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RbF/Ge(111) interface formation studied by LEED, XPS, and UPS

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The interface formation between rubidium fluoride (RbF) and the Ge(111)$c(2\times8)$ surface has been studied by low-energy electron diffraction, x-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy as a function of growth temperature. Three interface types have been identified. Sublimation of RbF at 750 K leads to a (3×1) symmetry with three domains induced by a chemisorbed submonolayer of Rb. An epitaxial RbF overlayer is observed at 500 K with rubidium bound to the substrate (F-Rb-Ge). Island growth mode is observed at room temperature. A disordered layer of RbF is then formed, with two types of interfacial bonding: Rb-F-Ge and F-Rb-Ge. The stability of the RbF film under the irradiation of various beams is also discussed. [S0163-1829(96)04128-8]

Because of their potential application in three-dimensional integrated circuits and other high-speed devices, epitaxially grown fluorides on semiconductors have been a subject of interest in recent decades. Most studies were performed with group-IIa-fluoride films on silicon,[1–3] and much less is known about the interfaces between other fluorides and silicon or other semiconductor surfaces.[4–7] Before novel devices can be developed and manufactured, several unsolved issues must be addressed, namely, interface roughness, epitaxial growth conditions, layer stability, interface reactions, and type of bonding in the fluoride/semiconductor interface region. Since all these problems are more or less related to the interface formation, surface analytical techniques, such as low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS), receive much attention in the study of fluoride films.

RbF crystallizes in the rocksalt structure with a lattice parameter of 5.65 Å. Since germanium has the diamond structure with a lattice parameter of 5.66 Å, the lattice mismatch between Ge and RbF surfaces with the same Miller indices is small (about 0.2%). The epitaxial growth of RbF(100)/Ge(100) and the interface interactions have been investigated by Konrad, Schug, and Steinmann,[6] who found, using core level photoelectron spectroscopy, that the Rb atoms bind on the top sites of the Ge surface whereas the F atoms adsorb in fourfold hollow sites.

In this paper we report on the interface formation between RbF and Ge(111) as a function of growth temperature and studied with a combination of LEED, XPS, and UPS. Three different interfaces are observed. In addition to confirming that the alkali-metal atoms bind to the germanium surface under epitaxial conditions (500 K), we find that a Rb submonolayer is chemisorbed at a growth temperature of 750 K, pointing towards a dissociative adsorption of RbF on Ge(111) at this substrate temperature. Moreover, another type of interfacial bond characterized by fluorine bound to the substrate is evidenced by photoemission spectra when the RbF film is deposited at room temperature (RT).

We will first examine the results of the LEED study for these three different substrate temperatures. Then we will discuss the XPS spectra in detail. At this point we will introduce a first model of the RbF/Ge interface, so that it will be easier to understand the UPS data.

The experimental setup combines two UHV chambers. The preparation chamber is equipped with LEED, a Knudsen cell, and a heating facility to control the substrate temperature during the film growth. The analysis chamber is equipped with an XPS system (Scienta ESCA-300) consisting of a rotating aluminum anode, a monochromator, and a high-efficiency electron spectrometer, as well as a He discharge lamp (Leybold) for UPS. The base pressure in these chambers was 1×10^{-9} and 1×10^{-10} mbar, respectively.

The Sb-doped (0.005 Ω cm) Ge(111) substrate was chemically degreased before introduction into the preparation chamber. A clean Ge(111) surface, characterized by a $c(2\times8)$ LEED pattern,[8] was obtained after several cycles of Ar^+-ion sputtering and annealing at 1000 K.

After thorough outgassing, the RbF powder (99.8% pure) was sublimated onto the Ge(111)$c(2\times8)$ substrate, from a Knudsen cell regulated to 1000 K. At this temperature, RbF sublimates in the molecular form with a deposition rate around 1 Å/min as monitored by a quartz oscillator. The deposition was carried out at various substrate temperatures. LEED, XPS, and UPS measurements were recorded after the sample was cooled down to RT.

The growth was first performed at RT. For a RbF coverage of 3 Å, corresponding to less than 1 monolayer (ML), no LEED spots were observed, which implies the formation of a disordered layer. The LEED pattern (not shown here) obtained for the same nominal amount of RbF deposited at a substrate temperature between RT and 400 K consisted of diffuse rings, indicating random rotations of crystalline domains around a common direction normal to the overlayer.

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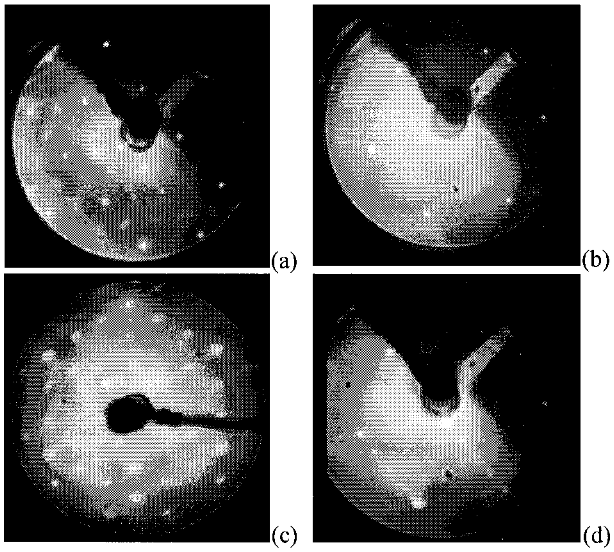

FIG. 1. LEED pictures of (a) the clean Ge(111)$c(2\times8)$, (b) epitaxial layer of RbF(111) on Ge(111), (c) Rb-terminated Ge(111) (3×1) surface symmetry with three domains, (d) (4×1) symmetry with three domains of Ge(111) after the annealing.

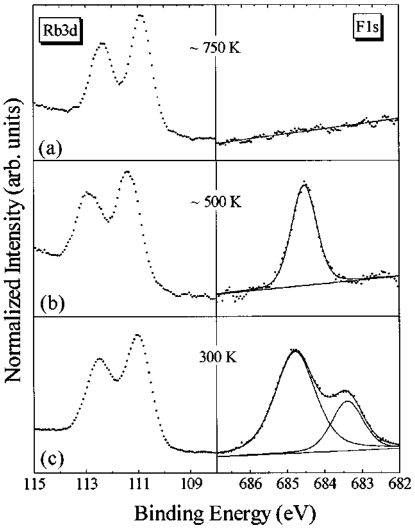

FIG. 2. XPS spectra of the Rb 3*d* (left panels) and F 1*s* (right panels) levels recorded at an electron emission angle of 75° for three typical growth temperatures of the films: (a) 750 K, (b) 500 K, and (c) room temperature. The thickness of films (b) and (c) is around $\frac{1}{10}$ ML.

For growth on a substrate near 450 K, each of these rings breaks into 12 short arcs, resulting from the formation of two domains with preferred orientations, rotated by 30°.

Figure 1 shows the LEED patterns for RbF deposition at various substrate temperatures, the LEED spots of the clean Ge(111)$c(2\times8)$ are depicted in Fig. 1(a) for comparison. For a substrate temperature of 500 K, a hexagonal LEED pattern is observed, indicating epitaxial growth. The recorded pattern was photographed with a very short exposure time since it degraded during the LEED observation. This implies that the epitaxial RbF film is not stable upon exposure to low-energy electrons. Deposition at a substrate temperature of 750 K results in a LEED pattern characteristic of a (3×1) symmetry surface with three domains [Fig. 1(c)], which remains stable under the electron beam. An exposure to a much higher RbF dose at the same substrate temperature has no influence on the LEED pattern. Figure 1(d) shows the effect of a postannealing at 750 K, which changes the (3×1) into a (4×1) symmetry.

According to these observations, we conclude that there are at least three types of RbF/Ge(111) interfaces, depending on the growth temperature: (1) a disordered interface formed for RT deposition, (2) an epitaxial RbF(111) layer grown at 500 K, and (3) a (3×1) or (4×1) surface symmetry with three domains for deposition at 750 K.

The films grown at these three specific substrate temperatures were then investigated in detail by photoelectron spectroscopies.

Hereafter, the zero of the binding energy scale will always be the Fermi level. XPS measurements of the Rb 3*d* and F 1*s* levels, recorded for depositions at three typical substrate temperatures, are plotted in Fig. 2. For the layer deposited at 750 K [panels (a)], only the Rb 3*d* doublet is observed with no appearance of the F 1*s* peak. This is interpreted as a dissociative adsorption of RbF on the Ge substrate. From the structural model of Ge(111)$c(2\times8)$,[9] we can see that there is only one-fourth of the atoms in the topmost layer in comparison with the bulk ones. It is most probable that these adatoms are the sites where the dissociative adsorption occurs. Since we observe a (3×1) LEED pattern, which can be explained by a (3×1) symmetry of the overlayer, we think that the amount of Rb adsorbed on this surface corresponds to less than 1 ML but we have no exact measure of the coverage.

Before investigating the peak positions in detail, it is important to note that reference photoemission spectra of the bulk RbF are very difficult to obtain. Since all fluorides are good insulators, the photoemission experiments and the data interpretation usually suffer from charging effects.[10] Using a flood gun to remove this surface charging cannot work because exposure of the fluoride surfaces to the electron beam modifies the chemical bonding.[11] In this study, we mainly focused on the initial growth stages where no charging effects appear.

For the Rb-terminated case, the Rb $3d_{5/2}$ peak is observed at 110.9 eV with a spin-orbit splitting of 1.49±0.01 eV between Rb $3d_{5/2}$ and Rb $3d_{3/2}$ peaks as obtained from a nonlinear least-squares fitting procedure. Since no shakeup structures, related with the plasma excitation of the free electrons,[12] appear in the Rb 3*d* spectrum, the Rb submonolayer is nonmetallic.

For the epitaxial RbF(111) layer deposited at 500 K [see panels (b) of Fig. 2], a single F 1*s* peak is observed at a binding energy of 684.6 eV. The Rb $3d_{5/2}$ peak is observed at 111.4 eV, which is about 0.5 eV higher than the rubidium in Rb-Ge bonding, due to the high electronegativity of the fluorine.

The RT deposition was performed at very low coverage to avoid the complication of multiple adsorption sites arising from steric effects at higher thickness. For a RbF film of around 0.25 Å, two distinct peaks are observed for the F 1*s* [see the right panel of Fig. 2(c)]: a dominant peak at 684.8 eV and a smaller one at 1.4 eV lower binding energy, indicating that a nonreported chemical state appears at this inter-

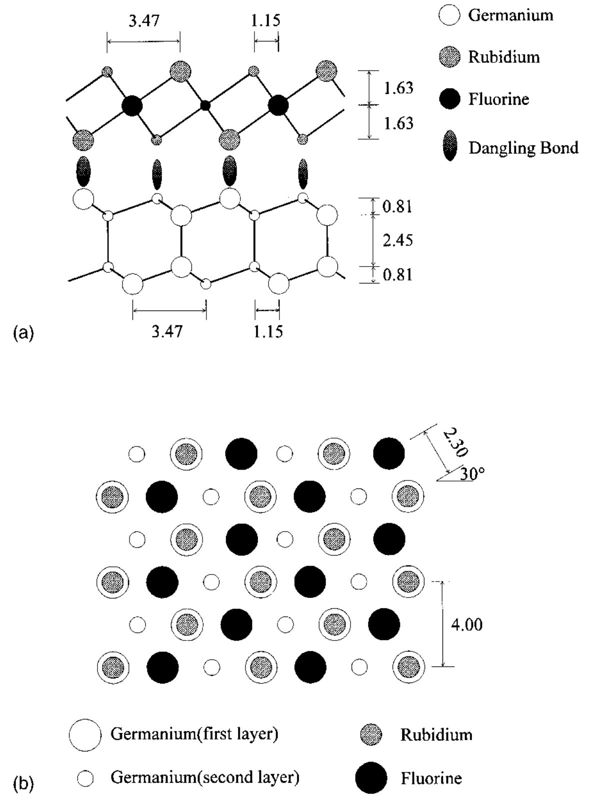

FIG. 3. (a) Side view of the RbF(111)/Ge(111) interface, where the atoms with larger size are in front; (b) top view of the RbF(111)/Ge(111) interface.

face. Since the mobility is significantly reduced at RT, RbF molecules are likely to be randomly distributed on the Ge(111) surface. We take the appearance of a second component as evidence for RbF adsorption with F bound to Ge; this introduces also a different site for Rb which can explain a downward shift of the Rb 3*d* binding energy at RT.

In the epitaxial conditions, we always observed a (1×1) LEED, even for very low coverage. It is thus reasonable to suppose that the deposition of RbF removes the $c(2\times8)$ reconstruction. This implies that the adatoms in the first layer of the Ge(111)$c(2\times8)$ surface are highly mobile around 500 K so that they could migrate to form additional Ge(111)-(1×1) islands at the interface. This high mobility was in fact observed for a temperature around 600 K at which an order-disorder phase transition occurs.[13] The RbF can perhaps act to reduce the temperature of this phase transition. In Figs. 3(b) and 3(c), we plotted the interfaces between RbF(111) and Ge(111) where we assumed that the RbF(111)/Ge(111) interface is abrupt. If this is the case, the Ge dangling bonds are perpendicular to the (111) surface, while the second layer of the hexagonal Ge lattice is 0.81 Å lower than the first one but shifted with respect to the first layer as shown in Fig. 3(a). We will suppose that Rb is adsorbed on the top site of the Ge, as has been suggested by Konrad, Schug, and Steinmann[6] for the (001) surface. Figure 3 shows a rocksalt structure on top of the Ge(111) atoms: the (111) cleave of a RbF lattice consists of alternate hexagonal layers of Rb and F separated by 1.63 Å. Although a RbF(111) surface can be terminated by either Rb or F atoms, it is hard to believe that there is a layer of F under the bound Rb because it would be too close to the second layer of Ge. Moreover, if one rotates the RbF lattice [Fig. 3(b)] by 30°, the F can sit either at the top or in the hollow sites of the Ge lattice, depending on the relative orientation of the RbF lattice with the Ge one, so that one should expect to see a chemical shift between these two positions. On the other hand, if the F atoms stay in the second layer of the RbF lattice, the rotation will have much less influence on the surrounding F, which is consistent with the fact that only one F 1*s* peak is visible.

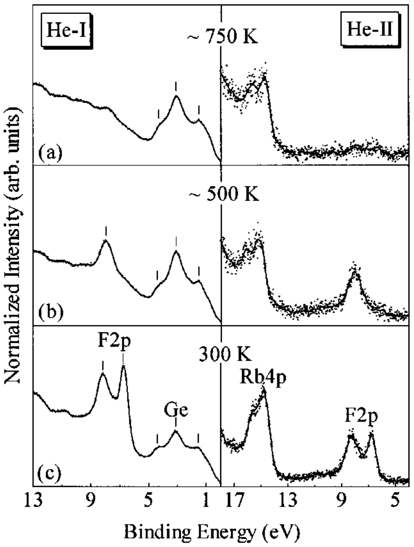

FIG. 4. He I (left panels) and He II (right panels) spectra of RbF films recorded at an electron emission angle of 40° for three typical growth temperatures of the films: (a) 750 K, (b) 500 K, and (c) room temperature. The thickness of the film (b) and (c) is around $\frac{1}{10}$ ML.

In order to collect more experimental evidence for a RbF species with F bound to Ge, we measured the Rb 4*p* and F 2*p* valence structures by UPS (Fig. 4). Because of the better signal-to-noise ratio, we will use the He I spectra to analyze the F 2*p* and valence bands of germanium. On the other hand, the Rb 4*p* level, with a binding energy near 15 eV, is superimposed on a huge secondary emission tail in the He I spectra and is thus better resolved in the He II spectra. As the spectral contribution of the Ge substrate is very weak, the He II spectra can be practically considered as the valence structure of the RbF.

UPS data confirm the conclusions from XPS: as seen in panels (a) of Fig. 4, for the film grown at 750 K, the Rb $4p_{3/2}$ valence structure appears at 14.7 eV. No F 2*p* states are observed, which indicates that, at this temperature, fluorine is dissociated and only rubidium sticks to the surface.

For the epitaxial RbF(111)/Ge(111) interface grown at 500 K [panels (b) of Fig. 4], a single F 2*p* peak around 8.0 eV and a Rb 4*p* doublet structure with the Rb $4p_{3/2}$ at 15.2 eV are seen. Comparing with the Rb-Ge bonding, it is 0.5 eV higher in binding energy, the same shift as was observed for the Rb 3*d*. This fact supports the above argument that this interface is terminated by Rb and all the F atoms stay in the second layer. As for the interface formed at RT, though the thickness of the RbF film is only 0.25 Å, an additional peak appears for the F 2*p* at 6.9 eV. This downward shift points again to a new interfacial bonding.

The initial growth stages at RT have been investigated

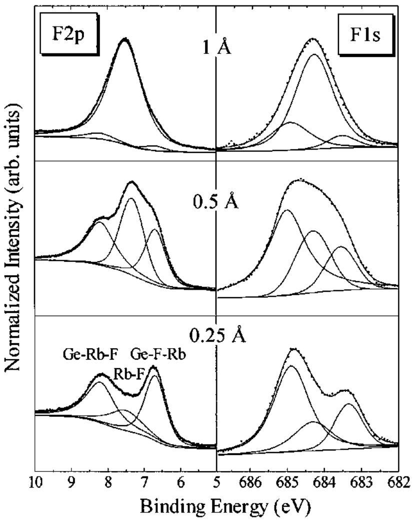

FIG. 5. He I spectra of the F 2*p* and XPS spectra of F 1*s* recorded from RbF films with different thickness grown at room temperature, where the dots are experimental data and solid lines are the results of a fit.

with different RbF thicknesses. Typical UPS (F 2*p*) and XPS (F 1*s*) spectra are plotted in Fig. 5. To fit the spectra from the 0.5-Å layer, it is necessary to introduce at least three components instead of the two we have used before in the case of the 0.25-Å film. Since there is only a small spin-orbit splitting of the F 2*p*, all the spectra of Fig. 5 can be fitted by three mixed Lorentzian-Gaussian peaks as plotted with solid lines. At a very low coverage of 0.25 Å, two peaks at 8.2 and 6.7 eV dominate the F 2*p* structure with a relatively small component at 7.5 eV. The intensities of these two dominating peaks are almost the same but the peak at higher binding energy is broader. Perhaps this can be explained by adsorption on different sites. With increasing coverage, the relative intensity of the middle peak increases rapidly, indicating that this is the ''bulk'' component. The peak at higher binding energy corresponds to the fluorine peak from F-Rb-Ge. The peak at lower binding energy can in this case be attributed to the Rb-F-Ge bond. The chemical shifts in this model are consistent with the Pauling electronegativity values. Meanwhile, the intensity of the other two peaks saturates very fast, judging from the intensity ratio between these two components and the valence structure of Ge below 5 eV (not shown), and their positions remain constant. From this, we can conclude that islands of RbF grow on Ge(111) at RT because the second layer appears before the saturation of the first ML.

It is important to ensure that the measurements induced no significant changes on the deposited layer. Therefore we exposed thin layers to UV and x rays during a period longer than the time of one set of measurements ($\approx$3 h) and we find the effect on the photoemission spectra to be negligible. On the other hand, the effect of low-energy electrons on RbF films is dramatic. By shining a flood gun (10 eV) on a RbF thick film for 1 h, the F 1*s* spectra shifted about 1.1 eV towards higher binding energy. In addition, a broadening of this peak is obvious and several components can be distinguished, testifying to the damage to the RbF bonding. Nevertheless, the area of the F 1*s* peak and the intensity ratio of this peak to the Rb 3*d* seems to be the same before and after the electron irradiation, suggesting that the electron only creates dissociation and defects in the RbF film but induces no desorption.

In conclusion, the formation of the interface between RbF and the Ge(111)$c(2\times8)$ surface has been studied by LEED, XPS, and UPS. Three typical interface structures are observed, depending on the substrate temperature during deposition. A submonolayer of Rb is formed at 750 K, an epitaxial film of RbF(111) grows on Ge(111) at 500 K, and a disordered layer of RbF forms at RT. For the 750-K deposition, a (3×1) adsorbate symmetry is observed due to chemisorption of Rb on Ge; this changes to a (4×1) adsorbate symmetry when part of the Rb atoms are desorbed. We confirmed previous results of interfacial bonding between epitaxial RbF on Ge, which is of the form of F-Rb-Ge. Moreover, we found it also possible to create interfacial bonds between fluorine and germanium when the interface is formed at RT. In this case, islands of RbF grow on the Ge(111) surface.

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