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Influence of Au overlayers on valence-band offsets for buried CaF_2/Si(111) interfaces

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High-resolution x-ray photoelectron spectroscopy has been used to characterize the electrical properties of Au/CaF_2/*p*-type Si(111). Our results show that the valence-band offset at the CaF_2/Si heterojunction varies with annealing temperature from 7.0 eV at 20 °C, to 7.7 eV at 700 °C, to 7.9 eV at 800 °C. Au deposition on (20–50)-Å CaF_2/Si interfaces produces an upward shift of the CaF_2 bands (from 0.8 to 1.3 eV), a corresponding Si band flattening (from 0 to 0.3 eV), and consequently, a large reduction of the valence-band offset at the buried interface (from 6.2 to 7.0 eV depending on annealing). The movement of the Fermi-level position at the Si surface and the variation of heterojunction band lineup correlate to the density of interface states and reflect charge redistribution and changes in dipoles at the interface.

The growth of epitaxial CaF_2 films on Si has attracted a great deal of attention because this system serves as a prototype for ionic-insulator–covalent-semiconductor interfaces and because it shows promise for applications in three-dimensional electronic devices. Various interface structural models have been proposed based on electron microscopy, ion channeling and backscattering, and photoelectron spectroscopy.[1-4] Recently, Phillips and coworkers[1] reported a reduction by 2 orders of magnitude of the density of interface states for a 250-nm thick CaF_2 film after a rapid thermal annealing to 1100 °C. Despite interesting studies, controversy remains about the electrical properties of the CaF_2/Si interface. In fact, the reported valence-band offset at this heterojunction ranges from 7.0 (Ref. 3) to 8.8 eV (Ref. 4).

In this paper we present a high-resolution x-ray photoemission study of the electronic structure of Au/CaF_2/*p*-type Si(111). The offset for the CaF_2/Si heterojunction varies with annealing temperature from 7.0 eV at 20 °C to 7.7 eV at 700 °C to 7.9 eV at 800 °C, and Au deposition alters the electrical properties at the buried CaF_2/Si interface by reducing the offset to 6.2, 6.8, and 7.0 eV, respectively. Our results indicate that the energy bands of sandwiched thin CaF_2 films remain spatially flat and the discontinuity of the vacuum level is accommodated by the buildup of dipoles at both interfaces. These studies provide new insight into the relationship between interface structure and band offsets for heterojunctions.

The x-ray-photoemission measurements were conducted using a Surface Science Instruments SSX-100 spectrometer with a monochromatized and focused Al *Ka* x-ray beam (spot size 300 μm) and a hemispherical analyzer (pass energy 25 eV). The full width at half maximum (FWHM) of Au $4f_{7/2}$ emission was 0.7 eV. Ultraviolet photoelectron spectroscopy and low-energy electron diffraction (LEED) studies were carried out in a separate chamber. Both chambers had base pressures of 8×10^{-11} Torr. Details of our experimental systems have been given elsewhere.[5]

Atomically clean *p*-type Si(111) wafer samples (~1 Ω cm) were prepared by cycles of Ar^+ bombardment and resistive annealing at 900 °C. Sharp 7×7 LEED patterns indicated that the surfaces were well reconstructed. Surface cleanliness was checked with Auger spectroscopy or photoemission. CaF_2 and Au were evaporated from W boats. LEED results for room temperature growth of thin CaF_2 films (20–50 Å) showed faded 1×1 spots with highly diffuse background indicating poor epitaxial quality. Post-growth annealing at 700 or 800 °C for 5 min resulted in well-ordered epitaxial CaF_2 overlayers on Si, as reflected by sharp 1×1 LEED patterns. CaF_2 film thicknesses were measured under room-temperature deposition conditions with quartz oscillators; they were reduced by thermal treatments because of partial evaporation of CaF_2 from the surface. No surface charging was observed.

To study the electronic structure and bonding character at the CaF_2/Si and Au/CaF_2 interfaces, we systematically examined the core-level (Si 2*p*, Ca 2*p*, Ca 3*p*, F 1*s*, and F 2*s*) and valence-band (VB) line shapes as a function of CaF_2 annealing temperature and Au coverage. The core-level energy distribution curves (EDC's) were analyzed using a curve-fitting program[5] to assess changes due to bonding and shifts due to band bending.

Line-shape analysis for room-temperature deposited CaF_2 revealed no variation in the Si $2p$ emission and only a single component in the CaF_2 core levels, suggesting CaF_2 growth on Si with minimal interaction. Annealing to 700 or 800 °C produced two small peaks at lower and higher binding energies with respect to the bulk Si $2p$ peak. Himpsel *et al.*[3] and Olmstead *et al.*[4] have suggested that they correspond to the Si atoms bonded to Ca and F at the interface, respectively. An interface component at -2.2 eV relative to the bulk peak was also evident in the Ca $2p$ EDC's, but no interface bonding features were discernible in the F core-level results, consistent with previous photoemission studies.[3,4]

To characterize the electrical properties of the heterojunction, we measured the valence-band offsets for CaF_2/Si as a function of annealing temperature. The results are summarized at the top of Fig. 1. In determining the offsets, the valence-band maximums (VBM's) were obtained by linear extrapolation of the valence-band edges to zero intensity. For the clean Si(111)-7×7 surfaces, because of the long inelastic mean free path of photoelectrons with kinetic energy of $\sim$1480 eV, the accuracy of this method ($\sim$0.05 eV) was not severely affected by the small contribution of Si surface states near the Fermi level.[6] Indeed, the energy separation between the Fermi level and the VBM was found to be between 0.57 and 0.63 eV, in very good agreement with the value reported in the literature.[7]

For as-grown CaF_2, the VBM was 7.0 eV below that of Si. This offset increased to 7.7 and 7.9 eV when the system was annealed to 700 and 800 °C for 5 min, respectively. This remarkably large change clearly indicates the dependence on the preparation process. Indeed, previous studies have suggested that interface fluorine atoms can diffuse into the Si substrate or can evaporate during thermal annealing so that most of the Si atoms in the outer layer are bonded to Ca in an epistructure known as *B*-type.[1,4,8] Annealing of the room-temperature-grown CaF_2 thin films results in higher crystal quality and a large reduction of interface state density because of the removal of interface F atoms[1] (see below for further discussion). Therefore, the observed increase in the VB offset with increased CaF_2 annealing temperature suggests that a perfect heterojunction free of interface F and free of interface states would have an offset value greater than 7.9 eV and that the offset is sensitively influenced by interface disorder and interface structure.[3,4] It is interesting to note that annealing had very little effect on the position of E_F in the Si gap, probably because of different substrate doping or different growth processes compared to Ref. 3.

To study the evolution of the CaF_2 electronic structure, we investigated the effects of overlayer thickness on the heterojunction VB offsets. Interestingly, band discontinuities for nominal 20 and 50-Å CaF_2 films on Si annealed at 700 °C were identical and the core-level spectra of CaF_2 differed only in the relative contribution of interface components. Further, the linewidths of all the core levels did not change.

To examine the influence of metal overlayer growth on the buried insulator-semiconductor interface, we deposited increasing amounts of Au onto formed CaF_2/Si heterojunctions. As schematically shown in Fig. 2 for two model cases, the energy levels of the sandwiched thin CaF_2 film would be determined by the Au overlayer and the Si substrate. Two different structures could be obtained because

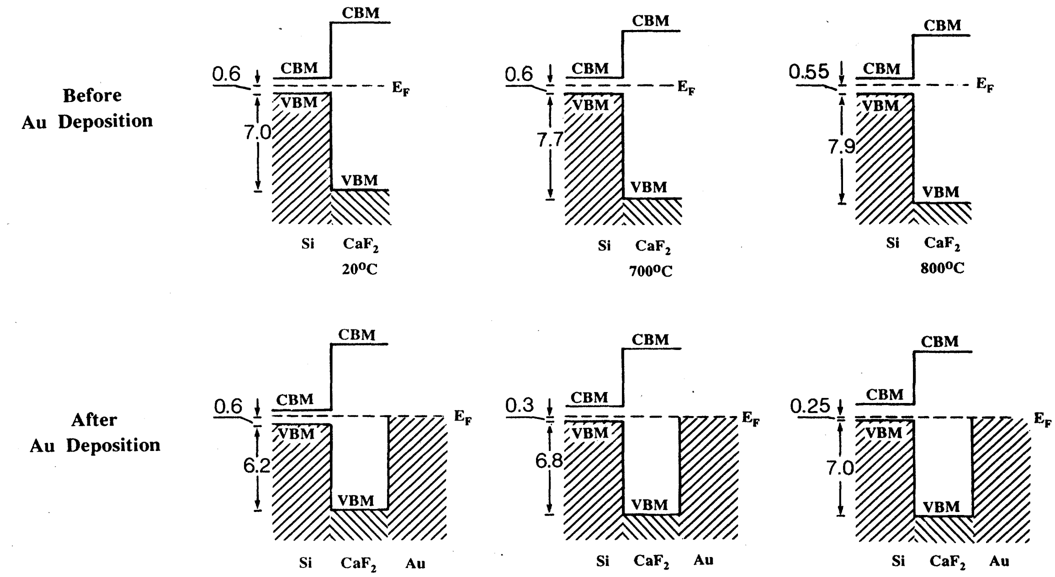
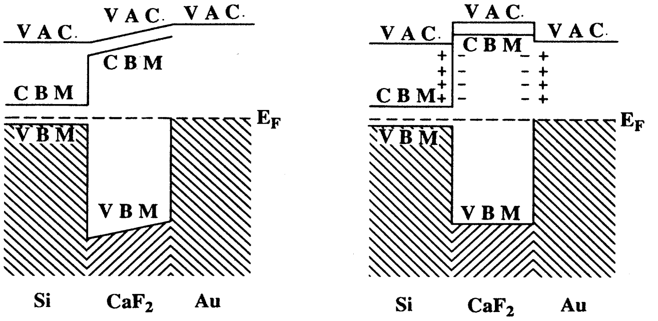


FIG. 1. Energy diagrams before and after Au deposition for CaF_2/Si heterojunctions annealed at 20, 700, and 800 °C. The influence of the Au overlayer on the band offset reflects charge redistribution and changes in the interface dipole at the buried CaF_2/Si interface. In particular, the presence of the metal layer alters the offset by up to 0.8 eV and leads to a band flattening of the Si surface of up to 0.3 eV.



(a) (b)

FIG. 2. Schematic energy levels for thin CaF$_2$ films, sandwiched between Au and Si. In case (a), the continuity of the vacuum level implies a nonuniform band bending across the CaF$_2$ layer which is not observed. Instead, our results show the presence of dipole layers at the interfaces to accommodate the discontinuity of the vacuum level, as shown in case (b). This condition is necessary to have flat bands for CaF$_2$. At the Au/CaF$_2$ interface a dipole layer may also be formed. The signs of interface dipoles are uncertain because the electron affinity of CaF$_2$ is unknown.

of the difference in work functions. In one case [Fig. 2(a)], the continuity of the vacuum level, E_{vac}, implies a spatially nonuniform band bending across the CaF$_2$ layer but this would introduce a directly observed broadening of the CaF$_2$ core levels. In the other case, a buildup, or a change, of the dipole layers at the interfaces [Fig. 2(b)] could accommodate the discontinuity of E_{vac} and provide the conditions necessary for CaF$_2$ to have flat bands with no increase of the core linewidth. In the absence of chemical interaction, it is straightforward to distinguish these two cases with photoemission measurements.

Our results show that Au adatoms induce rigid shifts in CaF$_2$ core-level binding energies but no changes in line shapes or linewidths. We conclude that their effect is to shift the CaF$_2$ bands while forming an abrupt interface without chemical reaction and that the energy bands of CaF$_2$ film are spatially flat over the thickness of 20–50 Å. Further, Au deposition results in the buildup of a dipole layer at the CaF$_2$/Si interface.

In Fig. 3 we show the movement of the Fermi-level position E_F relative to the VBM of CaF$_2$ and Si as a function of Au coverage for 20–50 Å CaF$_2$ films annealed at 20, 700, and 800 °C. The relative changes of E_F-E_{VBM} were obtained from the constituent-element core-level binding energies. These results show that the CaF$_2$ bands shift upward as the Au overlayer evolves (up to 1.3 eV). Simultaneously, the underlying Si substrate also undergoes a surface-band flattening (for a p-type sample) in the same direction (up to 0.3 eV). The difference between these curves gives the VB offset for the buried CaF$_2$/Si heterojunction, ΔE_{VBM}, as indicated. The energy diagrams presented at the bottom of Fig. 1 illustrate the formation of the Au/CaF$_2$ Schottky barrier and the effects of Au deposition on the band discontinuity at the buried CaF$_2$/Si interface for differently prepared CaF$_2$ thin films.

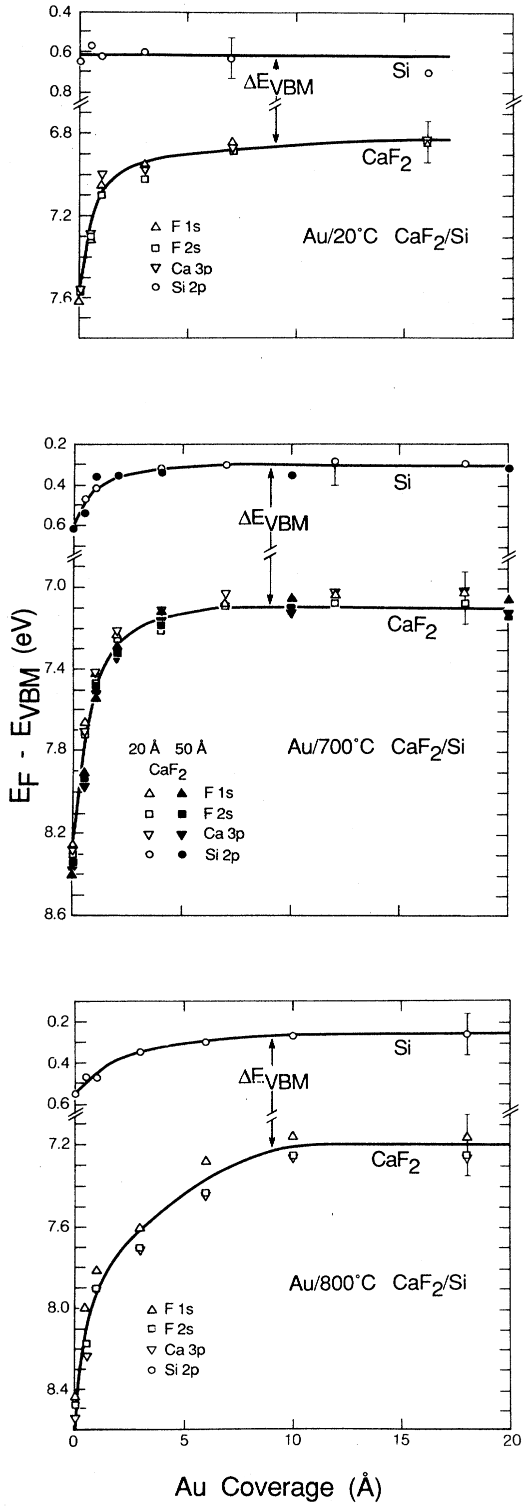


FIG. 3. Fermi-level positions in the Si and CaF$_2$ band gaps as a function of Au deposition for CaF$_2$ annealing temperatures of 20, 700, and 800 °C. The nominal CaF$_2$ thicknesses are 20, 20 and 50, and 40 Å, respectively. The difference directly gives the valence-band offset, ΔE_{VBM}, for the CaF$_2$/Si heterojunction. These results indicate the dramatic effect of the Au overlayer on the electrical properties at the buried CaF$_2$/Si interface.

They also show the Au-induced movement of E_F in the Si surface gap, an effect not observed for CaF_2 deposition (top of Fig. 1).

As can be clearly seen from Figs. 1 and 3, Au adatoms cause a large upward shift of the CaF_2 bands toward E_F. The shift is larger for better-ordered CaF_2 (1.3 eV at 800 °C vs 0.8 eV at 20 °C). We propose that this is due to the variation in the relative number of defects in the CaF_2 film and interface states created by CaF_2-Si bonding. For well-ordered ionic semiconductors or insulators such as CaF_2, the Schottky barrier height could be related to evolution of the metal surface work function of electronegativity and a dipole layer can also be formed at the Au/CaF_2 interface.[9]

For the buried CaF_2/Si interface, the Anderson electron affinity rule[10] predicts a constant band offset if both materials are bulklike, independent of the presence of a metal layer on the surface. In his interface dipole model, Tersoff[11] suggested that deviations in band lineup relative to that dictated by intrinsic properties of the constituent semiconductors would induce an interface dipole to screen such variations. More specifically, the upward shift of CaF_2 bands, $\Delta E_{\rm VBM}$ $(CaF_2)\cong 1.3$ eV, would induce a corresponding upward band flattening of Si so that the offset change would be within $\Delta E_{\rm VBM}(CaF_2)/\epsilon \cong 0.1$ eV, where $\epsilon \cong 9$ is the average of the static dielectric constants of Si and CaF_2. Such a nearly constant offset at the CaF_2/Si interface would imply the placement of the Si VBM above E_F, a situation which is physically very unlikely.

When the interface state density is very high, as for CaF_2 layers grown at 20 °C where unpaired electrons could be as many as 10^{14} cm^{-2}, any movement of the VB toward E_F would produce a large excess of interface charge and a giant interface dipole. Therefore, no change of E_F at the Si surface is expected. Indeed, our results in the upper panel of Fig. 3 show a constant E_F-$E_{\rm VBM}$ for Si during Au deposition, regardless of the ~0.8 eV band shift of CaF_2.

For annealed CaF_2/Si heterojunctions, the density of interface states is greatly reduced,[1] but not totally eliminated. The observation that better-ordered CaF_2/Si contacts have a larger offset and fewer interface states implies that the Tersoff dipole increases the offset. Therefore, the change of E_F-$E_{\rm VBM}$ in Si in response to the band shifting of CaF_2 upon Au deposition is a result of the balance between two dipoles with opposite sign. On the one hand, the Tersoff restoring dipole results from the further deviation of the band offset from the ideal value and tends to move the VBM of Si closer to E_F. On the other, emptying high-lying gap states of Si by reducing E_F-$E_{\rm VBM}$ results in excess interface charge and gives rise to another dipole which opposes such surface band bending. A total depopulation of the interface states, and thus a complete flattening of the Si bands (for *p*-type samples), is very unlikely. For a given CaF_2 band shift caused by Au deposition, charge redistribution occurs at the CaF_2/Si interface and the Fermi level readjusts to balance the two interface dipoles. The absolute magnitude of Si surface band bending depends inversely on the interface state density (see Figs. 1 and 3).

The spatial charge redistribution and a change of interface dipole at the buried CaF_2/Si interface upon Au deposition can be further inferred from the different binding energy shifts for the bulk and the interface Ca $2p_{3/2}$ components. Our results for annealed CaF_2/Si (not shown) indicate a shift in the interface bonding feature after Au deposition (0.5–0.6 eV) that is intermediate between those of the bulk Ca $2p_{3/2}$ (1.2–1.3 eV) and Si $2p_{3/2}$ (0.3 eV).

In conclusion, we have presented photoemission results of the electrical properties for Au/CaF_2/*p*-type Si. We have shown that metal deposition on 20–50-Å thin CaF_2 films causes a band shift in CaF_2 during the Schottky barrier formation but no band bending across the film, that the Fermi level at the Si surface also moves correspondingly, and that the VB offset at the buried CaF_2/Si interface can be dramatically changed. These results have demonstrated the critical role of density of interface states, charge redistribution, and change in interface dipoles in determining band discontinuity at the buried heterojunction.

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