influence on the electronic properties of the insulator-semiconductor interface. In the case of RbF and KF, where the mismatch to the GaAs lattice is very small and the overlayer is simultaneously desorbed for monolayers and multilayers, the observed differences in the core-level peak positions among various sample treatments are less than 0.6 eV, which is expected to be mainly due to the change in the charge density. Neither strong charging up of the overlayer nor band bending of the substrate for the multilayer could be observed. We assume that KF is islandlike epitaxially grown on GaAs, and RbF shows a direct interface bonding, as reported above.

LiF and NaF, with a large mismatch to GaAs, show a dissociation on the surface; NaF does for initial monolayer deposition and LiF does after annealing the sample. The polycrystalline multilayer of both species is strongly charged up. However, we think that the structure of the alkali fluoride overlayers on the surface depends very much on the preparation of these overlayers. A structure change of the overlayer can be easily induced due to the high reactivity of such strong ionic molecules.

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