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Surface photovoltage of Ag on Si(111)-7×7 by scanning tunneling microscopy

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Using a scanning tunneling microscope and light from a He-Ne laser, we have measured the surface photovoltage of the Si(111)-7×7 surface with coverages of Ag up to 1 monolayer. The data agree with a model for the photovoltage based on the recombination of photoexcited minority carriers with majority carriers thermally excited over the surface Schottky barrier. The surface Fermi-level positions derived from these data are consistent for n- and p-type Si decreasing from 0.60 eV above the valence-band maximum for the clean surface to 0.40 eV near 1 monolayer coverage. Although our photovoltage data are spatially resolved on an atomic scale, we have not observed any spatial variation in the photovoltage on the clean surface or on surfaces partially covered by Ag islands. This can be understood on the basis of the finite surface conductivity of the Si(111)-7×7 reconstruction.

Several research groups are currently exploring the influence of light on the operation of a scanning tunneling microscope (STM).[1–3] For STM experiments on the Si(111) (Ref. 4) and Si(001) (Ref. 5) surfaces, we have found that the dominant effect is the surface photovoltage: the change in band bending produced by photoexcited carriers. To better understand how changes in surface properties may influence the photovoltage, we have studied a simple metal-semiconductor interface. Ag on Si(111)-7×7 provides an experimentally convenient and well-characterized system for this study.[6] These experiments are also motivated by the recent rediscovery of photovoltage effects in x-ray photoemission studies of Schottky-barrier formation.[7–9]

In this connection, Hecht[10] has published a calculation predicting the size of this effect. Our study of the photovoltage as a function of Ag coverage on both n- and p-type Si supports the validity of Hecht's model.

Shining light on a semiconductor surface has long been known to produce a change in the potential of the surface[11] known as the surface photovoltage (SPV) effect. Surface electronic states with energies within the bulk band gap create band bending and a near surface region depleted of majority carriers. Electrons and holes produced by above-band-gap illumination diffuse to the surface and are separated by the built-in electric field of this depletion layer. The injection of minority carriers into the near surface region produces a reduction in band bending that we refer to as SPV.

Hecht[10] has modeled the SPV by equating the current of minority carriers produced by optical or x-ray excitation to a current of majority carriers flowing through the depletion layer. If the surface is the dominant site for recombination, the photocurrent density of minority carriers arriving at the surface $J_{\rm pc}$ is simply proportional to the flux of photons illuminating the sample. For the geometry of our experiment, $J_{\rm pc} \simeq 40P$ A cm^{-2} where P is the laser power in watts. Majority-carrier transport through the depletion region[12] $J_{\rm th} = J_0 \exp(qV/nkT)[1-\exp(-qV/kT)]$ includes a nonideality factor $n \geq 1$ that allows for deviations from the theory of thermionic emission. Setting $J_{\rm th} = J_{\rm pc}$ gives an expression for the change in the surface potential under illumination. In the small- and large-signal limits,

$$V = kT/q\ (J_{\rm pc}/J_0), \quad V \ll kT/q \tag{1}$$

$$V = nkT/q \ln(J_{\rm pc}/J_0), \quad V \gg kT/q\ . \tag{2}$$

The sensitivity of the surface potential to illumination is set by J_0 which is in turn exponentially dependent on the Schottky-barrier height ϕ_b, $J_0 = A^* T^2 \exp(-q\phi_b/kT)$. For Si, the value of A^* is $\simeq 30$ A cm^{-2} K^{-2} for holes and $\simeq 100$ A cm $^{-2}$ K^{-2} for electrons.[12] For n-type Si, ϕ_b is the difference in energy between the conduction-band minimum and the Fermi level measured at the surface. For p type, ϕ_b is the difference between the valence-band maximum and the Fermi level at the surface.

We perform all experiments at room temperature in ultrahigh vacuum (base pressure 1×10^{-10} Torr) using a STM similar to the one described by Demuth *et al.*[13] and commercial, polished wafers supplied by the Virginia Semiconductor (0.1 Ω cm As doped and 0.1 Ω cm B doped). Samples are cleaned with methanol before loading into the UHV chamber and then degassed for 8 h at 1030 K using resistive heating. Cleaning proceeds by successive flashes to increasingly higher temperatures ending with flashes to 1425 K for n-type Si and 1475 K for p type.[14]

Ag was evaporated from a bead on a resistively heated Mo filament. Coverage was measured by a commercial, quartz-crystal oscillator. After Ag deposition, we found that a clean Si surface could be regenerated by a single flash heating to 1425 K.

Light from a 10-mW He-Ne laser is modulated by an electro-optic crystal followed by a crossed polarizer. p-

polarized light, coarsely focused by a 75-mm focal length lens mounted outside the chamber, passes through a window and onto the tip-sample junction at an angle of 70° from the surface normal. The STM junction is approximately 2.5 cm behind the focal point of the lens giving a spot size of $\sim 0.3 \times 1$ mm.

We determine the SPV by a double modulation technique:[5] the tunneling current is modulated by periodic illumination from the laser and by a sinusoidal modulation $v = 30$ mV rms added to the sample bias. The rms amplitude of these current modulations are measured by separate lockin amplifiers; the two different frequencies of modulation are chosen to be outside the response of the feedback loop that controls the tip-sample separation. The bias-induced modulation of the tunneling current $\Delta I_{\rm bias}$ is proportional to the differential conductance $dI/dV = \Delta I_{\rm bias}/v$. The light-induced modulation of the tunneling current $\Delta I_{\rm light}$ measures the surface photovoltage SPV$= \pi/\sqrt{2}\Delta I_{\rm light}(dI/dV)^{-1}$. The factor $\pi/\sqrt{2}$ is needed to convert the rms value of $\Delta I_{\rm light}$ to the desired peak-to-peak amplitude of the square-wave modulation. This measurement scheme relies on the fact that for small changes in the surface potential the I-V curve can be locally approximated by a straight line, i.e., we can reliably measure the SPV only for values that are small compared to the average sample bias. This condition is met for the data reported here: the sample bias is in the range 1–1.6 V and the SPV is always < 150 mV.

For both n- and p-type Si, we observe that the sign of the SPV always corresponds to a decrease in band bending with illumination. Therefore, only the magnitude of the SPV is discussed below.

In Fig. 1 we show data for a clean Si surface with a few atomic-size defects. The top left image is the topography of this surface obtained at negative sample bias which probes the filled electronic states of the surface. At top right (b) is the differential conductance dI/dV measured simultaneously. At bottom left (c) is the modulation of the tunneling current $\Delta I_{\rm light}$ resulting from the square wave, on-off, modulation of light from the He-Ne laser. The fact that these two images are almost identical shows that the SPV is independent of position; dividing the $\Delta I_{\rm light}$ data by the dI/dV data gives the SPV image shown at bottom right (d). In this gray-scale representation of the SPV data the average value is shown as middle gray while deviations of -10% correspond to black and $+10\%$ to white; we use this highly compressed gray scale range to demonstrate the degree of precision in our measurement. (The atomic scale variations in the SPV data of ~ 1 mV are the result of some small systematic errors in the experimental method and should not be interpreted as true variations in the SPV.) We conclude that the SPV is independent of position within the unit cell and is unaffected by the atomic-size defects shown here.

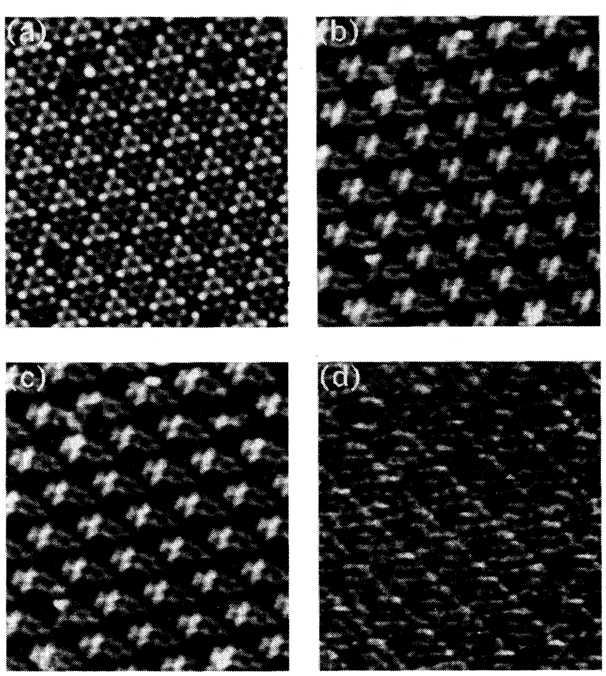

FIG. 1. (a) Topography, (b) differential conductance, (c) light-induced modulation of the tunneling current, and (d) surface photovoltage of the clean Si(111)-7×7 surface. Area 150×175 Å, sample bias -1.0 V, average tunneling current 0.25 nA, and laser power 50 μW. The average surface photovoltage is 35 mV and is shown as middle gray—gray scale is set to a total range of $\pm10\%$.

The results shown in Fig. 1 disagree with a recently published report[4] that found spatial variations of 5–10 % in the SPV measured within a defect-free unit cell of the Si(111)-7×7 and much larger variations at surface defects on a length scale of ~ 20 Å. Spatial variations in the SPV at surface defects were also observed by Kuk *et al.*[2] on a similar length scale of ~ 20 Å. The decrease in SPV at surface defects was attributed by both groups[2,4] to an increase in the recombination rate of photoexcited carriers at surface defects. Both of these efforts used a null technique to measure the position of the Fermi level at the surface; the sample bias was adjusted by a feedback loop to null the tunneling current. This null technique places stringent requirements on the electronic states of the probe tip and the surface because the gain of the feedback loop controlling the sample bias is proportional to the differential conductance at zero current. If some regions of the surface do not have any electronic states at the Fermi level, then extremely slow scanning speeds will be needed for the feedback loop to accurately measure the photovoltage. In this way, the SPV measurements at defects reported previously[2,4] may have been influenced by changes in the electronic structure of the surface at these sites. The double modulation technique that we use avoids these difficulties by operating at a bias voltage of 1–2 V where the tunneling conductance is larger, typically 2×10^{-10} Ω. We also stress that our technique gives data that are independent of the electronic structure of the probe tip; dI/dV and $\Delta I_{\rm light}$ can vary dramatically with changes in tip electronic structure but the ratio of these quantities, the SPV, does not.

Our SPV experiments on the Si(001) surface[5] show a

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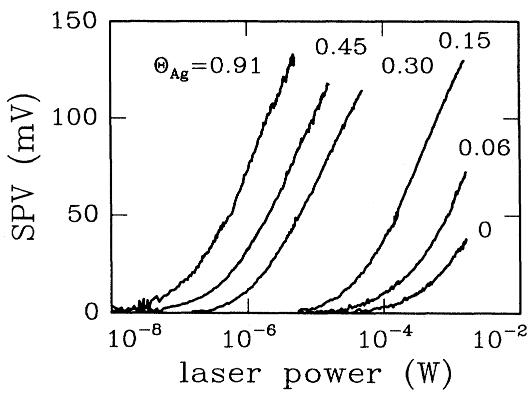

FIG. 2. Surface photovoltage (SPV) as a function of laser power and Ag coverage for n-type Si. Each curve is labeled by the Ag coverage in monolayers of Ag (1 monolayer Ag = 7.8×10^{14} atoms cm^{-2}).

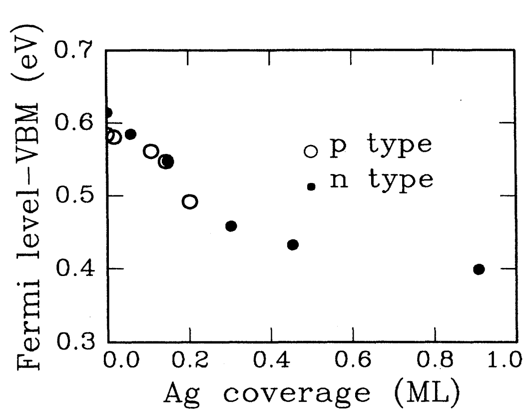

FIG. 3. Difference between the Fermi-level position at the surface and the valence-band maximum (VBM) from an analysis of the data using Eq. (1). On n-type Si silver was deposited with the sample at room temperature. Data for p-type Si was obtained on samples held at ~ 150 °C during deposition.

strong dependence on the tunneling current that can be used to measure charging of the surface electronic states by the tunneling current. In contrast, SPV data for the Si(111)-7×7 is independent of tunneling current up to the largest currents, 30 nA, we have attempted. The difference is likely due to the large density of surface electronic states on the Si(111)-7×7 that pin the Fermi level and make SPV insensitive to charging of the surface by the tunneling current.

To test the model of the SPV proposed by Hecht,[10] we have measured both n- and p-type Si for several coverages of Ag. Example data for n-type Si are shown in Fig. 2. (We are not able to measure the SPV at laser powers > 5 mW because of a competing modulation of the tunneling current resulting from thermal expansion of the probe tip.[5]) All curves are fit well by Eqs. (1) and (2) using two free parameters; J_0 is determined by fitting the small signal regime to Eq. (1) and n is determined from the large signal regime and Eq. (2). The nonideality factor n is consistently found to be greater than 1, typically in the range $1.1 < n < 1.3$.

The Fermi-level position at the surface can be directly inferred from the measured values of J_0 (see discussion above) and are plotted as Fig. 3. We obtain consistent results for n- and p-type samples. The Fermi-level positions shown in Fig. 3 are also consistent with core-level photoemission experiments.[6,15] We feel that the data shown in Figs. 2 and 3 support the validity of Hecht's model. Other models of the SPV (Refs. 11 and 17) lead to nearly the same functional dependence of the SPV on light intensity and Fermi-level position as Eqs. (1) and (2). The success of Hecht's model is in predicting the *magnitude* of the SPV given only the position of the Fermi level at the surface.

Although the SPV is an extremely sensitive function of Ag coverage (see Fig. 2), we have not observed any spatial variation of the SPV when the surface is covered with Ag. To increase the likelihood of observing these variations, we deposited Ag with the sample held at elevated temperatures. This procedure is known to produce separated Ag islands coexisting with clean Si(111)-7×7 reconstructions.[16] In this way, we can clearly compare SPV obtained on Ag islands to SPV of the bare Si(111)-7×7. Typical results of these experiments are shown in Fig. 4.

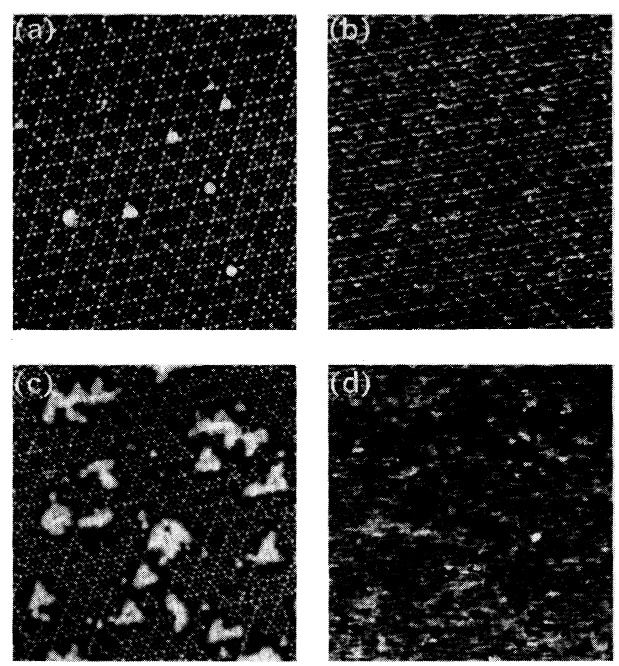

FIG. 4. (a) Topography and (b) SPV of p-type Si(111)-7×7 covered with 0.02 monolayers of Ag deposited with the sample held at ~ 150 ° C. Area 310 × 360 Å, bias −1.4 V; current 0.35 nA, and laser power 50 μW. Average SPV shown in (b) is 50 mV. (c) Topography and (d) SPV of p-type Si(111)-7×7 covered with 0.20 monolayers of Ag deposited with the sample at ~ 150 ° C. Area 360 × 400 Å, bias −1.6 V, current 0.30 nA, and laser power 500 μW. Average SPV shown in (d) is 25 mV. Gray scale images of the SPV, (b) and (d), have a black-to-white range of ±10%.

At a very low coverage of 0.02 monolayer of Ag [see Fig. 4(a)], Ag forms islands one-half the size of the Si(111)-7 × 7 unit cell. The average SPV of this surface is only ∼ 20% less sensitive to illumination than a clean surface [J_0 in Eq. (1) is smaller by ∼ 20%, a difference comparable to the variations we observe between different clean samples] but Fig. 4(b) shows that even directly over the Ag islands there is no change in the SPV. These data contradict the interpretation[2,4] that local changes in the recombination rate of carriers at the surface lead to spatial variations in the SPV. We expect that the Ag islands would introduce additional mid-gap electronic states that would increase the surface recombination rate yet we do not observe any localized changes in the SPV.

At a much higher coverage of 0.20 monolayer of Ag, the Ag islands have coalesced to form large patches of Ag separated by undisturbed regions of Si, see Fig. 4(c). At this coverage, the SPV is now 100 times less sensitive to illumination than the clean surface. [J_0 in Eq. (1) is 100 times smaller than for the clean surface.] The spatially resolved SPV is shown in Fig. 4(d); again, the SPV is independent of position.

One explanation for the absence of lateral variations in the SPV shown in Fig. 4 is that the lateral dimensions of the inhomogeneities are small compared to depth of the depletion layer. The scale of the inhomogeneities in Fig. 4(c) are ∼ 60 Å compared to a depletion layer depth of ∼ 300 Å for this 0.1-Ω cm *p*-type sample. We have tried to use more heavily doped Si to shrink the size of the depletion layer but unfortunately the SPV is strongly suppressed in this case. In heavily doped Si, majority carriers can tunnel through the surface Schottky barrier instead of being thermally excited over the barrier; tunneling leads to an enhanced rate of carrier recombination and suppressed photovoltage. We do find it intriguing, however, that even though these two length scales differ by only a factor of 5, the SPV is constant to within 10% (2 mV).

Another factor that could account for the negligible spatial variation in the SPV is that charge transport within the surface electronic states could act to short out potential differences created by the photoexcited carriers. Assume for the following argument that the photoexcited minority carriers (electrons) arrive chiefly at the clean Si(111)-7×7 (the areas with the largest band bending) and then must recombine at the surface with holes that are most prevalent at the Ag covered regions (the areas with the smallest Schottky barrier). This scenario requires a current to flow in the surface states between the clean and Ag covered regions. We can now estimate the size of this current: for the experiment shown in Figs. 4(c) and 4(d), using a current density of photoexcited electrons of ∼ 20 mA cm^{-2} (created by a laser intensity of 500 μW) and the length scale of inhomogeneities of 60 Å gives a current of 10^{-15} A. To sustain even a small potential drop of 0.1 mV between clean and Ag covered regions would require a surface resistance of at least 10^{11} Ω per square. This is an enormous value for the surface resistance considering that in electron-energy-loss spectroscopy experiments the Si(111)-7×7 behaves as a two-dimensional (2D) metal[18] and that even 2D metals that are amorphous typically have a resistance of only ∼ 10^4 Ω per square. Charge transport within the surface electronic states is a likely explanation of the lack of spatial variations in our SPV data.

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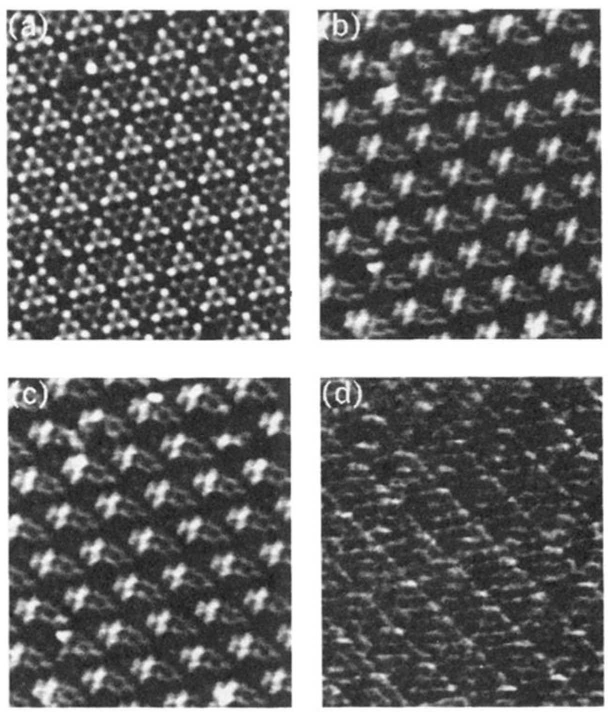

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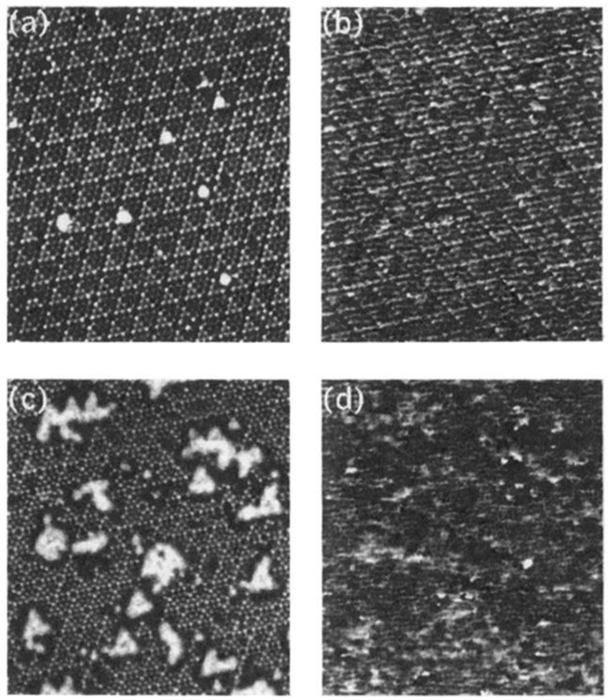

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