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Scanning probe nanolithography of conducting metal oxides

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The scanning tunneling microscope (STM) was used to form nanometer-size holes in thin conducting films of thallium (III) oxide. Hole formation was only observed when the process was performed in humid ambient conditions. The hole formation was attributed to localized electrochemical etching reactions beneath the STM tip. Etching reactions consistent with the observed hole formation are a direct electrochemical reduction of thallium (III) oxide to soluble Tl (I) at negative sample bias, and local reduction of pH at positive sample bias. The fastest etching was observed at negative sample bias. Holes as small as 10 nm or as large as 1 μm in diameter could be etched in the films. © *1997 American Institute of Physics.* [S0003-6951(97)00138-1]

Scanning probe microscopes, such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM), can be used to both image and modify the surface of materials. Several groups have shown that nanometer-scale features can be formed on surfaces in the presence of adsorbed water.[1–8] Snow and Campbell have used *in situ* electrical measurements to control the fabrication of 10 nm diameter Ti wires and Ti-TiO$_x$-Ti junctions with the conducting tip of an AFM,[9] and Matsumoto *et al.* have produced a single electron transistor by nanometer-scale oxidation in a STM.[10]

We have previously shown that we can electrodeposit various metal oxide thin films and superlattices.[11–15] In this letter we discuss STM tip-induced oxidation and reduction on the surface of electrodeposited thallium (III) oxide thin films. Thallium (III) oxide is a degenerate *n*-type semiconductor that can be electrodeposited from an aqueous solution at room temperature. It has a bixbyite crystal structure (space group Ia3). Films grown at 300 mV overpotential for this study have an intrinsic band gap of 0.50 eV, resistivity of 7.8×10^{-5} Ω cm, majority carrier concentration of 8.7×10^{20} cm^{-3}, majority carrier mobility of 93 cm^2/V s, and conduction band effective mass of 0.29 m$_o$.[16] The band-to-band optical transition is shifted 1.15 eV by the Moss-Burstein effect.[16] These optical and electronic transport properties are similar to tin-doped indium oxide (ITO).

A commercial STM (Nanoscope E, Digital Instruments Inc.) for surface modification and imaging was employed for this study. The tunneling probe tips employed here were electrochemically etched platinum-iridium (80:20) wire. For surface modifications, a bias voltage ($\pm$ 2.5 V) was either scanned or applied between the tip and substrate (with the tip stationary) with the feedback of the STM disabled. All STM images reported in this study were acquired at a 200 mV bias voltage and 0.5 nA set-point current. A positive bias voltage indicates that the sample potential is positive relative to that of the tip. The thallium (III) oxide thin films were electrodeposited with an overpotential of 300 mV from an aqueous solution of 100 mM TlNO$_3$ in 1 M NaOH (caution: thallium salts are extremely toxic). The film thickness is 0.1 μm and

the average grain size is 150 nm. All STM experiments were performed in ambient conditions with the relative humidity above 50%. Chemical dissolution rates of thallium (III) oxide films in solutions of various pH were measured using a Seiko EG&G quartz crystal analyzer (model QCA917). The thallium (III) oxide films were electrodeposited on gold sputtered, 9 MHz, AT-cut quartz crystal substrates at a deposition current density of 5 mA/cm^2.

We first observed hole formation on the thallium (III) oxide films during an attempt to probe the electronic energy structure by scanning tunneling spectroscopy (STS) in air. STS has been used to characterize the band structure of semiconductors under ambient conditions by several groups.[17–19] We had previously shown that the STM can be used to image cleaved electrodeposited superlattices in cross section.[12,13] Our goal in the STS experiment was to probe the band structure in the supperlattices on a nanometer scale. The STS spectra were obtained by sweeping the bias voltage between $+1$ and -3 V, after setting the tip height with a current of 0.5 nA and bias of $+200$ mV. Although the I-V curve in Fig. 1 could be interpreted in terms of tunneling into the conduction band at positive bias and out of the valence band at negative bias for an *n*-type semiconductor with a band gap of
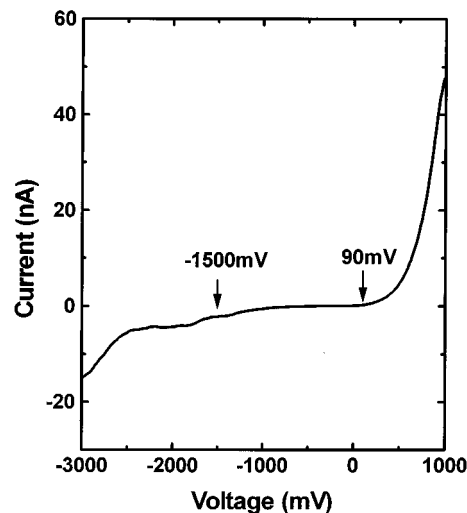

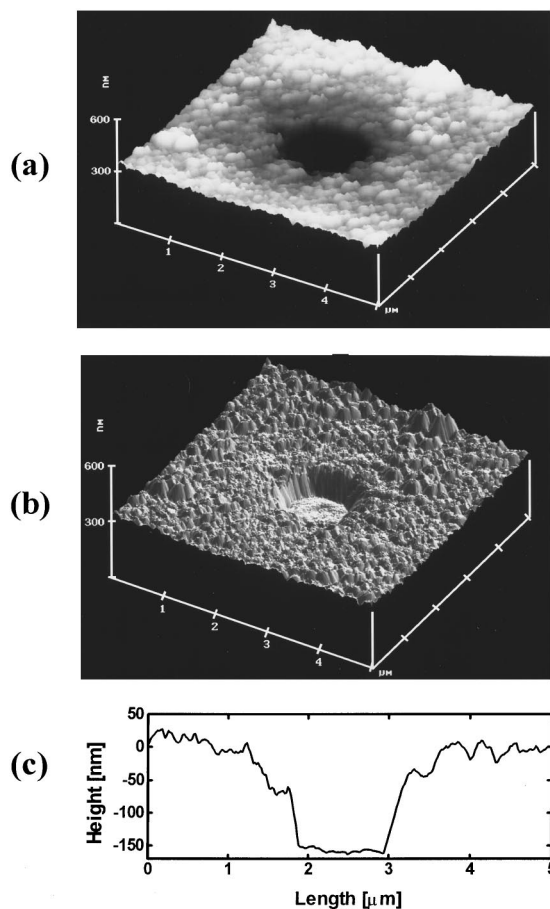FIG. 1. Scanning probe current-voltage spectrum of thallium (III) oxide in air.

FIG. 2. (a) A STM image of a hole formed with a scan bias=±2.5 V for 20 minutes. The hole is 1 μm in diameter. (b) The same image in illumination mode. (c) The cross-sectional profile through the hole.

FIG. 3. Schematic illustration of possible (a) cathodic etching reaction and (b) anodic etching reaction.

approximately 1.6 eV, we observed that holes formed in the thallium (III) oxide after the I-V curves were obtained. We attribute the hole formation to localized electrochemical reactions of the conducting metal oxide film. The I-V curve could result from anodic reactions at positive bias and cathodic reactions at negative bias rather than by direct electronic tunneling between the tip and surface.

Fig. 2(a) shows the STM image of a hole formed after sweeping a bias of ±2.5 V for 20 minutes. Fig. 2(b) shows the same image in illumination mode clearly showing the features of the hole. The cross-sectional profile through the hole is shown in Fig. 2(c). The hole is approximately 1 μm in diameter. The primary reason for use of this etching process is thought to be the presence of adsorbed water on both the tip and sample surfaces. The tip and sample would then act as the anode or cathode of an electrochemical cell, which is similar to the scanning electrochemical microscope.[20] We propose that the etching reactions are the reduction of the thallium (III) oxide and oxidation of water at the surface of the thallium (III) oxide (Fig. 3). When the thallium (III) oxide is biased negatively, the reduction of the thallium (III) oxide to soluble Tl^+ will proceed at the interface of the thallium (III) oxide and water according to

$$Tl_2O_3 + 3H_2O + 4e^- \rightleftharpoons 2Tl^+ + 6OH^- . \qquad (1)$$

An anodic etching reaction occurs when we apply a sample positive bias voltage. The oxidation of the water would pro-

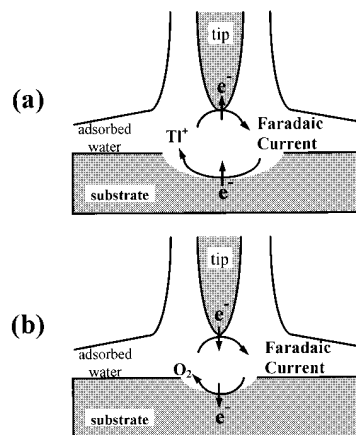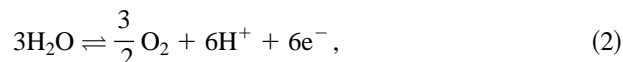duce protons on the surface of the thallium (III) oxide and therefore reduce the local pH directly beneath the tip [Eq. (2)]. Lowering of the local pH would cause dissolution of the thallium (III) oxide to soluble Tl^{3+} [Eq. (3)].

$$3H_2O \rightleftharpoons \frac{3}{2} O_2 + 6H^+ + 6e^- , \qquad (2)$$

$$Tl_2O_3 + 6H^+ \rightleftharpoons 2Tl^{3+} + 3H_2O . \qquad (3)$$

This process can be reversed in the area away from the tip and sample junction where the local pH is higher. The quartz crystal microbalance was employed to monitor the chemical dissolution of the bulk thallium (III) oxide films in different pH buffered solutions. The dissolution rates are listed in Table I. The dissolution rate increases from 9×10^{-5} nm/s at pH 6.7 to 1.6×10^{-1} nm/s at pH 0.

Additional information about the mechanism of this etching process was obtained under different conditions. In Fig. 4, a grain 0.2 μm in diameter was completely removed after applying a bias of −2.5 V for 1 minute as indicated in Fig. 4(a). By varying the polarity of the bias voltage, the etching rate was decreased significantly. A positive bias voltage of 2.5 V was applied to the tip and sample junction for 1 and 10 minutes as shown in Fig. 5. The holes are 10 and 160 nm in diameter, respectively. There are some small grains around the edge of the 160 nm hole as shown in Fig. 5(b). We attribute this to redeposition of the thallium (III) oxide in areas of higher local pH. Hole formation was not observed when the experiments were performed under low humidity conditions (<10%), and this is consistent with the proposed electrochemical etching mechanism.

TABLE I. The chemical dissolution rates of bulk thallium (III) oxide films in different pH solutions measured with a quartz crystal analyzer.

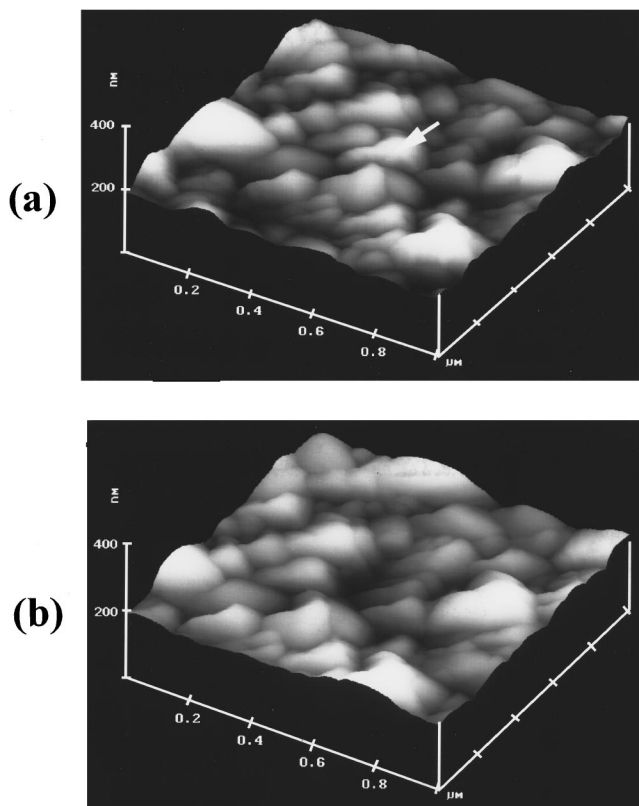| pH	6.7	4.0	1.1	0.3[a]	0[b]
Dissolution rates (nm/s)	9×10^{-5}	1.4×10^{-3}	4.6×10^{-3}	1.6×10^{-2}	1.6×10^{-1}

[a]0.5 M nitric acid.
[b]1 M nitric acid.

FIG. 4. STM images of the thallium (III) oxide surface (a) before etching and (b) after applying a bias of -2.5 V for 1 minute. A 0.2 μm grain indicated in (a) was etched out in (b).
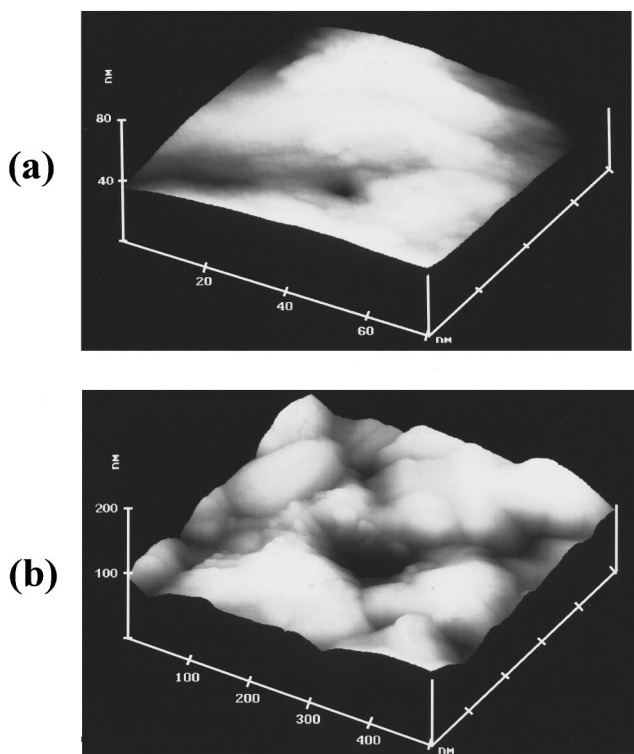

FIG. 5. STM images of a hole formed with an applied bias of $+2.5$ V for (a) 1 minute and (b) 10 minutes. The holes are 10 and 160 nm in diameter, respectively.

In conclusion, we have shown that STS results obtained in air may not represent direct electronic tunneling between the tip and substrate. Our results are more consistent with localized electrochemical reactions occurring beneath the STM tip. Both cathodic and anodic etching reactions can be performed on metal oxide surfaces. The size of the holes was found to be dependent on the etching time and the polarity. The different etching behavior of different polarity biases provides additional support to the view that the etching mechanism is electrochemical in nature. The etching rate is faster at negative sample bias, even though the observed currents are higher at positive sample bias. The etching technique we have outlined for thallium (III) oxide may be applicable to other conducting metal oxides with redox-active metal ions such as ITO, SnO_2, ZnO, PbO_2, and RuO_2, and can be extended to nanolithography applications of metal-oxide devices. Although the emphasis of this letter was the *etching* of conducting metal oxides in the STM, in future work we plan to study the contribution of localized electrochemistry to the *imaging* process under ambient conditions.

[1] T. R. Albrecht, M. M. Dovek, M. D. Kirk, C. A. Lang, C. F. Quate, and D. P. E. Smith, Appl. Phys. Lett. **55**, 1727 (1989).

[2] R. M. Penner, M. J. Heben, N. S. Lewis, and C. F. Quate, Appl. Phys. Lett. **58**, 1389 (1991).

[3] R. L. McCarley, S. A. Hendricks, and A. J. Bard, J. Phys. Chem. **96**, 10089 (1992).

[4] J. K. Schoer, F. P. Zamborini, and R. M. Crooks, J. Phys. Chem. **100**, 11086 (1996).

[5] H. Sugimura, T. Uchida, N. Kitamura, and H. Masuhara, J. Phys. Chem. **98**, 4352 (1994).

[6] H. Sugimura and N. Nakagiri, J. Vac. Sci. Technol. A **14**, 1223 (1996).

[7] A. E. Gordon, R. T. Fayfield, D. D. Litfin, and T. K. Higman, J. Vac. Sci. Technol. B **13**, 2805 (1995).

[8] D. Wang, L. Tsau, K. L. Wang, and P. Chow, Appl. Phys. Lett. **67**, 1295 (1995).

[9] E. S. Snow and P. M. Campbell, Science **270**, 1639 (1995).

[10] K. Matsumoto, M. Ishii, and K. Segawa, J. Vac. Sci. Technol. B **14**, 1331 (1996).

[11] J. A. Switzer, M. J. Shane, and R. J. Phillips, Science **247**, 444 (1990).

[12] J. A. Switzer, R. P. Raffaelle, R. J. Phillips, C.-J. Hung, and T. D. Golden, Science **258**, 1918 (1992).

[13] J. A. Switzer, C.-J. Hung, B. E. Breyfogle, M. G. Shumsky, R. Van Leeuwen, and T. D. Golden, Science **264**, 1573 (1994).

[14] B. E. Breyfogle, C.-J. Hung, M. G. Shumsky, and J. A. Switzer, J. Electrochem. Soc. **143**, 2741 (1996).

[15] T. D. Golden, M. G. Shumsky, Y. Zhou, R. A. VanderWerf, R. A. Van Leeuwen, and J. A. Switzer, Chem. Mater. **8**, 2499 (1996).

[16] R. A. Van Leeuwen, C.-J. Hung, D. R. Kammler, and J. A. Switzer, J. Phys. Chem. **99**, 15247 (1995).

[17] J. Jahanmir, P. E. West, A. Young, and T. N. Rhodin, J. Vac. Sci. Technol. A **7**, 2741 (1989).

[18] T. Oshio, J. Tanaka, A. Ono, T. Nagamura, Y. Kamizono, Y. Sakai, and S. Ehara, J. Vac. Sci. Technol. A **8**, 455 (1990).

[19] R. M. Silver, J. A. Dagata, and W. Tseng, J. Appl. Phys. **76**, 5122 (1994).

[20] A. J. Bard, F.-R. F. Fan, D. T. Pierce, P. R. Unwin, D. O. Wipe, and F. Zhou, Science **254**, 68 (1991).