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Local Fermi-level pinning at a single adatom (Cs) or vacancy (As) on a GaAs(110) surface

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Local surface photovoltage imaging with a scanning tunneling microscope is used to demonstrate two types of local Fermi-level pinning next to a single adsorbate or defect, taking advantage of the tip-induced band bending due to the lack of gap states at clean GaAs(110) surfaces. The pinning energy at a single cesium adatom location was determined to be 0.56 ± 0.04 eV above the valence-band maximum (VBM), while for As vacancy, the Fermi level cannot go below the top of a filled surface state, 0.62 ± 0.04 eV above the VBM. [S0163-1829(99)51828-6]

An electric field from an external source, whether in metal-insulator-semiconductor devices, under a scanning tunneling microscope (STM) tip, or due to an adsorbed charged species, can penetrate a semiconductor surface, and depending on the surface-state density and doping level, gives rise to a subsurface band bending and a depletion layer. The degree of such band bending can also affect the cross section for photodesorption or photodissociation of adsorbed species: Photoexcited electrons can couple to the adsorbate by exciting a transient negative ion state, which decays back to a neutral with vibrational excitation that can lead to bond breaking.[1] This process is crucially dependent on the lifetime of the electron in the adsorbate. The lifetime, in turn, is dependent on the degree of band bending caused by the adsorbate's temporary charge, since it controls the adsorbate-substrate states' overlap. In this paper we use surface photovoltage (SPV) imaging with a scanning tunneling microscope (STM) to explore the effect of a single adatom and a single-missing-atom defect, at the otherwise surface-state-free GaAs(110) surface, on the *local* screening of an external field. In addition, we show that electric-field penetration provides us with a tool to characterize and measure the energy of a single surface state, in the zero-coverage limit where no surface analysis tool is applicable.

When semiconductors are illuminated with super-band-gap energy photons, photocarriers flood the subsurface depletion layer. A SPV, which equals the resulting reduction of the band bending, evolves between the illuminated surface and the back of the dark sample. Its value can tell us about the extent of the local subsurface band bending in the absence of illumination.

The first attempts to image SPV on a nanometer length scale with a scanning tunneling microscope were made by Hamers and Market[2] and Kuk *et al.*[3] on partially oxidized Si(111)7×7 surfaces, through current nulling potentiometry. Both groups noticed a strong reduction in the photovoltage on the 15–25 Å length scale, around certain points at the surface, which they attributed to a locally enhanced carrier recombination rate. However, atomically resolved SPV imaging of silver ($\leq$1 ML) on the Si(111)7×7 surface[4] and Si(111):Ge5×5 surfaces,[5] found the photovoltage to be uniform within 10 mV over a 100-Å range. In a recent paper,[6] where the tip was brought closer to the surface while nulling the current in order to improve the accuracy to ±2 mV, no local SPV change was detected next to potassium atoms on Si(111)7×7 surfaces either.

The surface states of clean Si(100)2×1 surfaces do not cover the whole bulk band gap, hence *I-V* curves taken with a STM exhibit zero current for a range of sample bias values: As a result, a current nulling technique is no longer usable and the SPV imaging has to be carried out under a finite surface-tip potential difference and a finite tunneling current. Imaging the photovoltage on a clean Si(100)2×1 surface[7] revealed the existence of local charging produced by the tunneling current, due to slow transport between surface and bulk electronic states, causing band bending under the apex of the tip. The surface charge, and thus the appearance of atomic-size features in SPV images, was shown to be enhanced while tunneling at the bonded, type-B atomic step and at specific point defects. When the tunneling current set-point was lowered, the SPV features disappear.[7,8]

The effect of the electric field between the tip and the sample, which is mainly dictated by the sample bias in respect to the tip, though also by the tip's shape (and/or composition), was demonstrated by McEllistrem *et al.*[8] on *n*- and *p*-type Si(111)7×7, Si(100)2×1, and H:Si(111) surfaces. It was shown that in the lack of surface states that are able to screen the field from the tip locally, tip-induced band bending can occur. Further, subnanometer SPV features were observed on top of adsorbed oxygen molecules at the ''metallic'' Si(111)7×7 surface; here, only when the tip was positioned above areas with reduced density of surface states could it affect the band bending. Except for a recent work, where a change in SPV within $<$20 nm range from a step on WS_2 in air (no atomic resolution) was reported,[9] no other SPV features that are caused by local band bending due to defects, adsorbates, or even subsurface dopants, were imaged.

By keeping the tunneling current sufficiently low, where the SPV is independent on the current set point, one can eliminate charging under the STM tip. On the other hand, the electric field-induced band bending, and how it is affected by possible localized Fermi-level pinning, is what we wish to explore. Figure 1 illustrates local pinning through a solution of the Poisson equation in cylindrical coordinates for a single two-electron localized surface state, on a ''smooth'' GaAs(110)-like surface (no surface states elsewhere): **r** is the

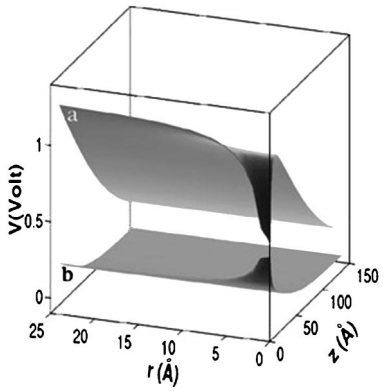

FIG. 1. A numerical solution of the Poisson equation, showing the electrical potential (V) as a function of the distance into the bulk (**z**) and the lateral distance (**r**) for a surface state (0.54 eV above VBM, at $\mathbf{r}=\mathbf{z}=0$) on a p-GaAs(110) surface, with tip bias of 2.5 V (a) and 0.3 V (b). See the text for details.

distance from the localized surface state parallel to the surface, and **z** is the distance into the p-GaAs-like bulk. The local density of the surface state was shaped as a Gaussian, centered at 0.56 eV above the valence-band maximum (VBM) with a full width at half maximum of 0.2 eV, and defined neutral when half filled (occupied with one electron). The single (two-electron) surface state was localized in a cylinder of 2-Å radius and 2-Å height at $\mathbf{r}=\mathbf{z}=0$. The tip-induced electric field was introduced through the positioning of a flat ''conductor'' at a bias of +2.5 V [Fig. 1(a)] or +0.3 V [Fig. 1(b)] in respect to the back of the GaAs sample ($\mathbf{z}=600$ Å), parallel to the sample surface and 12 Å away from it. At a lateral distance away from the localized surface state (large **r**), the electric potential increases (downward band bending) as **z** decreases, due to the penetration of the tip-induced electric field into the sample.[8] However, at $\mathbf{r}=0$, the Fermi level is locally pinned very close to the state's neutrality energy, thus keeping the degree of band bending nearly independent of the sample-tip bias.

When the surface recombination velocity of photocarriers is low, as at clean GaAs(110) surfaces, one can easily flatten the bands under super-band-gap illumination[10] and the SPV becomes a measure of the degree of band bending. Hence, it becomes possible to determine the energy of a surface state inside the band gap due to a single, atomic size defect or adsorbate that causes Fermi-level pinning locally; this can be easily and very reproducibly done by imaging the local SPV together with the topography at a few different tip-induced electric-field values.

The experiments were carried out in an ultra-high-vacuum chamber (1.0×10^{-10} Torr) equipped with a home built scanning tunneling microscope (STM, developed with the aid of Mezotronics), which was run using a commercial controller (RHK, model STM200). An in-vacuum low noise I-V converter (10 mV/nA), followed by a two-stage $\times100$ amplifier outside the vacuum chamber, allowed us to obtain stable atomically resolved images at tunneling currents as low as 10 pA. Imaging was obtained with an etched 0.25-mm-thick W-wire tip, whose apex was cleaned by radiative heating in vacuum. GaAs(100) wafers, [Zn-doped $\sim2\times10^{17}\,\mathrm{cm}^{-3}$, $(E_F-E_{\mathrm{VBM}})_{\mathrm{bulk}}=0.09\pm0.01$ eV] were cleaved in vacuum and placed 8 cm away from a Cs dispenser (SAES) through which current of 6 A was passed for 20 s (including warm-up time) during which the pressure rise was $\leqslant3\times10^{-11}$ Torr.

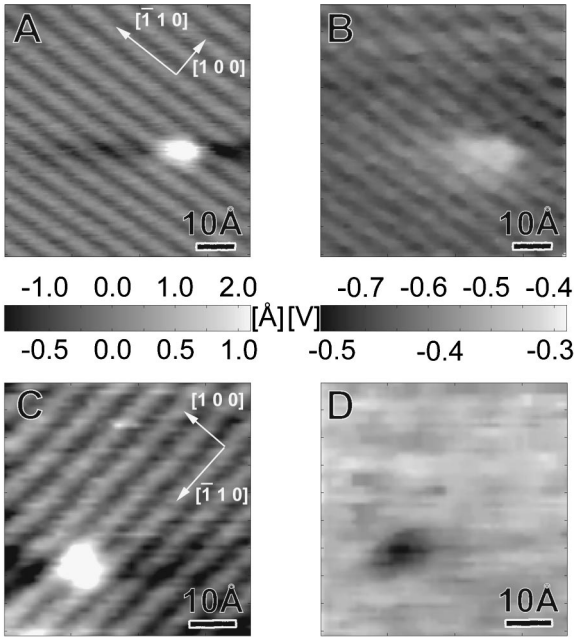

FIG. 2. CCT (a),(c) and the corresponding SPV [(b),(d), respectively] images, taken at $V_s=-2.5$ V ($I_{\mathrm{tun}}=29$ pA), of $<4\times10^{12}\,\mathrm{cm}^{-2}$ Cs/p-GaAs(110) surface. Images (a),(b) were taken with a sharper tip.

Local surface photovoltage (SPV) imaging was carried out with the STM, using a chopped light source in a similar manner to that described by McEllistrem *et al.*[8] A 20-mW continuous frequency-doubled Nd-YVO_4 laser (532 nm) was chopped with an acousto-optic modulator at 3–5 kHz and focused mildly at the sample-tip junction, yielding ~400 mW/cm^2 at the surface during light-on periods, and <1 mW/cm^2 during light-off periods (p polarization). Next, the sample bias was altered during the light-on period by a second feedback loop so as to compensate for the SPV and bring the tunneling current back to its value in the dark. Noise on the tunneling current due to capacitive coupling between the sample and the tip was minimized by feeding the inverted sample bias waveform to the tip through a 0.1-pF capacitor. Obviously, the current sampling windows were chosen to avoid the capacitive spikes due to the bias switching. The SPV value, which is the inverted bias modulation amplitude, was imaged simultaneously with the constant current topography (CCT) in the dark, and taken at both scan directions to check for artifacts due to possible insufficient speed of both feedback loops. The SPV reading remained unchanged when the light intensity was reduced by up to at least 25% of its operating value, indicating that the power used was sufficient to flatten the bands.

Figure 2 shows CCT [(a) and (c)] and the corresponding SPV [(b) and (d)] images of a p-GaAs(110) sample with single Cs adatoms at a coverage $<4\times10^{12}\,\mathrm{cm}^{-2}$. Often, the tip seemed to drag them along the chain direction. At higher coverages ($>2.5\times10^{13}\,\mathrm{cm}^{-2}$), we could observe Cs chains forming.[11] In this paper, we chose to concentrate on the isolated Cs atoms coverage regime. The images of Figs. 2(a) and 2(b) as well as Figs. 2(c) and 2(d) were taken at a sample

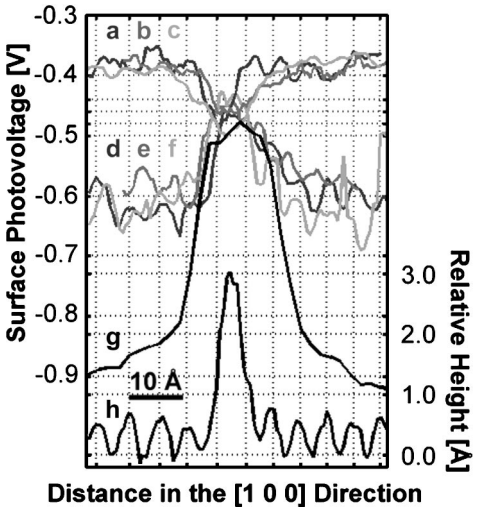

FIG. 3. Cross sections of the SPV images along the [100] direction around a single Cs adatom at the p-GaAs(110) sample, taken at (a),(b) $V_s=-1.8$ V ($I_{\mathrm{tun}}=36$ pA,) (c) $V_s=-2.5$ V ($I_{\mathrm{tun}}=29$ pA), (d) $V_s=-3.0$ V ($I_{\mathrm{tun}}=36$ pA), (e),(f) $V_s=-2.5$ V ($I_{\mathrm{tun}}=29$ pA), (g) $V_s=-3.6$ V ($I_{\mathrm{tun}}=18$ pA), (h) topography at $V_s=-2.5$ V.

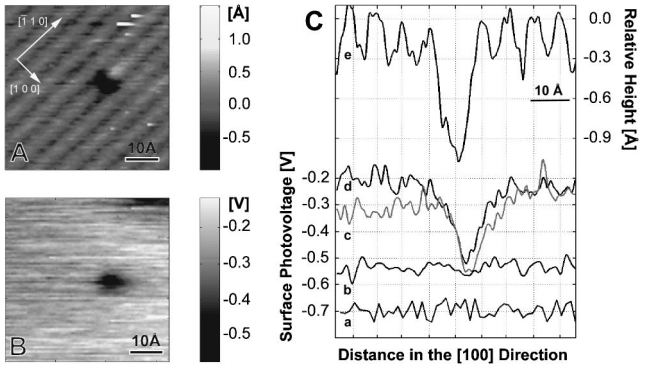

FIG. 4. Topography (a) and SPV images (b), taken simultaneously at $V_s=-2.8$ V ($I_{\mathrm{tun}}=25$ pA), around an As vacancy, and (c) cross sections in the SPV images along the [100] direction around V_{As}, taken at (a) $V_s=-3.5$ V ($I_{\mathrm{tun}}=29$ pA); (b) $V_s=-3.0$ V ($I_{\mathrm{tun}}=18$ pA); (c) $V_s=-2.5$ V ($I_{\mathrm{tun}}=29$ pA); (d) $V_s=-1.8$ V ($I_{\mathrm{tun}}=30$ pA); (e) $V_s<0$ topography.

bias of -2.5 V. However, because the tip had a different shape, the values of the SPV far from the Cs adatoms were different: A sharper tip in Figs. 2(a) and 2(b) gave rise to a higher SPV magnitude (b) and higher corrugation in the topography (a). At the Cs locations, the SPV had a maximum in (b) and a minimum in (d). Figure 3 shows cross sections of both the topography (h) and SPV images (a)–(g) of several scans, taken at different sample bias values or tip conditions, around a single Cs atom and along the [100] direction. For clarity, we present only low and high tip-induced field SPV traces, where on clean surface regions the SPV values were $\geqslant -0.4$ V [(a)–(c)] and $\leqslant -0.55$ V (d)–(g), respectively. Above the Cs adatom, traces (a)–(c) show a minimum at -0.48 ± 0.03 V while traces (d)–(g) show a maximum at -0.45 ± 0.03 V. These observations agree with the prediction in Fig. 1, i.e., with a surface state which is centered at about 0.47 eV above the flat bands Fermi-level energy (FBFLE), [$\sim$0.56 eV above the valence-band maximum (VBM)].

Detailed studies of Cs/GaAs(110) interfaces through core-level photoemission peak shifts showed an evolution of a strong downwards band bending on p-GaAs(110) surfaces at low coverages (0.8–1.0 eV at <0.1 ML at room temperature), while only little upwards band bending was observed on the n-type material:[12,13] Only at higher coverages (>1 ML) the Fermi-level position of both p- and n-GaAs approach the same pinning position, around 0.6 eV above the VBM. This asymmetry is interpreted as a consequence of the donor character of the alkali-metal atom: If positively charged at low coverages, the partially filled state in the energy gap will contribute to the screening of its charge, and the Fermi-level pinning energy will shift up within the state's energy width. Since we do not see a change in topography around the single Cs atom, as is evident for negatively charged oxygen on n-type GaAs(110) Ref. 14 [see Figs. 2(a) and 2(c)], we assume that the Cs adatom charge is screened by this state. Other photoemission experiments suggest that at coverages as low as $\sim$0.1 ML of Cs, a state is found at $\sim$0.35 eV above the VBM.[15] A clear Fermi-level pinning energy at about 0.35 eV above the VBM was observed for <0.05 ML Cs on n- and p-GaSb(110) surfaces.[16] A similar surface state at 1.6 eV above the VBM was detected at the GaP(110) surface for a similar Cs coverage.[17]

Note however, that the SPV absolute value at low tip-induced electric field [Figs. 3(a)–3(c)] was larger (more negative) by 0.04 ± 0.02 eV than the value at large field (e)–(h). We suggest that at higher fields, the positive tip ($V_s<0$) pushes the Cs atoms into the surface. If the Cs-induced surface state that causes the Fermi-level pinning is due to the interaction of the Cs 6s state with the Ga states (conduction-band surface resonances), the split between the resulting states will increase and the energy of the Cs-induced state in the gap will indeed shift down.

Arsenic vacancies (V_{As}) at (110) surfaces of p-type GaAs introduce a different type of Fermi-level pinning. They appear as dark spots at negative sample bias CCT images (of As-derived filled states), while at positive bias (Ga empty states) the nearest Ga atoms appear higher.[18] Recent calculations[19,20] showed that the surrounding Ga atoms may actually be slightly depressed, yet they appear higher due to additional vacancy-derived empty states above them. Figure 4 shows the CCT (a) and SPV (b) images at a sample bias of -2.8 V. Figure 4(c) shows several cross sections of the SPV images for different values of electric field at the tip-sample junction: As long as the SPV, due to the tip-induced band bending far away from the V_{As} site, is small in magnitude (SPV>-0.55V), the SPV value above the vacancy is pinned at -0.53 ± 0.03 V. However, a larger tip-induced field causes larger negative SPV that no longer shows Fermi-level pinning: This implies that the Fermi level is free to move from 0.53 ± 0.03 eV above the FBFLE and up due to the external electric fields. A filled state in the band gap, which has to remain filled to keep the surface neutral, and which extends below $\sim$0.62 eV above the VBM, will give rise to such an effect. Kim and Chelikowsky[20] indeed predicted a filled state that is centered at approximately 0.2 eV above the VBM, for an As vacancy which is $-1e$ charged (the charge required to maintain this ionic surface neutral). Note that the minimum in the SPV map does not coincide

precisely with the vacancy position, but occurs on the Ga atom chain where the dangling-bond states reside.

In conclusion, we used STM for imaging the local SPV at atomic resolution under various tip-induced band bending conditions to show the effective screening of external electric fields by a single adsorbate/defect-induced surface state. This effect turned out to be extremely instrumental in determining the local surface state occupancy and energy at surfaces that have no surface states in the bulk band gap when they are clean and perfect.

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