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Band-offset formation in the *a*-Si/Si(111) homojunction by a CaF_2 intralayer

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We performed a photoemission study on the (*a*-Si)/Si(111) homojunction with a thin intralayer of calcium fluoride (one monolayer). The intralayer and the amorphous silicon were grown *in situ* on cleaved Si(111) single crystals. From the core-level analysis we found a valence-band discontinuity of 0.35 eV due to the electrostatic dipole induced by the intralayer ionic bonds. Our results show that the intralayer forms an abrupt interface with Si and that the overlayer valence band has a lower binding energy than the substrate one. This implies that the most probable interface configuration is Si(111)-Ca-F-(*a*-Si), confirming the results of previous works on the CaF_2/Si(111) interface.

INTRODUCTION

The great progress in device engineering made in the last years is strongly related to the basic research performed on the properties of heterojunctions. One of the most studied problems is the formation of band discontinuities and the possibility of their tuning to modify the transport properties of the heterojunctions. Several theoretical models[1-11] were developed to calculate the band offsets of semiconductor-semiconductor junctions and several experimental works have been performed to test these theoretical predictions.[10,12] Indeed, the possibility of modifying the band offsets by the introduction of thin intralayers of different materials between the two sides of the junction was demonstrated,[13-21] and this effect was explained with the formation of an electrostatic dipole at the interface.

We will show that a similar effect can be induced in a homojunction inserting, at the interface, a thin layer of a material composed by molecules that have an intrinsic dipole.

We used CaF_2 to create an intralayer in the (*a*-Si)/Si(111) homojunction. Calcium fluoride has a fluorite structure, with a 0.6% lattice mismatch with respect to Si, and it maintains a molecular form during the evaporation process. Indeed, CaF_2/Si(111) is an abrupt junction (see Refs. 22–28), eliminating the difficulties, in the interpretation of the results, arising from interdiffusion during the interface formation. The growing processes of CaF_2 on an Si substrate has been widely studied in recent years with several techniques.[22-28] Different models have been proposed to explain the Si-Ca and the Si-F bond configurations at the interface.[24-26,29] For substrate deposition temperatures higher than 500 °C, the Si(111) surface behaves as a catalyst for a dissociation reaction transforming a CaF_2 monolayer in a CaF monolayer. The interface has predominantly Si-Ca bonds with limited interaction of Si with F. Hereafter, for substrate temperatures higher than 500 °C, we will refer to CaF instead of CaF_2 intralayers.

From the Si 2*p* core-level analysis in the (*a*-Si)/CaF/Si(111) system, we found that the valence-band edge of the *a*-Si overlayer is at a lower binding energy than the substrate one, with a discontinuity of 0.35 eV.

We attribute the band offset to the polar character of the Ca-F bonds at the interface. The strong electronegativity difference between Ca and F causes the formation of the electrostatic dipole, oriented from calcium to fluorine. This result confirms the previous structural studies predicting a bond sequence Si(111)-Ca-F-(*a*-Si) at the interface.[29]

We point out that similar results were obtained by introducing a Ga-As double layer at a Ge homojunction[17] or an Al-P mono, double, and triple layer in an Si homojunction.[18] In the first case, for example, the insertion of a Ga-As bilayer by successive evaporations of the two atomic species gives rise to some uncertainty for possible intermixing processes. This last difficulty is completely ruled out in our case because of the growing process of CaF with the calcium atoms sticking on the silicon substrate and forming an ordered Ca-F bilayer.[25,26,29]

EXPERIMENT

Photoemission experiments were performed on systems obtained from successive depositions of CaF and Si on Si(111) samples. The Si substrates were *n* type, *S* doped, with a carrier concentration of 4×10^{18} cm^{-3} and cleaved in ultrahigh-vacuum conditions (base pressure 1×10^{-10} torr).

A monolayer nominal thickness[30] of CaF was thermally evaporated on the Si bulk, kept at a temperatures between 500 °C and 600 °C. Silicon overlayers, deposited on the above system kept at room temperature, were amorphous, *p* type.[31] In both cases, nominal thicknesses were measured with a quartz microbalance.

Core levels and valence-band spectra were taken using a Perkin-Elmer double-pass cylindrical mirror analyzer and the synchrotron radiation emitted from the "ADONE" storage ring at the Frascati National Research Laboratories. We obtained monochromatic light by a toroidal grating monochromator, with three different interchangeable gratings and an overall resolution of 0.2–0.3 eV.

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The core-level data were analyzed with computer least-square fits. Each Si 2*p* core-level peak was deconvolved in bulk, surface, and overlayer components. We used a convolution of a Gaussian and Lorentzian line shape for each component.

RESULTS AND DISCUSSION

In Fig. 1 we present our experimental Si 2*p* core levels taken on a clean Si(111) surface and on the same surface after calcium fluoride and *a*-Si deposition. The spectra of Fig. 1, normalized to the photon flux, are a combination of different Si 2*p* contributions and show a quite complicated evolution. While the clean cleaved Si spectrum contains bulk and surface contributions, the spectrum obtained after one monolayer of CaF deposition is the convolution of many Si 2*p* components: bulk, Ca-Si, and F-Si chemically shifted components. This spectrum shows a reduced intensity, is broader than the clean Si 2*p* contribution, and has an evident shoulder on the high kinetic-energy side. The two top spectra of Fig. 1 shift towards higher binding energies, and the peak intensity increases with an increase of the *a*-Si overlayer coverage. The shift, confirmed by a movement of the same amount and direction of the Ca 3*p*, Ca 3*s*, F 2*s*, and valence-band edge (not reported here), is probably due to a change in the work function of the system. The Si 2*p* overlayer core level is the dominant contribution in the spectrum taken after 15-Å *a*-Si deposition.

In Fig. 2, we see the best fits of the Si 2*p* spectra shown in Fig. 1. It is very well established[32,33] that the clean cleaved silicon has a surface reconstruction where the Si dangling bonds rearrange to form chains along the [110] direction. The atoms in the chains suffer a different charge transfer with respect to the bulk atoms and give rise to differently shifted 2*p* components. This is also the result of the best fit of the bottom spectrum of Fig. 2 (the parameters of the fit are reported in Table I), where surface shifted component 1 (SS1) and surface shifted component 2 (SS2) are the two surface doublets shifted in the opposite side with respect to the bulk doublet. In disagreement with the results reported in Ref. 33 we find a different intensity of the two SS1 and SS2 peaks which could be due to the presence of multidomains in the Si(111)2×1 surface reconstruction.

One monolayer of CaF transforms the 2×1 in 1×1 reconstruction and the best fit reported in Fig. 2 gives indications on the Si-Ca and Si-F interactions. In the best fit we still have a strong bulk component and two doublets, 0.35 and 0.9 eV higher and lower in kinetic energy than the bulk peak. Since in the electronegativity scale there is a large difference in going from Ca to Si and F, the two doublets can be easily attributed to Si-Ca at higher kinetic energy and Si-F at lower kinetic energy than the bulk feature. We point out that the Si-F doublet is very small, supporting previous conclusions[25,26] showing that the interface is mainly formed by Si-Ca bonds with Ca atoms placed on H_3 and T_4 interface sites.

Deposition of 8 Å of *a*-Si gives rise to the third spectrum from the bottom of Fig. 2. The Si 2*p* core level is

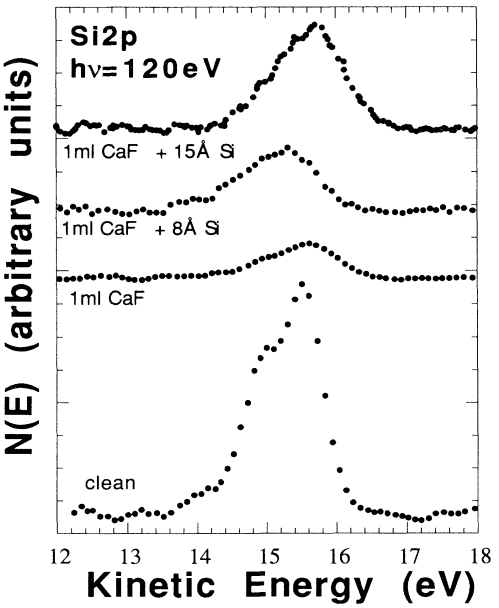

FIG. 1. Evolution of the Si 2*p* core levels taken at 120 eV for the clean cleaved Si(111) surface, and for the same surface after successive evaporations of one monolayer of CaF, 8 and 15 Å of *a*-Si.

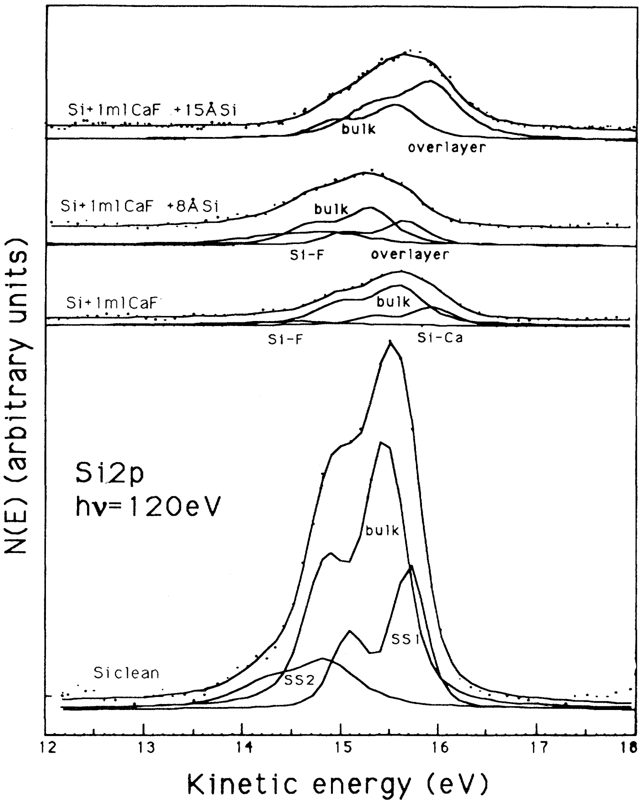

FIG. 2. Least-squares fits of the Si 2*p* core levels taking into account bulk, surface, and overlayer components. We used a convolution of Gaussian and Lorentzian line shapes for each doublet component.

TABLE I. Fit parameters for the first deconvolved spectrum of Fig. 2. FWHM denotes full width at half maximum.

	Spin-orbit	Branching ratio	Gaussian FWHM	Lorentzian FWHM
*SS*1	0.608	2.00	0.33	0.15
*SS*2	0.608	2.00	0.33	0.6
Bulk	0.608	2.00	0.33	0.29

again the convolution of three doublets. The broad peak at lower kinetic energy is still attributed to the Si-F interaction and the increasing intensity is due to the overlayer in the Si(111)-Ca-F-(a-Si) interface. The two other doublets are bulk and overlayer $2p$ components.

To discriminate between bulk and overlayer contributions we must consider the intensity evolution of both peaks with the increasing overlayer thickness. In the top spectrum of Fig. 2 (15-Å a-Si thickness) we see that the higher kinetic-energy doublet increases in intensity while the middle one decreases. The increasing intensity feature is attributed to the overlayer, while the decreasing one is attributed to the bulk. The two features maintain an energy separation of 0.35 eV.

In the top spectrum of Fig. 2 the Si-F component disappears, still demonstrating the abrupt character of the Ca-F intralayer and ruling out the possibility that the less bound $2p$ component could be attributed to an intermixed phase.

The splitting of the Si $2p$ core level into two components, one due to the Si substrate and the other to the a-Si overlayer, is an indication of the establishment of a band offset between the two sides of the Si homojunction. The 0.35-eV band offset reported in this work has to be compared with the 0.1-eV value found on the (a-Si)/Si(111) interface.[31] We point out that in Ref. 31 the results on interfaces, obtained by growing amorphous silicon (a-Si) on hydrogenated amorphous silicon (a-Si:H) or crystalline silicon [Si(111)] substrates, were predicting, in both cases, a valence-band maximum alignment, between substrate and overlayer, inside the experimental uncertainty (0.1 eV). This finding suggests that a-Si overlayer morphologies or doping level differences, induced by different Si-based substrates, do not play an important role in the establishment of a band offset.

In the interface under investigation, where we have a thin CaF epitaxial intralayer and the intermixing processes can be completely ruled out, the band-offset variation is more likely due to the intrinsic dipole created by the Ca-F intralayer species. Calcium and fluorine are in the opposite side of the electronegativity scale and a strong charge transfer between Ca and F occurs. The induced electrostatic dipole is directed from the Si(111) substrate to the a-Si overlayer determining the observed valence-band offset.

A rough evaluation of this dipole term can be done if we suppose that only Si-Ca bonds are present at the CaF/Si(111) interface. By a further schematization we consider the double junction Si(111)-CaF-Si as a sequence of planes of spheres representing the Si, the Ca, and the F atoms in the order Si-Ca-F-Si and we suppose that the electronic charge transfer occurs only between Ca and F planes.

The simple electronegativity approach, proposed by Sanderson,[13,34] allows us to evaluate this charge transfer by the equation

$$\rho_{\text{Ca-F}} = S_{\text{F}} - S_{\text{Ca}} / \Delta S_{\text{F}} \ ,$$

where $S_{\text{Ca,F}}$ are the Sanderson electronegativity values (1.22 and 5.75, respectively), and $\Delta S_{\text{F}} = 2.08 S_{\text{F}}{}^{1/2}$ is a normalization factor (Ref. 34). We obtained $\rho_{\text{Ca-F}} = 1.98$ electronic charges. The potential drop ΔV, occurring between the two planes, is $\Delta V = \sigma_{\text{Ca}} \rho_{\text{Ca-F}} e d / \varepsilon$, where σ_{Ca} is the density of Ca atoms at the interface with the substrate, e is the electron charge, d is the Ca-F bond length, and $\varepsilon = \varepsilon_0 \varepsilon_{\text{CaF}_2}$ is the relative dielectric constant of CaF_2 ($\varepsilon_{\text{CaF}_2} = 7.36$). We find a dipole term value $\Delta V = 1$ eV directed from calcium to fluorine. The 1-eV value is an upper limit with respect to the experimental value of 0.35 eV. In our experimental case, in fact, the substrate temperature during deposition was 500 °C–600 °C, determining a certain number of Si-F bonds and a reduction of σ_{Ca} used in the previous expression for ΔV. Indeed, we neglected the charge transfer from the overlayer and bulk Si atoms to the intralayer atoms, which is going to decrease the net charge transfer between Ca and F.

The above rough estimation indicates that one possible dipole term can explain the correct sign of the experimental band-offset change and gives an upper limit of the band offsets.

CONCLUSIONS

Performing the double interface (a-Si)/CaF/Si(111), we demonstrated the possibility of changing the band discontinuity of the (a-Si)/Si(111) homojunction. The band offset, 0.1 eV for the (a-Si)/Si case, becomes 0.35 eV for the new system. Since the overlayer valence band is found at lower binding energy than the substrate one, the interface dipole inducing the discontinuity is directed from the substrate to the overlayer. This is a complementary way to confirm previous structural studies.[25–27,29] that in our growing conditions, hypotize a Si(111)-Ca-F-(a-Si) interface configuration.

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