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The geometric and electronic structure of the ZnO(000$\bar{1}$) surface

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The scanning tunneling microscope has been used to examine the geometric and electronic structure of the ZnO(000$\bar{1}$) surface in ultrahigh-vacuum. Constant current images show that single crystal surfaces cleaned by vacuum annealing have numerous steps consisting mainly of (10$\bar{1}$0) and (11$\bar{2}$0) faces. Tunneling spectroscopy data demonstrate that spatially localized mid-gap electronic states are associated with these steps.

The reactions at transition metal oxide surfaces which underlie complex phenomena such as heterogeneous catalysis [1] and gas sensing [2] are strongly influenced by the geometric and electronic structure of the crystal's surface. The application of surface spectroscopies [3] and high resolution transmission electron microscopy [4] have provided the first insights into the structures of these surfaces, but the current information is still rather limited and many systems have not yet been investigated. Zinc oxide, the subject of this study, has several thermodynamically stable faces which are perhaps the most thoroughly studied transition metal oxide surfaces [5–9]. We have studied single crystal ZnO surfaces with the scanning tunneling microscope (STM), an instrument which has had enormous impact on the study of metal and covalently bonded semiconductor surfaces, but has been applied rather infrequently to ionic materials. This study has yielded a great deal of information including both real-space images of the microscopic surface structure and high spatial resolution tunneling spectroscopy of localized surface states at step edges. This Letter presents only results from the ZnO(000$\bar{1}$) surface, data from other faces and the effects of chemisorption will be discussed in a forthcoming paper [10].

The anisotropic etching of the ZnO(0001) and (000$\bar{1}$) faces was used to determine the polarity of the single crystal [5]. The oxygen terminated (0001) face was mechanically polished until there were no optically visible defects by sequentially reducing the size of abrasive alumina grinding media to 0.05 μm. After heating the sample in UHV at 600–700°C for 2 h, a hexagonally symmetric low energy electron diffraction (LEED) pattern was clearly observed and Auger electron spectroscopy (AES) indicated that the surface was free of carbon contamination. Previous work has indicated that such a treatment produces steps and facets on the surface [8].

The microscope consisted of a commercial STM head [11] contained in a UHV chamber and controlled by "home made" feedback electronics and software of conventional design. The mechanically formed Pt tip was "sharpened" in situ by applying a 90 V potential between the sample and tip and passing 1 μA of current for several minutes. The procedure had to be repeated periodically to maintain tip resolution and stability. The dependence of the tunneling current on sample-tip separation was used to gauge the integrity of the vacuum gap. Using the vacuum tunneling equa-

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tion, the apparent barrier height was determined to be 4.2 eV [12]. The images in this Letter were collected in the constant current mode using sample biases of -1.5 to -3.0 V and tunnel currents between 0.1 and 1.0 nA and are presented after the subtraction of a background plane which eliminates the tilt of the sample that would otherwise overwhelm small variations and make atomic features undetectable. Current–voltage (I–V) curves were acquired at pre-selected locations on the image during the scanning. When the tip reached one of the selected locations, the feedback loop was momentarily disabled and the current was recorded while the sample bias was ramped nearly from -3.0 to 3.0 V in less than 100 ms. After a brief stabilization interval, the process was repeated so that each spectrum is the average of ten sequential measurements. After the image was recorded, each I–V curve could be correlated to a specific point on the image. In each case, the dimensionless quantity $(\mathrm{d}I/\mathrm{d}V)/(I/V)$, which has been demonstrated to be related to the local density of states, was obtained by numerically differentiating the experimentally determined current [13]. Current data was disregarded when it fell below the level of 1 pA, which is near the detection limit of the sensor, and a straight, dashed line is substituted for the spectral data. This spectral region will be referred to as the apparent bandgap.

The constant current images of the ZnO(000$\bar{1}$) surface, shown in fig. 1, demonstrate that surfaces prepared by in situ annealing have a high density of surface steps. However, unannealed surfaces appeared even more disordered, presumably due to polishing damage. Atomically smooth flat areas

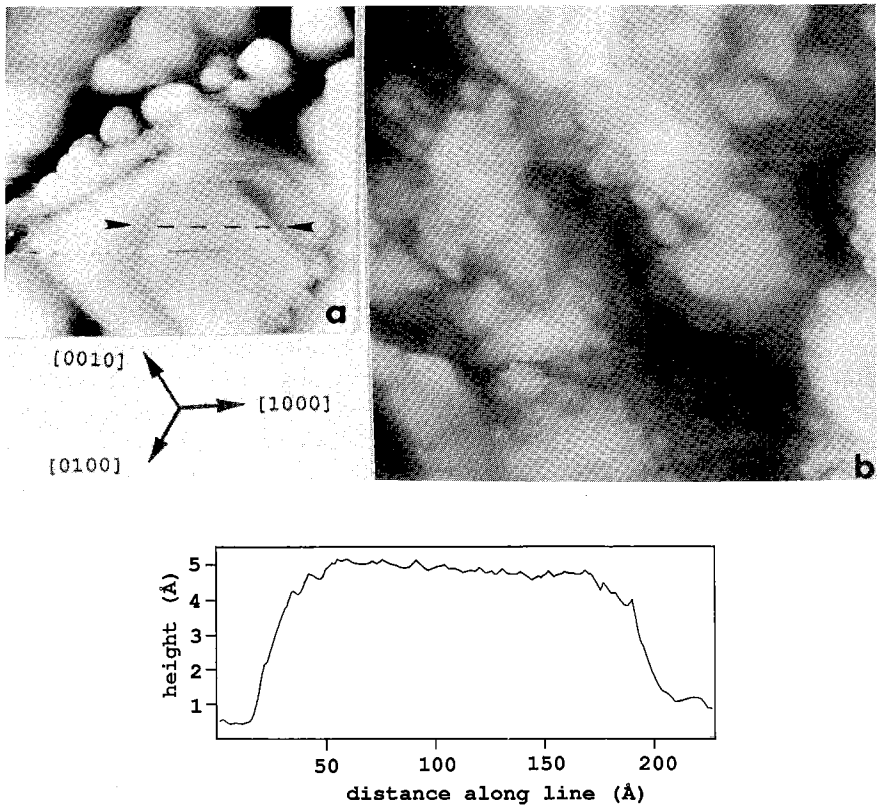

Fig. 1. (a) 766 Å × 766 Å image of the ZnO(000$\bar{1}$) surface acquired at -1.5 V sample bias and 0.3 nA tunnel current. The full scale displacement from black to white is 36 Å. The steps on the surface are oriented to form (10$\bar{1}$0) and (11$\bar{2}$0) faces. (b) 984 Å × 984 Å image of a different part of the surface shows the high step density on the surface. There is 50 Å of vertical resolution from black to white. (c) The topographic profile along the line indicated by the two arrows in (a).

are separated from one another by steps on the surface, which are predominantly aligned in the either the [10$\bar{1}$0] or [11$\bar{2}$0] direction. This is reasonable, since these are the nonpolar faces and are known to be thermodynamically stable [2]. Fig. 1c shows a profile of the topography across the large hexagonal plateau in the lower left part of fig. 1a. This plateau is formed by a step 5.21 Å in height, which agrees exactly with the ideal spacing between next nearest neighbor oxygen planes along the [0001] direction. Therefore, this step is exactly one unit cell in height and will be referred to as a single step.

We were not able to image the atomic structure of these surfaces, despite attaining a low signal to noise ratio. In fact, in all cases single steps such as the one shown in fig. 2 appeared rounded, their lateral extent being 15 to 30 Å. This unphysical rounding of the steps must be an artifact of the experiment and because it was observed reproducibly in numerous experiments with a variety of tips, we rule out the possibility that the resolution was tip-shape limited. Instead, we attribute the reduced resolution to the low conductivity of the sample. Flores and Garcia [14] have demonstrated that for poorly conducting samples ($\rho \sim 100$ Ω cm) the image resolution is space charge limited. This is in the range of the resistivity of intrinsic (not intentionally doped) ZnO crystals, such as the one used for this study [7]. We should remark, however, our success in imaging the atomic structure of the reduced titania(110) surface, a compound with a similar bandgap, suggests that it should be possible to obtain atomic resolution on a ZnO crystal with sufficient conductivity [15].

In the majority of the regions imaged, the average size of an atomically smooth area was approximately 100 Å in diameter (see fig. 1b), which implies that 0.7% of the atomic sites occur at edges. Spatially resolved tunneling spectroscopy was used to determine the effect of edge sites on the surface electronic properties. Fig. 2a shows gray-scale top view image of an 82 Å $\times$ 82 Å area of the ZnO surface containing a step which is oriented so that it forms a (11$\bar{2}$0) type face. One hundred tunneling spectra were acquired along the diagonal line which goes from the top left to lower right hand corner. Six of the tunneling spectra from this line are shown in figs. 2b–2g and a profile of the topography along this line is shown in fig. 2h. As the ledge is approached, a strong band appears at about -1.3 eV (see fig. 2c). This band apparently shifts to slightly lower energies, or is replaced by a related band, and eventually is centered at -1.75 eV (see figs. 2d–2f). Fig. 2i, which shows how the intensity of this band varies with position, clearly demonstrates that the band intensity peaks at the step and the state responsible for this band has a spatial extent of about 30 Å. This rather large "screeninglength" is in agreement with the estimate of the space charge limited resolution mentioned earlier.

Because of surface faceting, it is sometimes difficult to be certain which face has been imaged. However, based on larger images of the same area, we conclude that the relatively straight part of the topography in fig. 2h is a trace along the (000$\bar{1}$) plane (the tilt is a result of the plane subtract applied to the data) and that a series of steps are then encountered which are oriented to form a (11$\bar{2}$0)-type face. The initial increase in height near the center of fig. 2h is due to a double step (exactly two unit cell lengths) whereas the rest of the height change that occurs on the right side of the figure can be accounted for by two single steps separated by about 20 Å that are not individually resolved.

The features labeled E_V and E_C in figs. 2b and 2g are found consistently in the tunneling spectra and correspond to voltages where there is a dramatic increase in tunnel current. These features are separated by roughly 3 eV and are designated as the valence and conduction band edges, respectively. The fact that the Fermi level (zero bias) appears about 1 eV below the conduction band edge and some current is measured in the gap region is puzzling, since the tunneling spectrum of a 3.2 eV bandgap n-type semiconductor should show the Fermi level immediately below the conduction band edge followed by a roughly three volt bandgap as the bias is decreased to negative values [16]. In this case, the position of the Fermi level may be explained by the presence of some upward band bending and the current measured in the gap may be the result of disorder-induced surface states. Based on the AES results, we as-

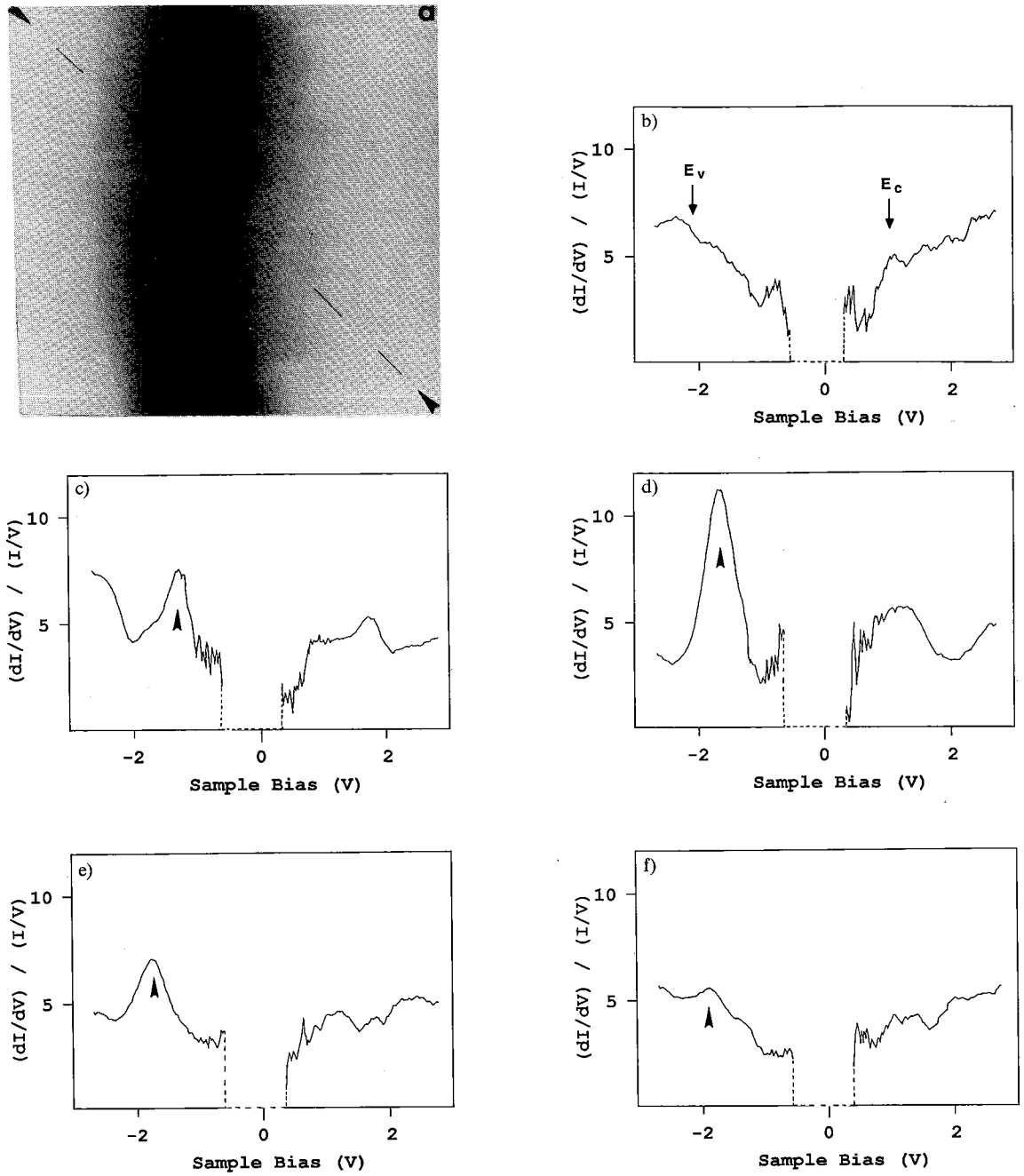

Fig. 2. (a) 82 Å × 82 Å image acquired at −3.0 V and 0.6 nA. 100 tunneling spectra were acquired along the line that goes from the upper left to the lower right corner. (b–g) six of the tunneling spectra. In (c–f), the state associated with the step is indicated by an arrow and in (b) and (g), the valence and conduction band edges are labeled E_V and E_C, repectively. The positions at which they were acquired are indicated in (h), where the topography along the diagonal line is shown. (i) The intensity of $(dI/dV)/(I/V)$, calculated from each tunneling spectrum at −1.3 V, is plotted as a function of position on the image. The intensity peaks at the step due to the associated localized state.

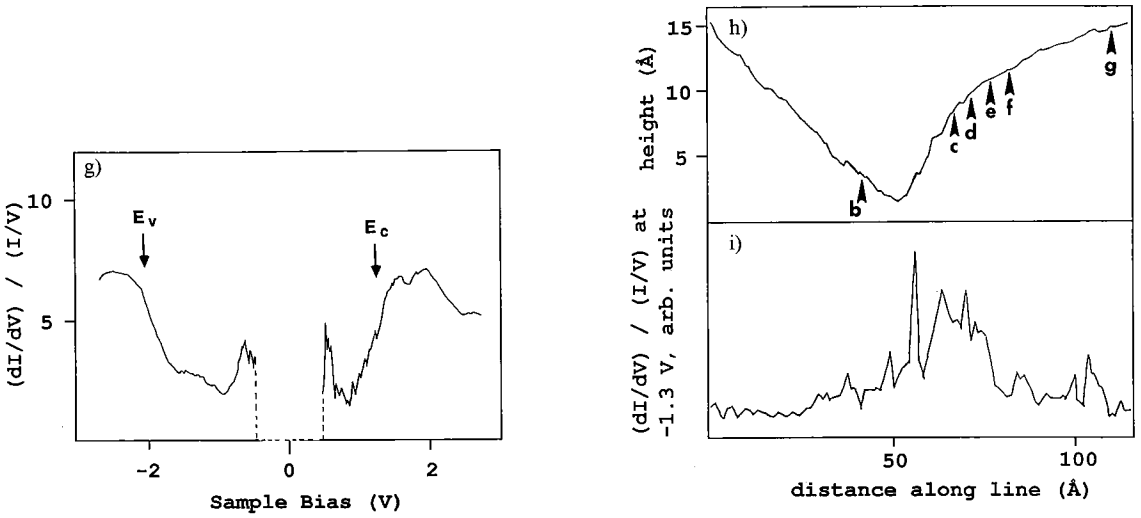

Fig. 2. Continued.

sume that this is structural disorder, although the influence of small amounts of surface contaminants can not be ruled out. Band bending on the order of several tenths of an eV has been noted in earlier studies of ZnO surfaces [17] and shifts in the positions of band edges have been noted in the tunneling spectra of other semiconductors [18]. The common and reproducible characteristics of the spectra from this surface, however, are represented by figs. 2b and 2g, which were acquired away from the step edge.

As the step edge is approached, a new occupied state appears below the Fermi level, its intensity grows and maximizes at the center of the step and then decreases as the tip moves away from the step. This state must be related to the different bonding configuration that occurs at the step. It is known that the three-fold coordination normally present at the surface does not create any mid-gap electronic states [9]. Therefore, this state might be associated with an atom in a lower coordination, or even an adsorbate, perhaps analogous to the chemisorbed O_2^- species which bond about 1 eV below the Fermi level on the (10$\bar{1}$0) surface [6]. We expect that such a species would be relatively unstable because of its reduced coordination and might, therefore, be a preferred reaction site.

Although the origin of these mid-gap states is not clear at this time, their detection is interesting because such states have not been observed by ultraviolet-photoelectron spectroscopy (UPS) experiments and are not predicted to exist on any of the perfect surfaces [2,9,19]. The very localized nature of STM measurements, the apparently large spatial extent of the state, and the fact that it was not detected at every ledge makes it impossible to accurately estimate the density of these states from the current data. However, it is possible to specify an upper limit of approximately $7 \times 10^{-12}/\text{cm}^2$ by assuming that one state is associated with each edge site. Considering this upper limit, which is almost certainly an overestimation, the absence of these states in UPS spectra is not surprising, since ZnO lattice imperfections with concentrations below 1/100 monolayer could not be detected [17]. For this reason, spatially resolved tunneling spectroscopy is the ideal technique to study these states, which are likely to influence the electronic properties and reactivity of the surface. We anticipate that ongoing experiments on crystals with different surface preparations and dopant concentrations will reveal the geometric configuration of the steps discussed here and thus allow the development of a more detailed model of the electronic states at these steps.

In conclusion, we have recorded the first images of a ZnO single crystal surface and found that crystals prepared by vacuum annealing have a

high density of surface steps and that there are mid-gap states associated with some of these steps. These states, which were not detected by previous UPS experiments, are likely to influence reactions which occur on these surfaces.

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