

A Morphological Study on a Spontaneous Photoelectrochemical Process of Cleaved CdTe(100)

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Photoelectrochemical processes on semiconductor surfaces, called as photocorrosion or photoetching depending on situations, are important in industrial applications. For examples, spontaneous photocorrosion under open-circuit potential is not desirable in solar cells, whereas intentional photoetching with potential control is crucial in fabricating surface features on semiconductors.¹

Scrutinized was a spontaneous photoelectrochemical process on cleaved CdTe(100) surface. This work is in conjunction with electrochemical digital etching (ECDE) of CdTe(100), whose object is electrochemically etching out surface features in a depth resolution of atomic scale.²⁻⁴ One of the strategies to etch out such features was proposed to be projection of a light image to control lateral reactivity of the reactions involved in the atomic manipulation,⁵ so that a spontaneous photoelectrochemical process on CdTe is likely to take place. If so, the effect of the photoelectrochemical process on ECDE should be understood for accurate manipulation. In that context, we studied the variation in surface roughness of cleaved CdTe(100) as a signal of the spontaneous photoelectrochemical process.

The cleavage of CdTe(II-VI Inc., U.S.A.), oriented toward the [100] direction, were performed by firmly pressing a nominal (100) surface with a diamond knife. This cleaving method reproducibly yielded atomically flat surfaces, which were perpendicular to the nominal (100) surface. The orientation of the cleaved surface was confirmed with TEM (Carl-Zeiss, EM-912 Ω Germany). We defined the surface prepared in this method as cleaved CdTe(100).

A photoelectrochemical process of the cleaved CdTe(100) surface was conducted under controlled illumination levels, in 0.1 M Na₂SO₄ (99+%, Aldrich, U.S.A.) equilibrated with air and without any potential control (i.e. at open-circuit potential). A light-tight box was used to control the light level reaching to the CdTe surface and the background light was negligible. Illumination was achieved with a halogen lamp, whose radiative power was controlled with supplied electric power. The illumination power was measured with an optical powermeter (Gentec Inc., TMP-310, U.S.A.).

The roughnesses of CdTe(100) surfaces were measured with an AFM (PSI, autoprobe CP, U.S.A.). A CdTe(100), subjected to a photoelectrochemical process, was rinsed with clean water and dried with N₂. The topographic images (1 $\mu\text{m} \times 1 \mu\text{m}$) of CdTe surfaces were obtained in air and were mathematically manipulated with a software (PSI, version 1.3) to calculate surface roughness (root-mean-square of height). Since a standard for height in 10 \AA regime was not

available, the height values reported in this work are uncalibrated ones.

Figure 1(a) is a typical micrograph of a cleaved CdTe(100). The image and its roughness value of $0.9 \pm 0.29 \text{ \AA}$ indicate that the cleaved surface is fairly flat in atomic scale. An exposure of the cleaved CdTe to a light ($\sim 5 \text{ mW/cm}^2$) for 8 minutes and 30 seconds in 0.1 M Na₂SO₄, led to randomly distributed pits (seen as black dots) whose diameters were less than 200 \AA as in Figure 1(b). After the development of the pits (Figure 1(c)), simple protrusions appeared at the expense of the pits (Figure 1(d)). Such small protrusions apparently transformed to quite larger features covering a considerable part of the surface, although pits were discernable among them in Figure 1(e). After a short extended exposure (35 seconds), the morphology of the surface rapidly changed to the one with homogeneously distributed pits and protrusions in Figure 1(f). The morphological variation following this change was much more dramatic. After 20 seconds, the morphology of the rough surface became quite smooth, as shown in Figure 1(g). The smoothness came from the disappearance of the pits and the reduction of the protrusions. With a prolonged exposure of the smooth surface, however, pits were formed again and the protrusions were not observed (Figure 1(h)). This particular morphology did not change further within the experimental time scale (2 hours).

Figure 2 is the variation in the surface roughness of the cleaved CdTe(100) as the photoelectrochemical process evolved. The slow increase of the roughness at the initial stage was obviously associated with the development of pits and small distinctive protrusions. With a greater rate, the surface roughness increased further as the surface was covered with the wide protrusions in Figure 1(e). When the morphology was similar to that seen in Figure 1(f), the maximum roughness of $23.7 \pm 2.71 \text{ \AA}$ was reached. Passing the roughness maxima, the roughness decreased instantaneously to show a minima, whose value was observed to be $6.5 \pm 0.85 \text{ \AA}$. After this minima, the surface roughness increased to $10.5 \pm 0.17 \text{ \AA}$ with formation of pits and depletion of protrusions. In addition, the time of the roughness maxima decreased with increasing illumination level.

Based on these morphological observations, the spontaneous photoelectrochemical process on the cleaved CdTe(100) surface may consist of five serial steps as depicted in Figure 2: pit formation, protrusion formation, wide protrusion formation, protrusion removal and pit formation. The transient roughness variation, associated with wide protrusion formation and protrusion removal, is the uniqueness of this work.

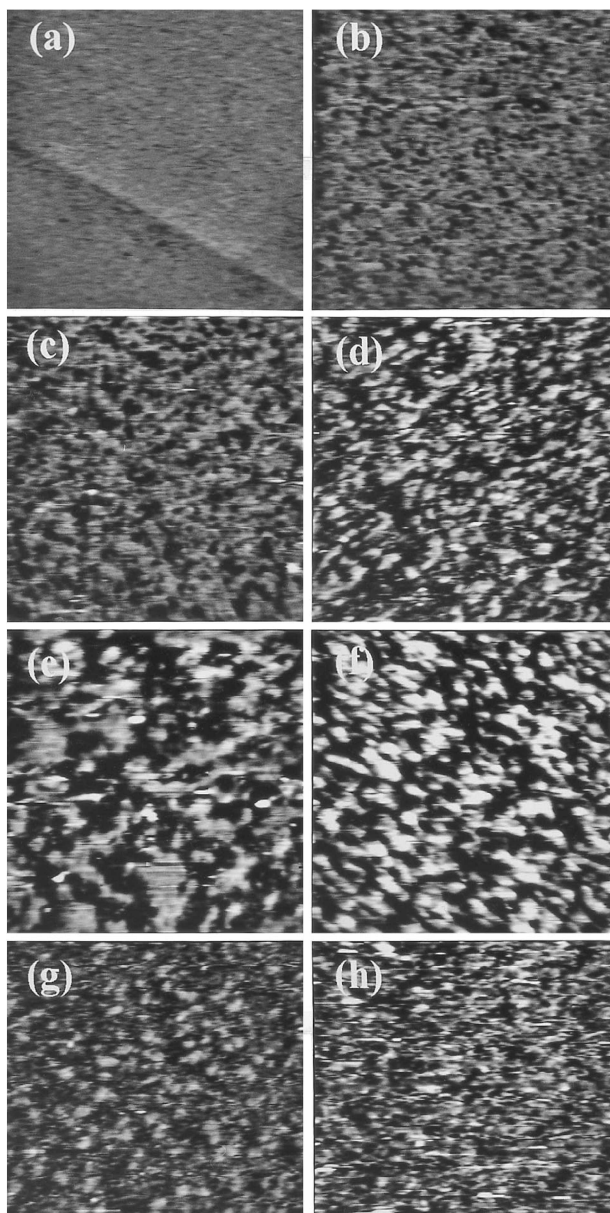


Figure 1. AFM micrographs ($1 \mu\text{m} \times 1 \mu\text{m}$) of cleaved CdTe(100) in 0.1 M Na_2SO_4 solution after exposures to the illumination of 5 mW/cm^2 for (a) 0 minutes, (b) 8 minutes 30 seconds, (c) 20 minutes, (d) 27 minutes 30 seconds, (e) 35 minutes 15 seconds, (f) 35 minutes 50 seconds, (g) 36 minutes 10 seconds, and (h) 45 minutes. Scan rate: 3 Hz. Set point: 2 nN.

In addition, these particular characteristics clearly indicate that more than a single mechanism are operational. This kind of morphological behavior during a spontaneous photoelectrochemical process on CdTe surface has not been reported, to our knowledge.

Concerning the change of the mechanism, it is sufficiently noteworthy that no oxidizing reagent was present in the solution employed in this work (0.1 M Na_2SO_4). In an open-circuit spontaneous photoelectrochemical process, known as "electroless etching",⁶ an oxidizing reagent should be presented in an etchant solution to inject holes into valence band under dark condition, or to consume photo-generated elec-

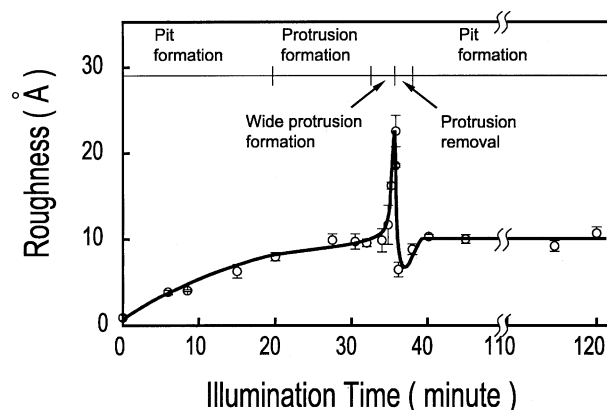


Figure 2. The variation in the surface roughness of cleaved CdTe(100) during the spontaneous photoelectrochemical process.

trons at valence band under illuminative condition. On the other hand, the collected holes at conduction band in both cases participate in oxidative removal of surface materials of semiconductor. Obviously, an oxidative removal process of the surface CdTe layer is involved in the change of the morphology. Due to the absence of any oxidizing species, a reduction reaction (or reduction reactions) responsible for the accommodation of the photo-generated electrons should exist. Any change in the unidentified reduction reaction(s) and/or its rate (their rates) is(are) may be crucial in understanding the observed morphological variation.

In conclusion, a photoelectrochemical process took place spontaneously on the cleaved CdTe(100) surface without any oxidizing reagent and the surface roughness varied in a peculiar manner. Although the reasons for these observations are not clear with the currently available data, identification of the reaction(s) consuming photo-generated electrons would be the key to understand the photoelectrochemical process on the cleaved CdTe(100) surface. In that particular direction, an investigation is in progress.

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