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Anomalous Au/Si barrier modification by a CaF_2 intralayer

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We show that a thin CaF_2 intralayer at the Au/Si(111) interface *increases* the Schottky barrier height, whereas all known growth properties of this intralayer would predict an interface dipole in the opposite direction. This unexpected result was obtained with internal photoemission and ultraviolet photoemission spectroscopy. Internal photoemission gave a Schottky barrier without intralayer of 0.81 ± 0.02 eV, in full agreement with other authors' results and confirmed by ultraviolet photoemission. After inserting the CaF_2 intralayer, we found with ultraviolet photoemission a barrier of 1.0 ± 0.1 eV, and a consistent internal photoemission-photocurrent threshold at 0.98 ± 0.02 eV.

I. INTRODUCTION

We found that a CaF_2 intralayer between gold and silicon modifies the Schottky barrier of this interface—an interesting possibility which could be used to tune the barrier to the specific need of specialized devices. If we consider only the CaF_2 intralayer acting as an interface dipole for the Au/CaF_2/Si system (positive on the Si side and negative on the Au one), the predicted Schottky barrier value Φ_B is lower than the Au/Si one. Our ultraviolet photoemission and internal photoemission measurements agree in finding an *increase* of the barrier height. This clearly shows that we have to take into account the intralayer interactions with the junction to explain the results. Our theoretical evaluations include the substrate-intralayer bonds and correctly predict the sign of the modification. The metal-induced gap-states theory could provide an alternate explanation.

Thin intralayers at semiconductor-semiconductor and metal-semiconductor interfaces are an effective way to modify and optimize the optical and transport properties of these junctions.[1-8] We investigated novel ways to control the barrier height of the prototypical gold-silicon interface, specifically by means of a CaF_2 intralayer. In order to avoid spurious results, the effects were investigated with two independent and complementary experimental techniques: ultraviolet photoemission spectroscopy (UPS) and internal photoemission (IPE). In the case of UPS, we took spectra during the first stages of formation of the interface, and evaluated the Schottky barrier height from valence-band edge and core-level energy positions. We then directly measured the Schottky barrier height of the fully formed interfaces by IPE.

The CaF_2/Si(111) interface was widely studied.[1,9-16] CaF_2 has a small lattice mismatch with Si(111) and its growth on this substrate is epitaxial at 700–800 °C; it evaporates in molecular form and forms an abrupt junction with Si. The Si(111) surface acts as a catalyst for the dissociation of CaF_2 into CaF+F, and the first layer of coverage is a CaF monolayer. The Si/CaF interface bonds are predominantly Si-Ca, producing a Si-Ca-F bond sequence.

Suppose now that an Au overlayer is deposited on the CaF intralayer: what is the resulting Au-Si Schottky barrier? Consider the Ca-F dipole: one would expect more positive charge on the calcium side, and therefore a dipole in the F-to-Ca direction. This approach would thus predict that the Schottky barrier Φ_B is lower than for Au/Si—a prediction in the *opposite direction* with respect to the experimental results. A more complete analysis of the interface dipoles suggests an explanation for this apparent paradox.

II. EXPERIMENT

IPE experiments were performed on Si(111) *n*-type wafers (3–7 Ω cm) cleaned in vacuum by annealing first at 600 °C to outgas and then at about 1100 °C for few seconds to obtain an ultraclean 7×7 reconstructed surface. The clean surface was subsequently covered with ≈ 2 ML (6–7 Å) of CaF_2 and 100 Å of Au.

Calcium fluoride films were deposited by thermal evaporation from polycrystals, keeping the Si substrate at 700–800 °C. The final 100 Å of Au were deposited at room temperature. A quartz microbalance monitored the layer's thickness. Ti contacts had been previously deposited on the back of the samples.

The IPE measurements were performed by illuminating the samples always from the Au side by a monochromatized chopped light in the 0.7–1.5-eV range. The photocurrent signal was amplified and lock-in detected. The estimated energy resolution is 0.02 eV. A more detailed description of the IPE apparatus was given elsewhere.[2] In order to test the reliability of the IPE mea-

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surements, we also studied the Au/Si(111) junction as a reference.

Similar samples were studied with the UPS technique at the Wisconsin Synchrotron Radiation Center on the 6-m toroidal grating monochromator beamline. We first studied the clean, reconstructed Si(111) surface. Then, we monitored the subsequent CaF_2 deposition by analyzing the Si 2*p*, the Ca 2*p* core levels taken at 140 eV, and the valence band at 60-eV photon energy. Approximately 2 ML of CaF_2 were deposited on the Si substrate heated at 700–800 °C.

Finally, we studied the room-temperature Au deposition by analyzing the Si 2*p*, Ca 2*p*, and Au 4*f* core levels taken at 140 eV. The overall energy resolution was about 100 meV. The Si 2*p* photoemission peaks were computer deconvolved into bulk, Si-Ca-, and Si-Au-reacted components. We used the convolution of a Gaussian and a Lorentzian line shape for each component. The fixed parameter used in the fit were the spin orbit (0.608 eV), the branching ratio (2), and the Gaussian full width at half maximum (FWHM) (0.2 eV). We best fitted the spectra by varying the Lorentzian FWHM and the energy position of each peak.

III. RESULTS

The IPE measurements consisted of illuminating the sample with monochromatic light and measuring the photocurrent.[2,8] The onsets of the photocurrent revealed the energy barriers of the system. The band diagram of Fig. 1 shows the possible optical transitions caused by the illumination of the Au/*n*-type Si(111) Schottky barrier.

The photoexcitation of the electrons from the metal to the semiconductor conduction band is revealed by the first threshold in the photocurrent, whose energy position corresponds to Φ_B. The Schottky barrier height was quantitatively derived by fitting the square root of the yield with a linear function, following the Fowler theory,[17]

$$\text{yield} \propto (h\nu - h\nu_0)^2 ,$$

where $h\nu_0 = \Phi_B$ is the photocurrent threshold.

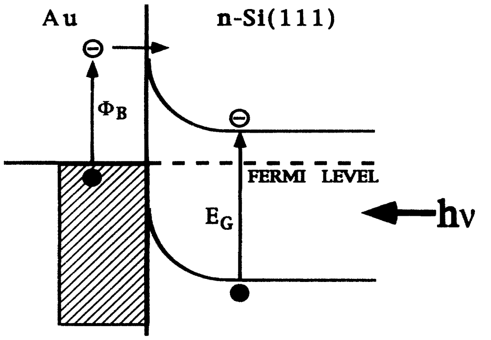

FIG. 1. Band diagram of the Au/*n*-type Si(111) Schottky barrier under illumination. The electron transitions that contribute to the photocurrent are schematically drawn and labeled as Φ_B (Schottky barrier height) and E_G (Si gap).

As the photon energy increases, we observe a second onset in the photoresponse, corresponding to the electron photoexcitation through the semiconductor energy gap E_G (see again Fig. 1).

Figure 2 reports the square root of the photocurrent yield versus the photon energy taken at 300 K for the 100-Å Au/*n*-type Si(111) Schottky barrier and for the 100-Å Au/2-ML CaF_2/*n*-type Si(111) system. For Au/Si(111) we derived $\Phi_B = 0.81 \pm 0.02$ eV, in full agreement with other authors' measurements.[18]

The insertion of 2 ML of CaF_2 at the 100-Å Au/Si(111) interface shifted the onset position to 0.98±0.02 eV. We therefore concluded that the intralayer increased the Schottky barrier height. Measurements at 77 K (to reduce the thermal noise) reproduced the 300-K results.

We also measured the samples under bias, to identify possible effects that can affect the data interpretation. We again found $\Phi_B = 0.98 \pm 0.02$ eV for the fully formed Au/2-ML CaF_2/*n*-type Si(111) system under −1- and 0.2-V bias. This ruled out possible mistakes in the Φ_B evaluation due to electrons tunneling across the barrier.

By increasing the forward polarization (Au side positive), we changed the photocurrent direction and reversed the Si band bending. The onset at 0.98 eV (as well as the onset at 0.81 eV in the Au/Si junction) disappeared because the electrons could flow from the Si to the Au side without encountering any potential barrier. This confirms that the measured thresholds are only due to the effects of the above interface barrier.

Some representative results of those obtained at the Wisconsin Synchrotron Radiation Center are reported in Figs. 3 and 4. In Fig. 3, we present the photoemission

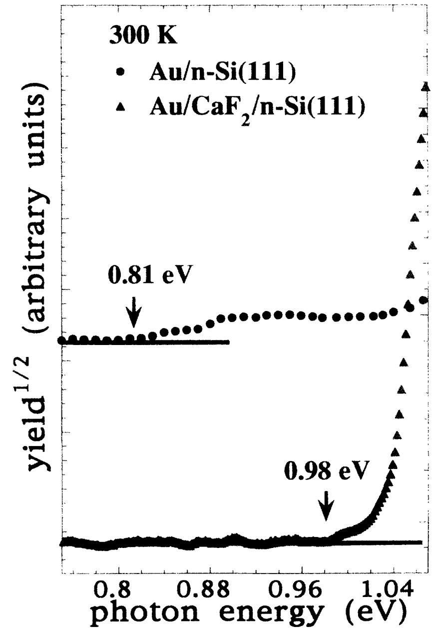

FIG. 2. Square root of the photocurrent yield vs photon energy for the Au/*n*-type Si(111) (dots) and the Au/2-ML CaF_2/*n*-type Si(111) (triangles) systems taken at room temperature. The onset positions obtained by a linear fit are marked.

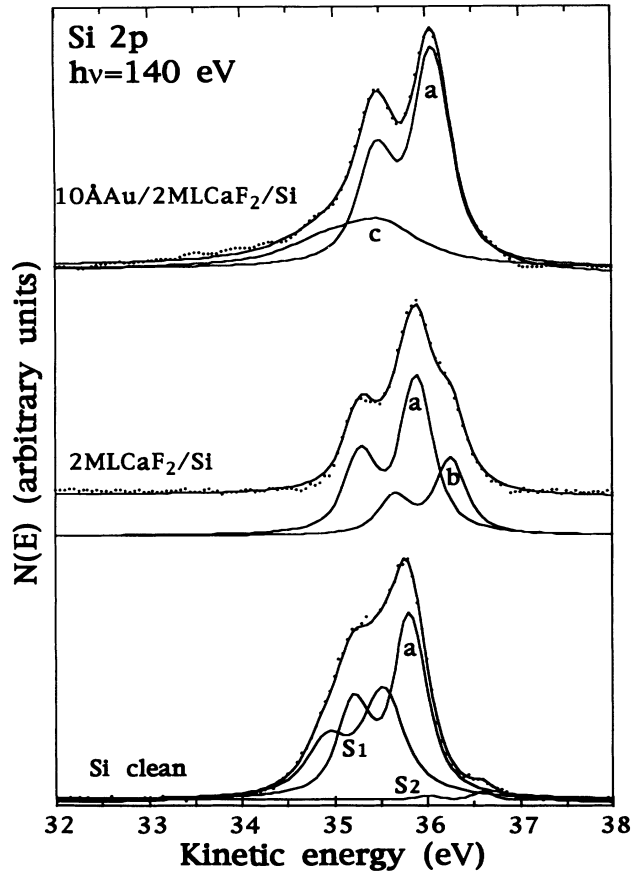

FIG. 3. Best fits of Si 2*p* core level from clean Si surface (lower), after 2 ML of CaF_2 deposition (middle) and after the Au evaporation (upper). The bulk component is labeled as "*a*." The surface doublets from the clean Si(111)-7×7 surface Si 2*p* fit are indicated as "S_1" and "S_2." The Si-Ca reacted peak is labeled as "*b*," and "*c*" is the Si-Au reacted component.

spectra of the Si 2*p* core level from the clean surface, after 2 ML of CaF_2 deposition, and after 10-Å gold deposition.

The annealing procedure performed on the Si(111) samples produces the 7×7 surface reconstruction as confirmed by the Si 2*p* line shape (Fig. 3, lower feature) deconvolved in three components. The clean surface of the Si(111)-7×7 has been widely studied[19] and the three fitted doublets are universally identified as the bulk (*a*) and the surface components (S_1 and S_2).

The CaF_2 deposited at 700–800 °C grows epitaxially on Si(111).[1,9–16] The interfacial bonds are mainly Si-Ca. The Si 2*p* peak presents two components after the CaF_2 deposition, the bulk (Fig. 3 middle feature, *a*) and the Si-Ca one (Fig. 3 middle feature, *b*) shifted at ≈0.4 eV higher kinetic energy than the bulk feature.[9–11]

The deconvolution best fit of the Si 2*p* core level after the 10-Å gold deposition on the CaF_2/Si system includes two components. We identified them as the bulk doublet (Fig. 3 upper spectrum, component *a*) and the Si-Au reacted doublet (Fig. 3 upper spectrum, component *c*). The latter was shifted by 0.6 eV to lower kinetic energies than the bulk doublet.[20]

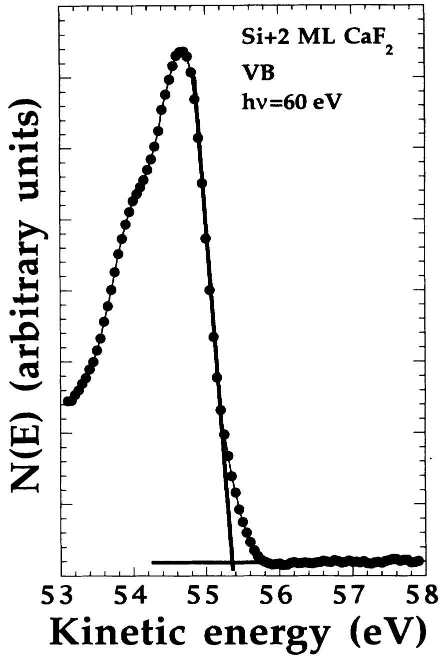

FIG. 4. Valence-band spectrum of the Si substrate after 2 ML of CaF_2 deposition taken at 60-eV photon energy.

The presence of the Si-Au reacted component indicates that the 2 ML of CaF_2 do not completely cover the Si surface. The atoms of the Si surface portions that are not covered by CaF_2 strongly react with the gold overlayer. This reaction is accompanied by Si outdiffusion, so that the signal from reacted Si is visible on top of the Au surface; for thick gold coverage, only the Si-Au reacted component is present in the Si 2*p* spectrum.

Recent scanning tunneling microscopy studies show that the 1 ML of CaF_2 coverage is not homogeneous on the Si substrate.[16] The CaF_2 islands are of the order of 1000 Å. This confirms our results.

The Si 2*p* bulk component itself shifts by $\Delta E_{\rm BB}=0.18$ eV to higher kinetic energy after the 10-Å Au deposition—where the symbol $\Delta E_{\rm BB}$ signifies the change in band bending. The valence-band edge position $E_{\rm VB}$ of the Si substrate after the 2-ML CaF_2 evaporation was derived from a linear fit of the edge data presented in Fig. 4.

We evaluated the Schottky barrier from the relation $\Phi_B=E_G-(E_F-E_{\rm VB})-\Delta E_{\rm BB}$, where E_G is the Si band gap at room temperature and E_F is the Fermi-level position. We found $\Phi_B=1.0\pm0.1$ eV in agreement with the IPE result.

We then analyzed the Au 4*f* core levels for the Au(10 Å)/Si and Au(10 Å)/2-ML CaF_2/Si systems, to obtain a second evaluation of the intralayer-induced Schottky barrier variation, $\Delta\Phi_B$. The Au 4*f* peak was deconvolved in bulk Au and reacted Au-Si doublets. We found that the reacted component was shifted to 0.6 eV lower kinetic energy with respect to the bulk doublet.[20] The Si 2*p* core level taken from the Au(10 Å)/Si junction was also deconvolved into Si bulk and Si-Au reacted components using the same fit parameters of Fig. 3, upper spectrum. We then calculated the energy distances between the bulk Si and bulk Au components with and without the CaF_2 intralayer. The difference between the two energy distances gives the Schottky barrier variation: we obtained $\Delta\Phi_B \approx 0.2$ eV, in agreement with the IPE value of 0.17 eV.

IV. DISCUSSION

The one-nominal-monolayer CaF_2 intralayer actually dissociates as CaF+F for a Si substrate temperature of 700–800 °C. The resulting CaF monolayer is spatially oriented, so that we can assume for the CaF/Si interface a bond sequence Si-Ca-F. The first interface layer is again CaF—producing the same bond sequence—also if more than one CaF_2 monolayer is deposited under the same conditions.

The strong electronegativity difference between Ca and F might suggest that the CaF intralayer acts as an electrostatic dipole, positive on the Si side and negative on the Au side. This would result in an intralayer-induced decrease of the Schottky barrier height.

The experimental results, however, rule out this possibility: we have seen that the CaF_2 intralayer *increases* the Schottky barrier by ≈ 0.2 eV. We can propose a very simple explanation of this apparent paradox.

We assumed that the interface dipole is mainly due to charge transfer between adjacent Si and Ca atoms. The resulting dipole is indeed negative on the Si side and positive on the Au/CaF_2 side, thus it increases the Schottky barrier. Recent x-ray diffraction studies[15] on CaF_2 overlayers on Si(111) conclude that the Si-Ca covalent bonds are stronger than the Ca-F ionic bonds. The CaF_2 overlayer is indeed still strained even for thick coverages, mirroring the Si(111)-(7×7) substrate lattice structure. This corroborates our interpretation based on a Si-Ca interaction stronger than the Ca-F interaction.

To roughly estimate the dipole, we considered the CaF/Si system as a plane capacitor and calculated the potential drop ΔV between the Si and CaF planes. The charge transfer on the Si after the formation of the CaF/Si system is obtained following the Sanderson-Carver approach[5,21]

$$\rho = \frac{(SR_{\mathrm{Si/CaF}} - SR_{\mathrm{Si}})}{\Delta SR_{\mathrm{Si}}} ,$$

where $SR_{\mathrm{Si/CaF}}$ and SR_{Si} are the Sanderson electronegativities or stability ratios[20] of the Si-(Ca-F) molecule and of the Si, and ΔSR_{Si} is a normalization factor. In our case $SR_{\mathrm{Si/CaF}}$ is

$$SR_{\mathrm{Si/CaF}} = (SR_{\mathrm{Si}} \sqrt{SR_{\mathrm{Ca}} SR_{\mathrm{F}}})^{1/2}$$

obtained considering the CaF as an independent molecule interacting with the Si atoms. We evaluated the potential drop from the equation

$$\Delta V = \frac{\sigma_{\mathrm{Si}} \rho e d}{\varepsilon} ,$$

where σ_{Si} is the Si(111) surface bonds density, e is the electronic charge, d is the Si-Ca distance and $\varepsilon = \varepsilon_0(\varepsilon_{\mathrm{Si}} + \varepsilon_{\mathrm{CaF}})/2$ is the mean relative dielectric constant of the Si/CaF system. We obtained an interfacial dipole $\Delta V = 0.1$ eV.

Realistically, we believe that this value should be considered as a lower limit since it ignores the screening effects of the Au overlayer. We tried to estimate the upper limit for the dipole by calculating the charge transfer from Ca to Si while ignoring the presence of F. The resulting ΔV is ≈ 1 eV. The experimental Schottky barrier variation falls between these two limits.

This is not, however, the only possible explanation for the results. One of the current dominant viewpoints on Schottky barriers is that the barrier height is dominated by a dipole due to the metallic screen from metal-induced gap states (MIGS), which pin the semiconductor E_F to maintain the local charge neutrality.[22] Under such a model, the Au/Si barrier is in the "pinned" limit, whereas the Au/CaF_2/Si is not as strongly pinned, but rather follows the original Mott-Schottky vacuum level matching system.[23] This model is also consistent with our results: the pinning induces the E_F near to the canonical midgap position in the Au/Si systems and gives a barrier substantially less than the difference between the large work function of Au (5.5 eV) and the electron affinity of Si (111)7×7 (≤ 4 eV). In the Au/CaF_2/Si case the addition of a thin insulating intralayer brings the barrier close to that associated with the vacuum levels alignment.

CONCLUSIONS

The results obtained with IPE and UPS show that the insertion of a thin CaF_2 intralayer (2 ML) increases the Au/Si(111) Schottky barrier of about 0.2 eV. Simple calculations based on the Sanderson electronegativity approach confirm the hypothesis of electron transfer from the CaF_2 intralayer to the Si substrate in agreement with the experimental data. The MIGS theory provides an alternate suitable explanation of the results.

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