*Communication to the Editor*

*Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 12    1299

the second protonated species(d) more easily so that breakdown of the intermediate, ③, would be the rate determining step.

This result is not commonly observed in amide hydrolysis and is likely to be caused by the structural feature of the *N*-acylimidazole.

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# Photoelectrochemical Stripping Behavior of Atomic Cd Layer on CdTe(100)

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Recently, Stickney[1-3] has suggested a new concept of electrochemical atomic layer etching, called "electrochemical digital etching (ECDE)", to etch compound semiconductor surfaces into a depth with an atomic depth resolution. The working principle of the atomic layer manipulation was an electrochemical stripping reaction confined to surface atomic layer, which is conceptually opposite to underpotential deposition (UPD).[4] An actual atomic layer etching was examined with CdTe compound semiconductor using cyclic removal of each atomic layers of Cd and Te in a sequential manner. By setting a digital number of removal cycles, an etching depth with an atomic resolution could be achieved.

Along with ECDE, we investigated the possibility of a photoelectrochemical way to fabricate a pattern on semiconductor surfaces. The main idea of the method is projection of a light image to control the local reactivity of CdTe surface toward the atomic layer stripping reactions. To achieve the goal, the stripping behavior of Cd layers under various illumination levels was scrutinized.

A CdTe(100) crystal, purchased from II-VI Inc., was cut to a plate (25 mm × 8 mm × 0.5 mm) and polished down to 1 μm. An ohmic contact was made by rubbing indium with a soldering iron at one end of the plate and a platinum wire (0.5 mm diameter) was soldered to it. A stoichiometric surface of the CdTe(100) electrode was prepared by chemical etching of the electrode in $Br_2$/MeOH solution followed by electrochemical reduction of a thick Te layer at -1.8 V.[5-7] The electrolyte used in this study was 0.1 M $Na_2SO_4$ (Aldrich) made from ultrapure water (> 18 MΩ) and its pH was 5.7. A light-tight box was used to control the light level reaching to the electrode. The background light was negligible. The illumination was achieved with a tungsten lamp and a halogen lamp, whose powers were ~0.1 mW/cm² and ~40 mW/cm², respectively.

A home-built potentiostat, manipulated by a computer, was used to control the potential of a conventional three-electrode system. The electrolyte was deareated with $N_2$ and the electrochemical cell was blanked with $N_2$ during the whole experiment. The reference electrode used in this work was Ag/AgCl([Cl⁻]=1.0×10⁻⁵ M), but the potential reported here is against Ag/AgCl([Cl⁻]=1.0 M).

In addition, surface analysis was performed using XPS (VG, ESCALAB 220i) for determination of relative surface concentrations of Cd and Te.

Figure 1 (a) is the cyclic voltammogram of a stoichiometric CdTe(100) surface in 0.1 M $Na_2SO_4$, taken in the

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anodic direction from an open circuit potential (- 0.5 V) under illumination of ~40 mW/cm². The voltammetric behavior of CdTe is well understood.[1] A brief description is as follows. Oxidative stripping of Cd via reaction (1) started immediately and showed a peak at +0.3 V.

$$CdTe + 2h^+ \rightarrow Cd^{2+} + Te \tag{1}$$
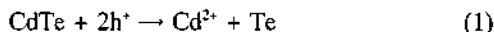
At potential more than +1.5 V, anodic dissolution of CdTe(100) was observed, although not shown here. In the reverse cathodic scan, three kinds of reduction currents were observed. A part of the previously dissolved Cd²⁺ ion was redeposited at - 0.7 V and a reduction current peak of Te, formed in reaction (1), was observed at - 1.6 V on a huge hydrogen evolution current. The reduction of Te took place according to reaction (2).

$$Te + 2e \rightarrow Te^{2-} \tag{2}$$
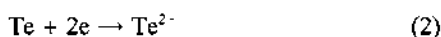
As shown in Figure 1(b) and (c), the reduction of illumination level changed the quite discernable oxidation peak of Cd (Figure 1(a)) to featureless one on an increased background. However, it is noticeable that the charge associated with the reduction of Te was remarkably decreased. Since it is known that a Te layer exposed to an electrolyte is electrochemically reduced until a Cd layer underneath the surface becomes the top layer,[5-7] the decrease of the Te reduction charge indicates that the amount of oxidatively stripped Cd decreased as the illumination level did. This observation clearly indicates that the oxidation of Cd was
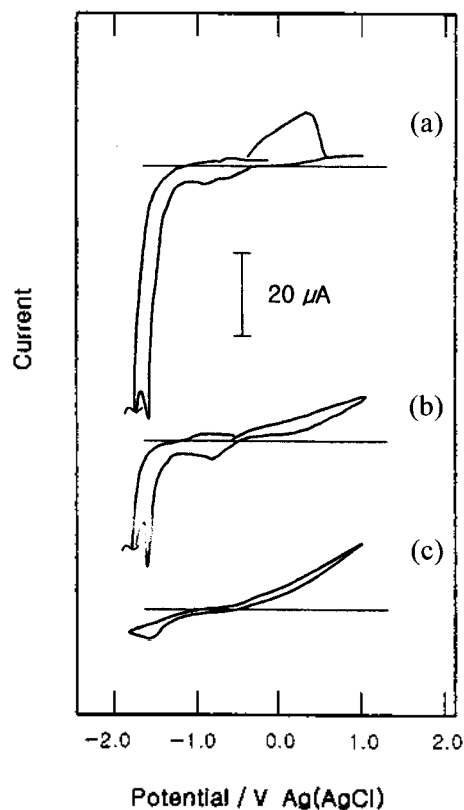
largely affected by the amount of light. Obviously, this behavior is due to the decreased concentration of the hole, generated via electron-hole separation by photons. Then, it is logical to state that the decreased amount of light vastly change the behavior of the oxidative stripping of Cd.

To specify the effect of illumination on the oxidation of Cd, the relation between the amount of oxidatively stripped Cd and potential was investigated. Direct measurement of the Cd oxidation charge was practically impossible, since the voltammetric behavior of the Cd oxidation under low level illumination did not show any distinctive feature as in Figure 1(b) and (c). Fortunately, because of the reductive behavior of Te as mentioned previously, the reduction charge of Te left after oxidative removal of Cd from a stoichiometric surface is equivalent to that of the Cd oxidation charge. The procedure for the determination of the Cd oxidation charge was as follows: holding a clean electrode at a certain potential for 2 minutes, rinsing the electrode throughly with 0.1 M Na₂SO₄ solution to remove any stripped Cd²⁺ ions at the potential and taking a negative potential scan from an open circuit potential to the hydrogen evolution region. In the cathodic scan, the Te layers left after the Cd oxidation were reduced and the reduction charge was determined by coulometry after correction with reasonably assumed background.

Figure 2 shows the relation between the amount of oxidatively stripped Cd and potential under the studied illumination levels. Regardless of illumination level, the oxidative charge of Cd clearly showed a general dependence on potential. As the oxidation potential became positive, the charge increased slowly and reached to a charge plateau of ~190 μC/cm². The theoretical oxidation charge of one Cd atomic layer, calculated from the CdTe structure and its lattice parameter,[8] is 153 μC/cm². Considering surface roughness of the studied CdTe electrodes and the uncertainty of the background assumed in measurement of Te charges, the two values are reasonably close to each other, we believe. At more positive potential than the plateau region, the observed charges reveals that more than one atomic layers of Cd were stripped. This observation clearly implies that one atomic layer of Cd can be stripped under any illumination level and that electrochemical atomic layer
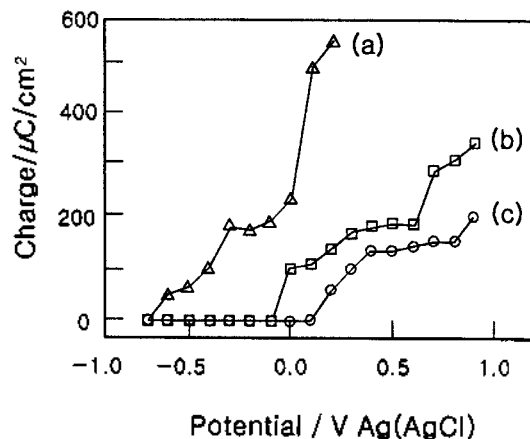


**Figure 1.** Cyclic voltammograms of a stoichiometric CdTe(100) surface in 0.1 M Na₂SO₄ solution under illumination of (a) ~40 mW/cm², (b) ~0.1 mW/cm² and (c) without light. Scan rate: 5 mV/sec.



**Figure 2.** Dependence of Cd oxidation charge on potential under illumination of (a) ~40 mW/cm², (b) ~0.1 mW/cm² and (c) without light. Refer the text for the details of charge determination.

Communication to the Editor

Bull. Korean Chem. Soc. 1998, Vol. 19, No. 12    1301

etching can be performed regardless of the presence of light.

The removal of one atomic layer of Cd was investigated further with a measurement of surface composition. In the measurement, the x-ray photoelectron spectroscopic $3d_{5/2}$ peaks of Cd (405 eV) and Te (573 eV) were utilized. The stoichiometric surface of CdTe, prepared with the previously mentioned method and known as Cd layer is the top one, showed the $I_{Te}/I_{Cd}$ value of $1.51\pm0.05$. After presumable removal of one atomic layer of Cd, the ratio was change to $2.14\pm0.12$, which indicates the amount of Te is more than that of Cd on the surface. A semiquantitative calculation[9] was performed to evaluate the surface concentration of Te, based on an assumption that the top layer is Te (for details, see reference 10). The surface concentration of Te was turn out to be $5.09\times10^{-14}$/cm$^2$, while the theoretical one calculated from the lattice of CdTe was $4.76\times10^{-14}$/cm$^2$. The closeness of the two surface concentration values strongly implies that only one atomic layer of Cd was oxidatively stripped.

Another interesting characteristics in Figure 2 is that the potential of the charge plateau shifts in the negative direction as the illumination level increases. This observation is very important in making a pattern during atomic layer etching. For an example, at $-0.2$ V, removal of one atomic layer of Cd can be achieved on a surface illuminated with light of ~40 mW/cm$^2$, while the oxidation of Cd can not be performed on an unilluminated surface. If a light image is projected on a CdTe surface during electrochemical atomic layer etching, a negative of the projected image can be etched in a depth with an atomic resolution.

In conclusion, one atomic layer of Cd on CdTe(100) was oxidatively stripped under any illumination level. However, the oxidation potential shifted in the cathodic direction as the illumination level increases. Such a photoelectrochemical behavior of CdTe(100) indicates that a light image projected on CdTe(100) surface can be utilized in etching out a pattern with an atomic depth resolution.

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# Convenient Conversion of Carboxylic Esters to Aldehydes by Oxidation of Alkoxyaluminum Intermediate with Pyridinium Chlorochromate or Pyridinium Dichromate

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The Oxidation of trialkyl borate[1] and trialkoxyboroxine[2] by pyridinium chlorochromate (PCC) affords a convenient procedure for conversion of alcohols and carboxylic acids into aldehydes. Similarly, the oxidation of alkoxyaluminum intermediate by PCC or pyridinium dichromate (PDC) provides another convenient procedure for such conversion under mild reaction conditions.[3] These methods involve the reduction of alcohols and carboxylic acids with reducing agent, BH$_3$·SMe$_2$ or AlH$_3$, followed by oxidation of the resultant reduction products, such as alkyl borate, trialkoxyboroxine or alkoxyaluminum, with oxidizing agent. From this mechanistic point of view, we decided to extend this procedure to the conversion of carboxylic esters into aldehydes. Herein we wish to introduce this new procedure which effects the transformation of carboxylic esters to aldehydes in excellent yields at room temperature.

Aluminum hydride,[4] a very versatile reducing agent, readily reduces carboxylic esters at room temperature to form alkoxyaluminum intermediate (1) as an initial reduction product, which then produces the corresponding alcohols upon hydrolysis[5] (eq 1). We believe this intermediate (without isolation) can be oxidized to aldehyde by PCC or