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In Situ Observation of a Dynamically Light-Induced Morphological Transformation at an n-MoS_2 Electrode Surface by a Scanning Tunneling Microscope

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Synopsis. A scanning tunneling microscope (STM) under photoelectrochemical control was used to investigate an in situ dynamically light-induced morphological transformation at an n-MoS_2 electrode surface in CH_3CN by the addition of I^- ions. The anistropic photocorrosion rate around the "disk-like" cavities was extremely slow due to the effects of the added I^- ions when compared to the results achieved by adding only H_2O.

In situ observation using a scanning tunneling microscope (STM) under potentiostatic control has been shown to be an important method for understanding electrochemical processes at various electrode/liquid interfaces.[1-8] Recently much attention has been focused on observing semiconductor electrode/liquid interfaces using the STM under potentiostatic control. Itaya et al. reported using the STM to research both oxide semiconductors such as TiO_2[9] and ZnO,[10] and also the topography and surface electronic structure of p- and n-Si.[11] Bard et al. studied high resolution photoelectrochemical etching for a sp-semiconductor n-GaAs,[12] Uosaki et al. produced result concerning the surface structure of n-GaAs during photoanodic dissolution,[13] and photoelectrochemical deposition of Au on n-GaAs was studied by Thundat et al.[14] However, reports of in situ photoelectrochemical studies on the layer-type semiconductor electrode using the STM under potentiostatic control have not yet been published, and led to the presented report's study of the photoelectrochemical behavior of n-MoS_2, a representative layer-type semiconductor electrode. The investigation was conducted to determine the effect of adding I^- ions in order to suppress the photoelectrochemical corrosion of n-MoS_2. MoS_2 is a technologically important material which is used as both a catalyst and lubricant. Stupian and Leung,[15] Sarid et al.,[16] and Ichinokawa et al.[17] have investigated the MoS_2 surface by STM in an air or vacuum environment. Tributsch et al.[18-20] were the first to investigate photoelectrochemical reactions of n-MoS_2 for use in solar energy conversion applications. However photoanodic corrosion was the dominant process in the absence of an effective redox system. Research performed from a surface chemistry perspective is very important to expand the understanding of photocorrosion processes. Investigations were conducted of in situ photoelectrochemical processes at the n-MoS_2 electrode surface in various solutions using the STM under photoelectrochemical control, and also interfacial photoelectrochemical processes were characterized in: (1) KCl, (2) KI, (3) CH_3CN, (4) CH_3CN+H_2O (4 vol%).[21-27] In this study I^- ions were added to a CH_3CN nonaqueous organic solvent, and a dynamically light-induced morphological transformation of n-MoS_2 was observed using the STM under anodic polarization. The effect that these I^- ions have on suppressing photoelectrochemical corrosion of n-MoS_2 when added to an organic solvent is discussed.

Experimental

A new type of electrochemical STM unit was used, consisting of a "Standalone" type microscope (Digital Instruments, USA) and a locally manufactured electrochemical cell.[21,22] The main advantage of the unit was that in situ photoelectochemical measurements could be performed both in aqueous and organic solutions by controlling the potential of the working electrode (E_W) and the tunnel tip (E_T) against a common saturated calomel reference electrode (SCE). The potential of the tip (E_T) with respect to the SCE in this four electrode system is given by $E_T=E_W-T_B$ (V vs. SCE), where T_B is the tunnel bias voltage (working electrode (WE) / tip(ground)). The background current in CH_3CN/10 mM TBAP (M=mol dm^{-3}) was less than 0.05 nA, and slightly increased by the addition of 1 mM KI (4 vol%). All images were observed in a constant current mode (6.0 nA). Glass coated $Pt_{0.8}Ir_{0.2}$ tips (Longreach Scientific Resources, USA) were used for measurements in solutions. The electrochemical characterization of these insulated tips is discussed in Sakamaki et al.[8] The cell was illuminated by an optical fiber guided 30 W Halogen-lamp, and a series of time-dependent STM images under photoelectrochemical control were observed by a Nanoscope (II) microscope (Digital Instruments, INC., USA) which had a six image buffer system.

The 2H-MoS_2 single crystals (n-type) used in the presented study were produced naturally in Japan. The donor concentration of MoS_2 (1.3×10^{18} cm^{-3}) was calculated by the Mott-Schottky relationship.[28] Fresh MoS_2(0001) crystal surfaces were prepared by cleaving with Scotch tape just before STM measurements. A Ga-In alloy was attached to the back of the freshly cleaved surface to ensure ohmic contact. The exposed surface area of n-MoS_2 in the electrochemical cell was 0.126 cm^2. A spectrograde CH_3CN nonaqueous solvent (Dojin) containing H_2O of less than 0.1 vol% was used. Tetra-*n*-butylammonium perchlorate (TBAP), (Tokyo Kasei's guaranteed reagent) was used as a supporting electrolyte. Solutions were prepared using super grade KI and ultra-pure water (Millipore-Q). The CH_3CN/10 mM TBAP (1 cm^3) was poured into a Teflon cell using a micropipette.

Results and Discussion

Figure 1(a) shows a STM top view image of n-MoS_2 in CH_3CN/10 mM TBAP under anodic polarization (E_W=+0.9 V vs. SCE), over an area of 2000×2000 nm shown in depths up to 5 nm. In situ observations were

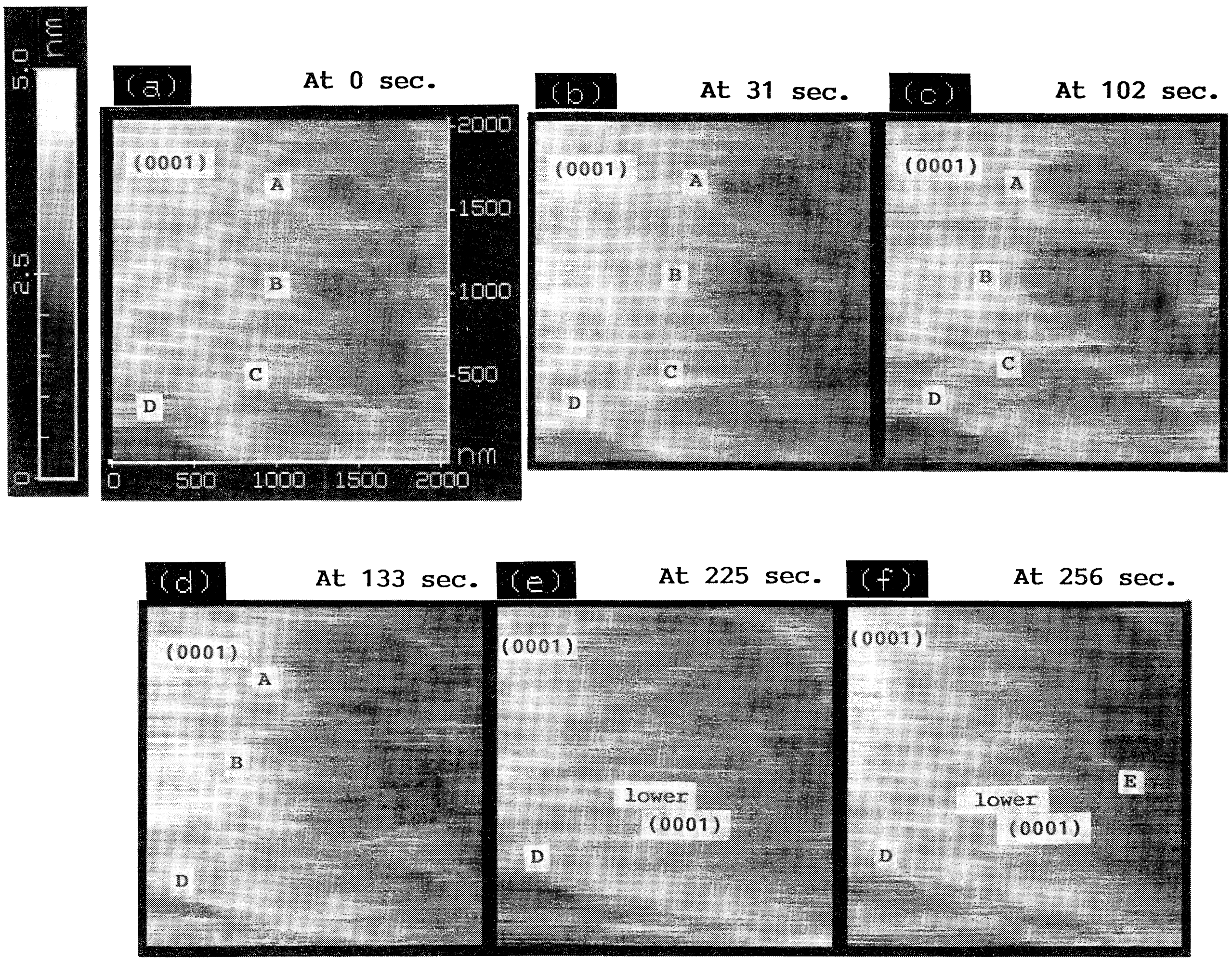

Fig. 1. A series of STM images of n-MoS_2 under photoelectrochemical control over an area of 2000×2000 nm. All images were observed at E_W=+0.9 V vs. SCE, T_B=+800 mV (WE/tip(ground)), E_T=+0.1 V vs. SCE, in a constant current mode (6.0 nA). (a) was observed in CH_3CN/10 mM TBAP. (b), (c), (d), (e), and (f) were respectively observed at 31, 102, 133, 225, and 256 seconds after the addition of 1 mM KI (4 vol%) into the solution used in (a). The observed times after the adding I^- ions were indicated on the top of each figures.

performed under the following STM conditions. The tunnel bias voltage and the potential of the tip were respectively set at T_B=+800 mV, E_T=+0.1 V vs. SCE. Care was taken to ensure that the potential of tip was set in a voltage potential window of electrolyte in order to gain reliable STM images. The flat-band potential and conduction band edge of n-MoS_2 in CH_3CN were respectively +0.30 V and +0.20 V vs. SCE.[29] STM observation was performed at E_T=+0.1 V vs. SCE, and therefore electron tunneling occurred from the tip to the conduction band of n-MoS_2. During 15 minutes of observation, photoelectrochemical corrosion in CH_3CN/10 mM TBAP proceeded extremely slowly due to the slight amount of H_2O (0.1 vol%) contained in CH_3CN (see Fig. 1(a)). The light-induced photoanodic reactions at n-MoS_2 in an inert electrolyte are classified into two processes:

$$MoS_2 + 8H_2O + 18h^+ \longrightarrow Mo^{6+} + 2SO_4^{2-} + 16H^+ \quad (1)$$

$$MoS_2 + 2H_2O + 4h^+ \longrightarrow MoS_2 + O_2 + 4H^+ \quad (2)$$

with reaction (1) being most predominant.[19,20,28] It sould be noted that light-induced disintegration of n-MoS_2 occurs in the presence of H_2O. Evidence supporting the existence of anisotropically enhanced photoelectrochemical reactions around surface depressions and vacancies by adding H_2O (4 vol%) to CH_3CN/10 mM TBAP has been reported, however the well-ordered n-MoS_2(0001) surface was found to be resistant to photocorrosion.[21,23] In a KCl solution, light-induced corrosion originated from "layer-island" structures, step edges, and defects, all of which served as active reaction sites, and then the electrode surface was morphologically transformed by photoelectrochemical processes into a stable van der Waals' surface.[24,25] The effect of I^- ions on the suppression of photocorrosion of n-MoS_2 in an "aqueous" solution (KI) was additionally investigated.[24,25] Discussed here is the effect that the addition of I^- ions into a "nonaqueous" organic solution (CH_3CN/10 mM TBAP) had on the suppression of photocorrosion of n-MoS_2. A microsyringe was used to carefully add a 1 mM KI (4 vol%) solution to the solution which gave the results shown in Fig. 1(a). Figures 1(b), (c), (d), (e), and (f) were respectively observed at 31, 102, 133, 225, and 256 seconds after this addition. In Fig. 1(a), two "disk-like" cavities (A and B), two depressions (C and D), and the top layer of the MoS_2(0001) face can be seen. These two "disk-like" cavities gradually grew as the anisotropic photocorrosion processed (see Fig. 1(b), (c), and (d)). The anisotropic growth of these "disk-like" cavities was expected because of the anisotropically structural property of MoS_2. However this anisotropic photocorrosion rate was extremely slow when compared to the results achieved by adding H_2O (4 vol%) to CH_3CN/10 mM TBAP,[21,23] because the I^- ions effectively suppressed the photocorrosion of n-MoS_2. Figure 1(e) clearly shows that the two "disk-like" cavities have disappeared, as a result of the photoelectrochemical reactions. These cavities were morphologically transformed into the large single "disk-like" cavity that is shown in Fig. 1(e). A new, stable van der Waals' surface appeared from underneath the top layer (see lower (0001) in Fig. 1(e) and (f)). Figure 1(f) shows that photoelectrochemical corrosion continued at the defects (see point E) located in the newly visible van der Waals' surface.

In conclusion, using these series STM observations, the dynamically light-induced morphological transformation at the n-MoS_2 surface was clearly visualized in situ. The well-ordered (0001) face was found to be stable against photo-corrosion in CH_3CN. The photocorrosion was significantly suppressed around the "disk-like" cavities due to the effects of the added I^- ions when compared to the results achieved by adding only H_2O (4 vol%). However the concentration of I^- ions was not strong enough to achieve long term stability of n-MoS_2. The photocorrosion that did occurred in Fig. 1(e) and (f) was attributed to the H_2O in the added KI solution.

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