APPLIED PHYSICS LETTERS VOLUME 79, NUMBER 16 15 OCTOBER 2001

Nanospark at the interface between organic solvents and tin-doped indium oxide

Hiroshi Uji-i, Koji Hatanaka, Jonathan Hobley, and Hiroshi Fukumura[a]
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

(Received 17 July 2001; accepted for publication 10 August 2001)

A nanometer-scale surface modification of tin-doped indium oxide (ITO) in organic solvent was performed using a scanning tunneling microscope (STM). The surface modification was attributed to localized field evaporation upon applying 10 V between the tunneling gap. White light sparking beneath the STM tip (nanospark) was observed during and after the surface modification. The addition of ionic species into the otherwise pure solvent also induced a nanospark even when applying lower voltages, but in this case, surface modification did not occur. Thus, it is proposed that a part of the ITO becomes dissolved in solution as ions, which results in electron avalanche in the presence of these induced ions. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1412429]

A scanning tunneling microscope (STM) can be used to modify surfaces on the nanometer scale.[1–7] Combining this technique with the detection of photon emission from the tunneling gap can open further possibilities in STM measurements.[8] This STM-induced luminescence technique has the potential to induce and probe localized chemical reactions and excitation processes of electronic states on a surface. Thirstrup *et al.* reported STM-induced photon emission from dangling bonds formed on hydrogen-terminated silicon.[9] Some groups have investigated the relation between surface structure and electroluminescence efficiency within nanometer dimensions for organic light-emitting diodes.[10,11]

Under atmospheric pressure, particularly in solution, we can reveal mechanisms of surface changes and discover phenomena by adding other chemicals during STM measurements. Several groups have shown that nanometer-scale fabrications can be controlled in the presence of adsorbed water.[3–7] It has been demonstrated that localized oxidation occurs during surface modifications of metals[3] and semiconductors.[4] Also, nanometer-scale modifications driven by redox reactions beneath a STM tip have been performed on metal,[5] semiconductor,[6] and conductive metal oxide surfaces.[7]

In this letter, we confirmed STM-induced nanometer-scale surface modification of tin-doped indium oxide (ITO) covered with an organic solvent phase. ITO is mainly used as a transparent conductive substrate for optoelectronic devices, e.g., flat panel displays, solar cells, and organic electroluminescence devices. These devices are based on interfacial charge injection from electrodes[12] and their structures are inevitably going to be reduced to the nanometer scale by applying recent technology. Here, we have investigated mechanisms of surface modification by changing the chemicals in contact with an ITO surface and by detecting photon emission emanating from the tunneling gap.

All experiments were performed using a commercial STM (NT-MDT, P-47) at the solvent/ITO interface in ambient laboratory conditions. The ITO substrate used in this study was a commercial one that was made by ion sputtering. STM tips employed in this study were mechanically cleaved platinum–iridium (7:3) wire or electrochemically etched tungsten wire. The STM tip was immersed in the solution (1-phenyloctane or heptylcyclohexane) and scanned at the solvent/ITO interface. STM images were taken in the constant current mode with the set point currents in the range 0.1 to 1.0 nA. For surface modification, 1 ms pulsed voltages, at 50 Hz repetition, were applied between the tip and substrate for 500 ms at each point (25 pulses in total). Here, a positive bias voltage indicates that the sample potential is positive relative to that of the tip. In order to avoid the STM tip touching the surface, the feedback system of the STM was turned on while applying the pulsed voltage. Two types of STM-based luminescent measurements were performed: (i) measurements of the emission intensity dependence upon the bias voltage; and (ii) emission spectra measurements. The emission intensity was measured using a cooled photomultiplier (Hamamatsu R464) collecting the light with an objective lens having a long working distance (Mitutoyo M Plan Apo SL 50, N.A. $=0.42$). In order to perform spectroscopic measurements, photons were collected with a low *f*-number lens and guided through an optical fiber into a spectrograph equipped with a multichannel photodetector (Otsuka electronics MCPD-7500). In both cases, photons were collected from the free surface of the sample at an angle of approximate 35° with respect to the surface.

We first investigated the dependence of surface changes upon the bias voltage for ITO covered with pure 1-phenyloctane or heptylcyclohexane. Figure 1(a) shows a STM image of a fresh ITO surface in a 1 μm^2 area, which exhibits an irregular granular surface morphology with a typical grain size of a few tens nm. No surface change was observed for applied pulsed voltages of between -9 and $+10$ V. Further, the tunneling current remained constant at its set point value during measurements made between these voltages. However, as shown in Fig. 1(b), a large surface modification resulted after -10 V was applied and this was associated with a current surge detected at the same time. The cross sectional profile through the modified area is shown in Fig. 2. The extent of the modified area was ap-

---

[a] Electronic mail: fukumura@orgphys.chem.tohoku.ac.jp

0003-6951/2001/79(16)/2660/3/$18.00

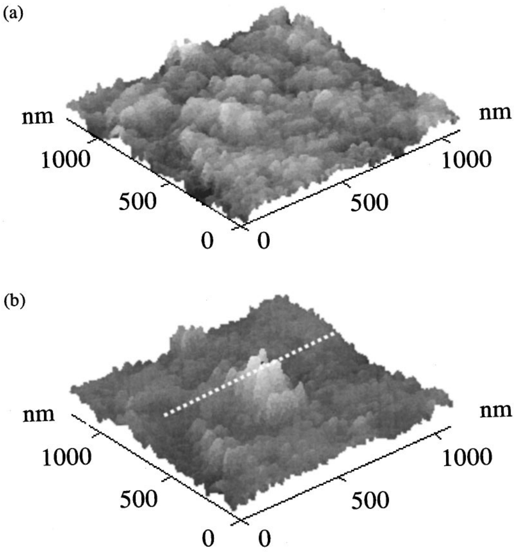

FIG. 1. STM images of an ITO surface covered with pure phenyloctane. Tunneling current and voltage are 1.0 nA and 0.1 V (sample negative), respectively. (a) Before applying the pulsed voltage at −10 V (sample negative). (b) After applying the pulsed voltage at −10 V. A clear modification could be confirmed.

proximately 200 nm in width. Once the surface was modified, massive random current flow occurred even at the lower applied voltages, of between −9 to +10 V, over a 1 μm region surrounding the modified area. Notably, we confirmed that no further surface change occurred in this case. We can conclude that the initial large surface change was induced by field evaporation resulting from the applied electric field, that was of the order of 10^9 V/m, and not by the massive current flow itself. Although in the macroscopic case an electric field of the order of 10^9 V/m is too low to produce field evaporation, it can occur easily in a typical STM configuration.[13] The possibility of electrochemical etching can be ruled out since this process should in general occur at a lower voltage.[7]

To investigate the mechanistic details of this phenomenon, experiments were carried out combined with light emission measurements. Figure 3 shows the dependence of the emission intensity upon the applied voltage in 1-phenyloctane with a Pt/Ir tip. No photon emission was detected until a surface change occurred as shown in Fig. 3, and once the surface was modified, the emission threshold was drastically reduced. Figure 4 shows the emission spectrum obtained when applying a voltage of +8 V between the substrate and tip after modification. The spectrum was broad from 400 to 800 nm having no obvious peaks. Because the emission from this nanometer region was so weak, the spectrum we obtained had many spikes due to the detection limitation of the photodetector. The spectral shape was not dependent upon bias polarity or its voltage, as expected, in the limited range available using our STM setup. Further, the same spectral shape was observed in different solvents used and was independent of the STM tip materials (Pt/Ir and W). Based on all of these results, we can suggest that the photon emission is caused by a current surge occurring either as a result of property changes at the ITO surface or by fragments of the ruptured ITO present in solution. The latter is more plausible because the extended area, over which the current surge and the photon emission could be detected after surface modification, was much greater than the area of the surface modification itself.

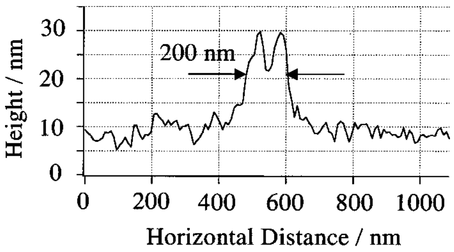

FIG. 2. Line profile along the white dashed line shown in Fig. 1(b).

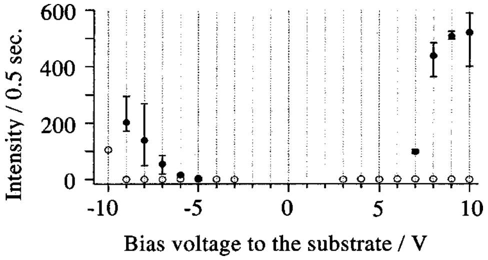

FIG. 3. Emission intensity as a function of the voltage. Open circle: before a surface modification. No photons were detected. Closed circle: after a surface modification. The emission threshold was drastically redeced.

To further clarify the origin of the light emission that, from the aforementioned discussion, is firmly linked to the concurring current surge, experiments were carried out in heptylcyclohexane solutions containing iodine (Aldrich) or tetramethylammonium perchlorate ions (Tokyo Kasei). For the solutions containing iodine, the result was the same as in the case of the neat solvent. On the other hand, for the ionic solution, both the current surge and the photon emission were observed even when the surface remained intact. The dependence of the emission intensity upon bias voltage followed a similar trend as that shown by the closed circle symbols in Fig. 3 and a similar broad emission spectrum was observed to that shown in Fig. 4. This result clearly indicates that the current surge was caused by the presence of ions in the solvent, since no surface modification occurred in this case. The difference between the results with iodine and with the ions is attributed to their dissociation energies. Although ions are bound to their counter ions in nonpolar solvents, they can be dissociated by an applied electric field more easily than iodine molecules, which require 7.4 eV to form iodine cation and anion pairs.

In the pure solvent case, we propose that fragments of ITO became released into the solvent as charged species due to an electric-field induced rupture of the ITO. The observed

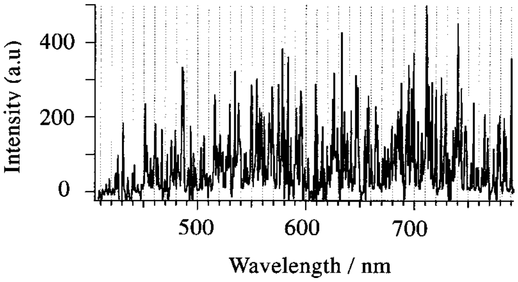

FIG. 4. Emission spectrum when pulsed voltages (+8 V) were applied at eight different points. The exposure time was 5 s.

current surge can be explained as an ion-initiated electron avalanche occurring in the following sequence: Ions are dissociated and accelerated by the intense electric field and electrons are generated from other ions or the STM electrodes ionized by collision with the accelerated ions; the secondary electrons, in turn, form further electrons along their paths. Thus, generated electrons collide with molecules and ions under the high electric field in the nanometer-scale region, which results in photon emission predominantly by bremsstrahlung radiation. We conclude this because the emission has a broad and featureless spectrum that is not dependent upon polarity biases, solutes, solvents, or STM tip materials.

In conclusion, nanometer-size surface modification of ITO was performed in organic solvents with a STM. We confirmed that the ruptured ITO ions became dissolved in solvent near the surface, using the photon emission measurements. We consider that nanometer-region electron avalanche in the tunneling gap was caused by the existence of ions resulting in this photon emission. We have shown that STM combined with photon emission measurements should be a useful and promising technique for the study of the electronic excitation process at liquid/solid interfaces due to the high spatial resolution and the ability to control the distance between two electrodes.

The authors acknowledge Otsuka Electronics Co. for generously supplying the MCPD-7500. Thanks are also due to Daicel Chemical Industries, Ltd. for their supply of ITO substrates. This work was supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, Sports, and Culture (Nos. 11355035 and 13440204).

[1] M. A. McCord and R. F. W. Pease, J. Vac. Sci. Technol. B **4**, 86 (1986).
[2] J. W. Lyding, T.-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abeln, Appl. Phys. Lett. **64**, 2010 (1994).
[3] H. Sugimura, T. Uchida, N. Kitamura, and H. Masuhara, J. Phys. Chem. **98**, 4352 (1994).
[4] J. A. Dagata, J. Schneir, H. H. Harary, C. J. Evans, M. T. Postek, and J. Bennett, Appl. Phys. Lett. **56**, 2001 (1990).
[5] Z.-X. Xie and D. M. Kolb, Electroanal. Chem. **481**, 177 (2000).
[6] H. Sugimura and N. Nakagiri, J. Vac. Sci. Technol. A **14**, 1223 (1996).
[7] C.-J. Hung, J. Gui, and J. A. Switzer, Appl. Phys. Lett. **71**, 1637 (1997).
[8] R. Berndt, R. Gaisch, J. K. Gimzewski, B. Reihl, R. R. Schlittler, W. D. Schneider, and M. Tschudy, Science **262**, 1425 (1993).
[9] C. Thirstrup, M. Sakurai, K. Stokbro, and M. Aono, Phys. Rev. Lett. **82**, 1241 (1999).
[10] M. Klemenc, F. Meghdadi, S. Voss, and G. Leising, Synth. Met. **85**, 1243 (1997).
[11] C. S. F. Alvarado, L. Rossi, P. Muller, P. F. Seidler, and W. Riess, IBM J. Res. Dev. **45**, 89 (2001).
[12] V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bassler, J. Appl. Phys. **84**, 848 (1998), and references therein.
[13] T. T. Tsong, Phys. Rev. B **44**, 13703 (1991).