

Probing the surface chemistry of polycrystalline ZnO with scanning tunneling microscopy and tunneling spectroscopy

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Scanning tunneling microscopy and spatially resolved tunneling spectroscopy have been used to examine polycrystalline ZnO surfaces in ultrahigh vacuum after bake-out, after a low temperature anneal that cleaned the surface, after a high temperature anneal, which segregated bismuth to the surface, after being dosed with O₂ and H₂O, and after exposure to air. The tunneling spectra depend both on the proximity to structural features, such as grain boundaries, and on the chemical composition of the surface. For example, the segregation of bismuth to the surface causes the tunneling spectra to have a *p*-type rectification. Our results also indicate that the rectification of tunneling spectra acquired in air is caused by surface hydration and that images of surfaces that have not been heated in vacuum have inferior resolution due to a reduction in the height of the apparent tunnel barrier. Spatially resolved tunneling spectroscopy has been used to demonstrate that surface hydration has a greater effect on the crystallite surfaces than on the grain boundary surfaces.

I. INTRODUCTION

Although scanning tunneling microscopy (STM) and tunneling spectroscopy (TS) are potentially very powerful probes of the local structure and electronic properties of polycrystalline materials, studies of these materials have been rather limited.¹⁻⁹ Most previous work was carried out in air, or in vacuum without *in situ* surface preparation, conditions that make a reliable interpretation of images and spectroscopic data difficult. Even for a clean surface, spatial variations of the surface chemistry might be coupled to, or independent of, topographic variations. Recently we have attempted to resolve some of these problems by the simultaneous acquisition of spatially resolved tunneling spectroscopy data and current images from clean polycrystalline ZnO in ultrahigh vacuum (UHV).¹⁰ The detection of local variations in the electronic properties by TS allows the source of image contrast to be identified as geometric, electronic, or a combination of both. The goal of the present paper is to use the same spatially resolved tunneling spectroscopy technique to probe the surface chemistry of ZnO and, in light of our previous work, draw some general conclusions concerning the analysis polycrystalline samples by STM.

The ZnO sample used in this study was doped with cobalt, manganese, aluminum, and bismuth; components that are commonly added to commercial varistors to aid in sintering and enhance electrical properties. Several factors make this an excellent prototype system for testing the capability of STM analysis of polycrystalline materials. First, it can be synthesized as a relatively fine grained material (grain size = 5000 Å) so that there is a high density of interfacial regions that can be located with the STM. Second, it is well known that the segregation of bismuth to the grain boundary regions produces a chemically and electronically inhomogeneous material. The electrical inhomogeneity arises because the grain boundary regions possess a net negative charge that causes the formation of a space-charge region in

the vicinity of the grain boundary.¹¹ Third, ZnO surfaces are known to chemisorb gases from the atmosphere, which alter the surface electronic properties.¹² Our earlier work demonstrated that STM can be used to probe the electrical properties of grain boundary space-charge regions on clean surfaces and here we demonstrate that changes in surface chemistry caused by the segregation of impurities or adsorption of species from the gas phase can be detected by tunneling spectroscopy.

II. EXPERIMENTAL

Sintered ZnO with additions of 0.1 mole % MnO, 0.1 mole % CoO, 0.1 mole % Bi₂O₃, and 150 ppm Al₂O₃ was prepared by a previously described method.¹³ Wafers approximately 2 mm thick were cut with a diamond saw and then polished by sequentially reducing the size of abrasive diamond grit down to 0.25 μm. After ultrasonic cleaning with acetone and then ethanol, the sample was heated in air at 140 °C for 30 min and then at 500 °C for 30 min. Although the surface conductivity of the sample following this treatment was insufficient for tunneling in air, it increased to acceptable levels after evacuation and bake-out of the STM chamber. Samples were analyzed in this condition and after two different heat treatments. The first treatment is a 10–30 min anneal at approximately 400 °C to remove chemisorbed gases and the second treatment is a 30 min high temperature anneal (700 °C), which causes irreversible changes in the surface composition. In other experiments, analysis was carried out after O₂ or H₂O was introduced into the chamber.

The microscope, which is of a standard design and described elsewhere, was attached to an UHV chamber with a base pressure of less than 5 × 10⁻¹⁰ Torr.⁵ Mechanically formed Pt tips were cleaned by field emission or continuous scanning. Images were made in the constant current mode (0.2–5 nA) at -3 V sample bias and current-voltage (I-V) curves were acquired at preselected 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 linearly from -3.0 to 3.0 V in less than 100 msec. After a brief stabilization interval, the process was repeated so that the data for each location is the average of ten curves. After the image was recorded, each $I-V$ curve could be correlated to a specific point on the image. Differential spectra are not presented, since a comparison of $I-V$ curves acquired under the different conditions is sufficient to demonstrate the results. A more detailed discussion of the spectroscopy of clean ZnO surface is presented in Refs. 10 and 14. The dependence of the current on sample-tip separation was measured using an interrupted-feedback technique similar to the one used to acquire the $I-V$ curves. In this case, after disabling the feedback circuit, the tip was pulled several angstroms away and then ramped toward the sample while measuring the current and maintaining a constant bias. Auger electron spectroscopy (AES) was performed in a separate chamber following transfer of samples through the atmosphere. Although zinc oxide surfaces have been reported to be rather inert, this technique probably leads to an overestimation of contamination levels.¹⁵

III. RESULTS

Images of the polycrystalline ZnO surface was acquired in air, in UHV before and after the thermal treatments, after several minutes of exposure to O_2 or H_2O , in the 10^{-5} range, at a pressure of 1×10^{-2} Torr H_2O and, subsequently, in air. After several days exposure to the ambient atmosphere, however, a reduction in surface conductivity made imaging impossible. The most detailed images (see Fig. 1), which revealed surface steps approximately 5 Å in height, were acquired in UHV from samples, which were cleaned by a 400 °C anneal. Space-charge formation at the surface of these low conductivity samples limited the lateral resolution, preventing the observation of the atomic surface structure.

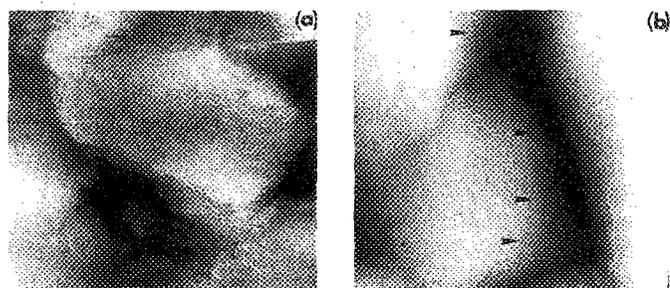


FIG. 1. Typical STM images of the polycrystalline ZnO surface. (a) $4950 \text{ \AA} \times 4950 \text{ \AA}$ gray-scale top view acquired at -2.75 V sample bias and 0.5 nA. This surface was cleaned with the 400 °C thermal treatment. (b) $5500 \text{ \AA} \times 5500 \text{ \AA}$ image acquired using similar parameters (current, bias, and feedback) in UHV before any attempt was made to clean the sample. The image shows less detail and the "streaky" sloped area indicated by the black arrows occurs because of the tip's inability to respond quickly enough to the rapidly changing topography of the sample surface, due, in part, to the reduced gain of the tunnel junction under these conditions.

The tunnel current depended only weakly on sample-tip separation following evacuation and bake-out. The apparent barrier height (ϕ), computed from the vacuum tunneling equation, is only 0.82 eV, which indicates that tunneling does not occur through a vacuum gap.¹⁶ The $I-V$ curves acquired under these conditions varied somewhat with position, but for the most part resembled the one shown in Fig. 2(a). The $I-V$ curves are rather featureless and vary weakly with sample-tip separation. Auger electron spectroscopy (AES) of samples that did not receive *in situ* heating indicated that the surface was composed primarily (60%) of carbon. Heating to 400 °C in vacuum reduces the level of carbon contamination to between 5% and 18%. The apparent barrier height measured after this treatment is 5.06 eV and a typical $I-V$ curve is shown in Fig. 2(b). The curve is less rectified than those acquired before the heat treatment. The difference in the $I-V$ curves is a clear indication that tunneling spectra are affected by surface contamination.

After cleaning, the surface was exposed to 4×10^{-3} Torr of O_2 for 5 min. The $I-V$ characteristics of this surface measured after return to UHV conditions were essentially unchanged. The sample was then heat treated again at 400 °C and exposed to 1×10^{-4} Torr H_2O for 3 h. Since this treatment had no effect, the sample was then exposed to 1×10^{-2} Torr of H_2O for 14 h. The typical $I-V$ curve acquired after this treatment is shown in Fig 2(c). The rectification apparent in the curve disappeared after pumping the chamber back to the UHV pressure region, indicating that the change is reversible. The $I-V$ curves acquired from the hydrated sample are identical to those recorded after the chamber was vented to air [see Fig. 2(d)] and the reduced tunnel barrier height was observed.

In an attempt to completely eliminate the carbon contamination, one of the samples was heated to 700 °C for 30 min. Before this treatment the sample was light green in color, but afterward, it appeared yellow. Scanning Auger electron spectroscopy indicated that this high temperature treatment significantly altered the surface composition; it was bismuth rich and was decorated with small precipitates rich in bismuth and manganese. Current-voltage curves acquired after this treatment exhibit a strong p -type rectification [see Fig. 2(e)].

Several sets of spatially resolved tunneling spectroscopy data were collected during the exposure to 1×10^{-2} Torr of water vapor and the results from a representative set are summarized in Fig. 3. The most prominent feature of the image shown in Fig. 3(A) is a valley or depression, about 85 Å deep, which extends about halfway down the image and then divides into two separate valleys. Based on the results of earlier experiments, we assume that this is the interfacial region between two grains.¹⁰ Current-voltage curves were acquired at each data point on the line indicated by the arrows. The current measured at each point when the bias was 2.0 V is plotted as a function of position in Fig. 3(B) and a profile of the topography along this line is presented in Fig. 3(C). The fact that the current increases in the proximity of the topographic depression, clearly shows that there is an electrical inhomogeneity, which correlates with the grain boundary. If the surface electrical properties were uniform,

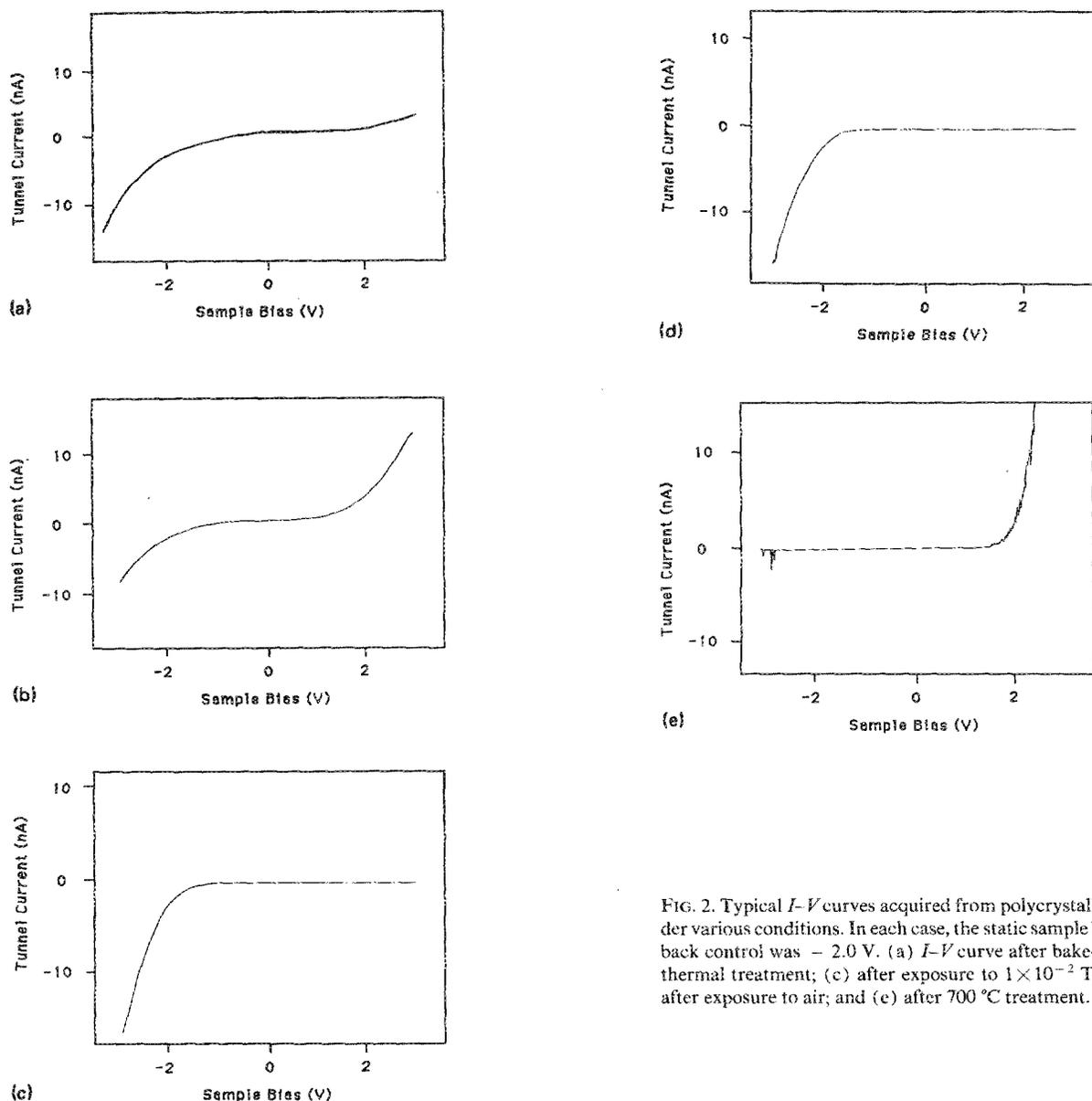


FIG. 2. Typical I - V curves acquired from polycrystalline ZnO surfaces under various conditions. In each case, the static sample bias while under feedback control was -2.0 V. (a) I - V curve after bake-out; (b) after 400°C thermal treatment; (c) after exposure to 1×10^{-2} Torr water vapor; (d) after exposure to air; and (e) after 700°C treatment.

the current measured at each point on the image should be the same, providing the bias and sample-tip separation is constant. Selected I - V curves from different points along the line [see Figs. 3(D)-3(G)] illustrate the two characteristic tunneling spectra acquired from different positions on the image. Spectra from the crystalline surface [Figs. 3(D) and 3(G)] are similar to those recorded in air while those from the vicinity of the interfacial regions [Figs. 3(E) and 3(F)] are much different. It was not possible to detect this difference in the spatially resolved tunneling spectroscopy data recorded in air, which showed a uniform response, with absolutely no correlation to the observed topography.

IV. DISCUSSION

Images of clean surfaces in vacuum show far more detail than those of dirty samples in vacuum or of samples exposed to air. The reason for this is clearly the size of the tunnel

barrier, which is much greater on a clean surface. When scanning on a contaminated sample, the sensitivity of the tunneling current to small changes in sample-tip separation (surface topography) is greatly reduced so that the topographic details are effectively filtered out. The most probable reason for the decrease in the tunnel barrier height is that the tip is in contact with the surface through an insulating contamination layer in such a way that the displacement of the tip is not necessarily equal to the change in the sample-tip separation, an effect discussed previously by Coombs and Pethica.¹⁷ Therefore imaging and spectroscopy data acquired from samples exhibiting reduced barrier heights cannot be strictly interpreted in terms of the conventional vacuum tunneling theory.

The primary goal of this work was to determine the cause of the strong rectification of the tunnel current that occurs during STM analysis in air. The observation that surfaces exhibited rectified tunneling characteristics on exposure to

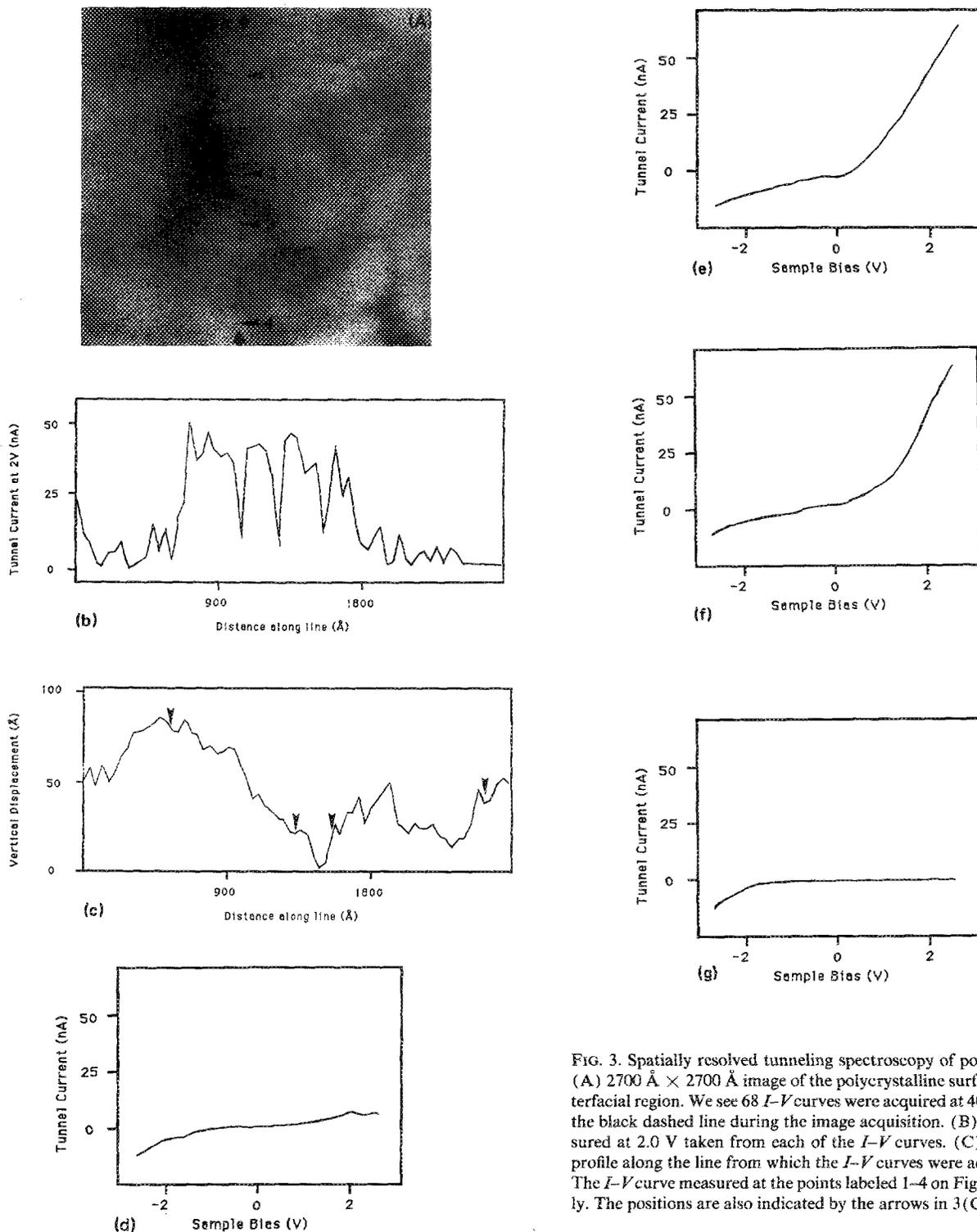


FIG. 3. Spatially resolved tunneling spectroscopy of polycrystalline ZnO. (A) $2700 \text{ \AA} \times 2700 \text{ \AA}$ image of the polycrystalline surface showing an interfacial region. We see 68 I - V curves were acquired at 40 \AA intervals along the black dashed line during the image acquisition. (B) The current measured at 2.0 V taken from each of the I - V curves. (C) The topographic profile along the line from which the I - V curves were acquired. (D)-(G) The I - V curve measured at the points labeled 1-4 on Fig. 3(A), respectively. The positions are also indicated by the arrows in 3(C).

large amounts of water vapor suggests that it is the absorption of atmospheric water, which causes this rectification. The effect of 1×10^{-2} Torr water vapor was not as great as what occurs in air, since it was still possible to detect spatial variations in the electrical properties. The dipolar character of the water molecule presumably allows it to trap charge carriers at the surface and thereby induce band bending and a subsurface depletion layer. The changes in the tunneling

spectra are consistent with the formation of a depletion layer, an effect illustrated schematically in Fig. 4. The absorption process apparently continues for several days with an associated growth of the depletion region that eventually renders tunneling impossible. Apparently the water interacts very weakly with the surface, since an extremely large dose was required to affect the surface in any significant way and the surface returned to normal after pumping the gas

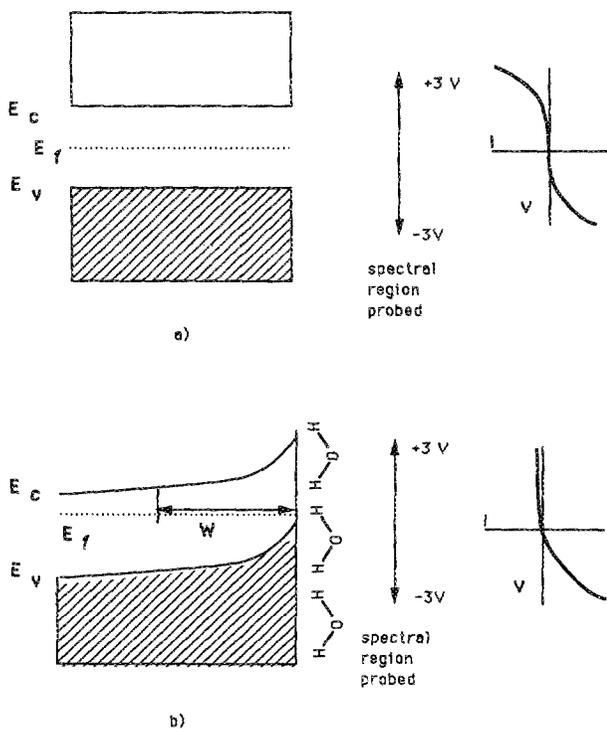


FIG. 4. Schematic illustration of the effect of water absorption on the electronic properties of the ZnO surface. (a) The nearly flat band conditions of the cleaned surface and (b) the band bending that occurs in air as a result of water absorption. The properties of an uncleaned sample in vacuum would be represented by an intermediate case. Schematic illustration of the I - V curves that would be measured in each instance are shown to the right.

away. It is possible that other electrophilic species such as O_2 could contribute to this process, but at the doses used here, no effect was detected.

The tunneling spectra show an opposite rectification after the sample was heated to 700 °C. The cause of this change is certainly related to the segregation of bismuth to the surface. One possible explanation is that a layer of bismuth oxide or a related compound was formed at the surface. The observed tunneling spectra are consistent with those expected from a poorly conducting p -type semiconductor, and Bi_2O_3 is known to reduce easily to become a p -type semiconductor.

The spatially resolved spectroscopy data indicate that the absorption of water does not occur uniformly on all parts of the polycrystalline surface. Regions that are away from the grain boundary have I - V curves typical of those measured in air while those nearer to the boundary are much different. The increases in the measured current near the grain boundary [see Fig. 3(B)] indicates that there is a greater density of states above the Fermi level, a result that suggests that there is a reduction of band bending in the region. The implication is that water does not adsorb at the interfacial regions as readily as on the crystallite surfaces. The surface of the material in these regions, is apparently not as hygroscopic.^{10,11} The complete uniformity of surface properties in air, however, suggest that these regions eventually do absorb water or that the depletion regions in the neighboring crystallites

grow large enough to include the grain boundaries.

Our results have several implications that are relevant to the study of all polycrystalline materials and multicomponent systems. The first is that while local variations in the electronic properties of inhomogeneous surfaces can certainly be measured using scanning tunneling microscopy, only very limited results can be obtained in air or on contaminated surfaces in vacuum. The interaction of the surface with adsorbed species can create a space charge region, which overwhelms other local variations and reduces the effective tunnel barrier. This may not be a problem for inert surfaces, which remain clean in air. The second conclusion is that *in situ* preparation treatments intended to clean the surface may change the surface composition by segregating impurity species to the surface or by causing a precipitation reaction in multicomponent systems. In this case, a middle ground must be achieved such that the sample is cleaned as thoroughly as possible without causing a reaction. The compromise position in the present study was the 400 °C anneal. Last, the importance and utility of spatially resolved spectroscopy experiments have been demonstrated. Polycrystalline surfaces do not have a unique electronic response and the spectroscopy must be mapped so that correlations with topographic features can be established and sources of contrast identified. This, of course, allows a whole range of local electrical measurements to be performed on complex, inhomogeneous materials.

V. CONCLUSIONS

Our results demonstrate that the strong rectification of I - V curves acquired in air is a result of the absorption of water, which causes the formation of a space-charge region. In limited doses, water absorption occurs primarily at the crystallite surfaces rather than at the intergranular regions. Also, the tunneling spectra measured after the segregation of bismuth show strong p -type behavior, possibly due to the formation of a reduced bismuth oxide at the surface. Although the surfaces of polycrystalline materials are rather complex, the simultaneous acquisition of topographic and spectroscopic data under controlled conditions allows chemical changes caused by absorption and segregation reactions to be probed.

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