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Characterization of the native oxide on CdTe surfaces

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This study focuses on the description of oxidation of CdTe monocrystal surfaces after selective chemical etching. Measurements of surface morphology of the oxides occurring in short time are valuable for deeper understanding of the material degradation and fabrication of reliable devices with enhanced performance. The samples with (1 1 1) orientation were selectively etched and cleaned of oxide. Exposure of the oxide-free surfaces of CdTe to air at normal atmospheric conditions over 24 hours leads to an appearance of characteristic surface features. The oxidized surfaces were investigated by scanning electron microscopy, scanning probe microscopy, Raman spectroscopy and ellipsometry. The results indicate clear differences in the oxidation of Cd-terminated and Te-terminated surfaces.

Keywords: *selective etching; scanning probe microscopy; ellipsometry; Raman spectroscopy*

1. Introduction

Cadmium telluride (CdTe) is a promising material for sensing applications. Estimation of surface condition is one of the key problems for design of devices. Surface processing and preparation influence the quality and reliability of the electronic components [1–5].

The surfaces of CdTe monocrystals are susceptible to alteration upon exposure to ambient conditions. Oxidation is one of the factors affecting surface morphology. X-ray photoelectron spectra of amorphous $CdTeO_x$ were investigated in detail by Amezaga et al. [6]. Optical characterization of long-term (in the range of weeks and months) CdTe oxidation was presented by Zázvorka et al. [7]. In spite of the number of studies on CdTe oxidation, a lot of information is still needed to build a comprehensive description of the effect of oxidation on CdTe surfaces.

Here, for the first time, we have observed the morphology of both Cd- and Te-terminated surfaces after short time exposure to air at normal atmospheric conditions. The study of the surfaces is supported by Raman spectroscopy and ellipsometry. Previous scanning probe microscopy (SPM) studies proved to be informative for characterization of CdTe surface behavior after various surface treatments, including selective etching after annealing [8], and sputter-anneal processing [9]. We applied semi-contact mode and phase contrast imaging for characterization of oxidized surfaces. A suitable choice of the methods from the SPM family allows surface inspection at the nanoscale level [10–15].

2. Materials and methods

Monocrystals of CdTe were selectively etched and subjected to oxidation at normal conditions. Exposure of an oxide-free surface of CdTe to air leads to the appearance of characteristic surface

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features. Experiments show differences in morphology between A and B surfaces after 24 hours oxidation in air.

A Renishaw inVia with a green laser was used to obtain Raman spectra. The power of the laser was 12 mW. Raman spectroscopy is a local technique, for this reason the measurement was done on two samples at several random points to obtain reliable data and all experiments were carried out in the same laser exposure time. We decreased the laser power down to 10 % to avoid heating of the sample and degradation of the thin amorphous oxide layer. The use of low power laser helped us to avoid laser-induced Te aggregation and bond dissolution [16].

The oxidized surfaces were inspected by a Verios scanning electron microscope. Morphological contrast, in addition to electron microscopy, was studied by atomic force microscopy (AFM) in semi-contact mode with phase contrast imaging. The NTEGRA Prima setup was used for AFM investigation by NSG01 probes with 6 nm tip curvature radius. Optical properties of the crystal surfaces were studied by VASE ellipsometry at three angles of incidence (50°, 60° and 70°) to obtain the highest sensitivity of the surface properties. The accuracy of ellipsometry allows for the estimation of the layer thickness with a precision of several angstroms. This is valuable in the case of thin oxide layers studied here. According to the literature [17], the thickness of the oxide layer should be about 0.5 nm. We used Fresnel equations (existing in VASE-software) and materials (CdTe, CdTe oxide) for evaluation of the surface thickness. The ellipsometric spectra contain both experimental measurements (psi, delta parameters) and modeling curves, calculated with consideration of the surface roughness obtained by AFM.

3. Results and discussion

This study explores difference in oxidation and emphasizes the variation of properties at the two faces of a CdTe monocrystal. Here, we compare the results of the examined Cd-terminated surface (A) and Te-terminated surface (B), obtained by independent measurement techniques.

The A-surface is more homogeneous: the surface roughness measured in a 5 μm × 5 μm area is half of that of the B-surface (Fig. 1a and Fig. 1b). A larger scan area (20 μm × 20 μm) reveals the presence of surface features with up to 300 nm height for the B-surface, while the maximum height in topographic maps of the oxidized A-surface is about 100 nm (Fig. 1c and Fig. 1d). The same features are observed in phase contrast imaging. Fig. 1e and Fig. 1f show the qualitative comparison of the surfaces where we can follow the appearance of new features at the morphology for the B-surface, indicated by the scale of the phase shift of the cantilever oscillations (twice as large for A-surface as for B-surface). This result is in agreement with the literature [18], where it is mentioned that Te-oxide is responsible for a rougher topography and lower homogeneity surface structure. Wavelet analysis allows evaluation of surface texture [19, 20]. Fig. 1c and Fig. 1d represent results of continuous wavelet transform which was performed using Gwyddion software.

Physical microstructure, shown in the SEM images (Fig. 2a and Fig. 2b), reveals characteristic features of the A and B surfaces. The SEM images are closer to phase imaging than SPM. It could be explained by the fact that SEM imaging also takes information from several near surface atomic layers and is defined by physical properties of the surface. AFM deals only with topography [21–23]. The presence of difference between phase contrast and topographical imaging obtained by AFM is also supported by the SEM measurements.

Ellipsometric spectra in Fig. 3a to Fig. 3c refer to a thin (few monoatomic layers) oxide film on the surfaces of the monocrystal: dotted lines are experimental data and solid lines are modeled data. The delta parameter best reveals the difference between the two surfaces after oxidation. Simulation (taking into account surface roughness and CdTe oxide thin film presence) provides the thickness of the oxide layer equal to 0.3 nm for both surfaces. The spectra (Fig. 3a) measured at the angle of incidence of 50° do not exhibit any difference in psi-parameter for A and B surfaces. The difference in the data for the two surfaces is better observed at the highest angle of incidence (Fig. 3c).

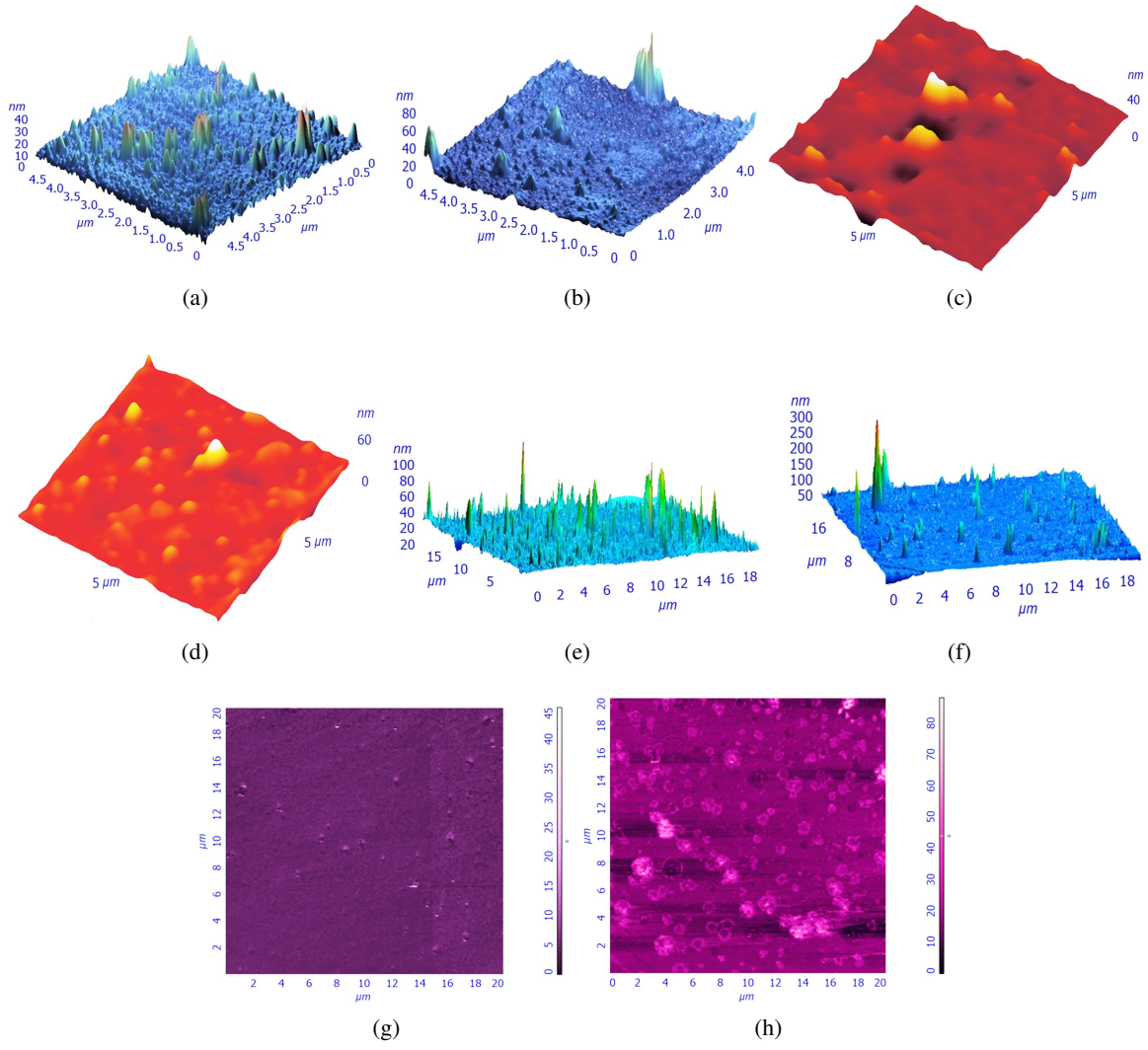


Fig. 1. Atomic force microscopy images at different scales (a), (b), (e), (f); wavelet-transformed images (c), (d) and phase contrast imaging (g), (h); (a), (c), (e), (g) for Cd-terminated surface; (b), (d), (f), (h) for Te-terminated surface.

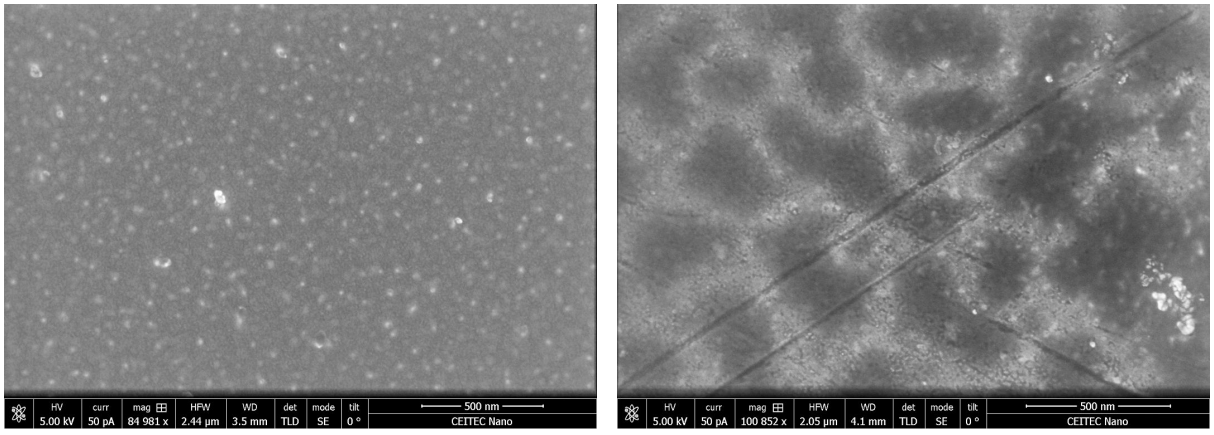
Ellipsometry results indicate lower Psi-parameter and larger Delta-parameter of Te-terminated surface (red line) in comparison to Cd-terminated surface (black lines).

Raman spectra have several peaks with different parameters for A and B oxidized surfaces. The dotted lines (Fig. 4a and Fig. 4b) are Raman spectra of A and B surfaces without oxide, immediately after cleaning. Two solid lines (black and red) are the spectra of two different samples with Cd-terminated (Fig. 4a) and Te-terminated (Fig. 4b) surfaces after exposure to air. This helps to present average information and to avoid errors and artifacts in the measurement.

Changes in intensity ratio of the three peaks at 90 cm^{-1}, ~125 cm^{-1} and ~142 cm^{-1} (which refer to Te (TO of E and A_2 symmetry), Te (LO of A_1 symmetry) and CdTe (TO) + Te (E symmetry) respectively) indicate more significant changes of the tellurium chemical bonds at Te-terminated surface.

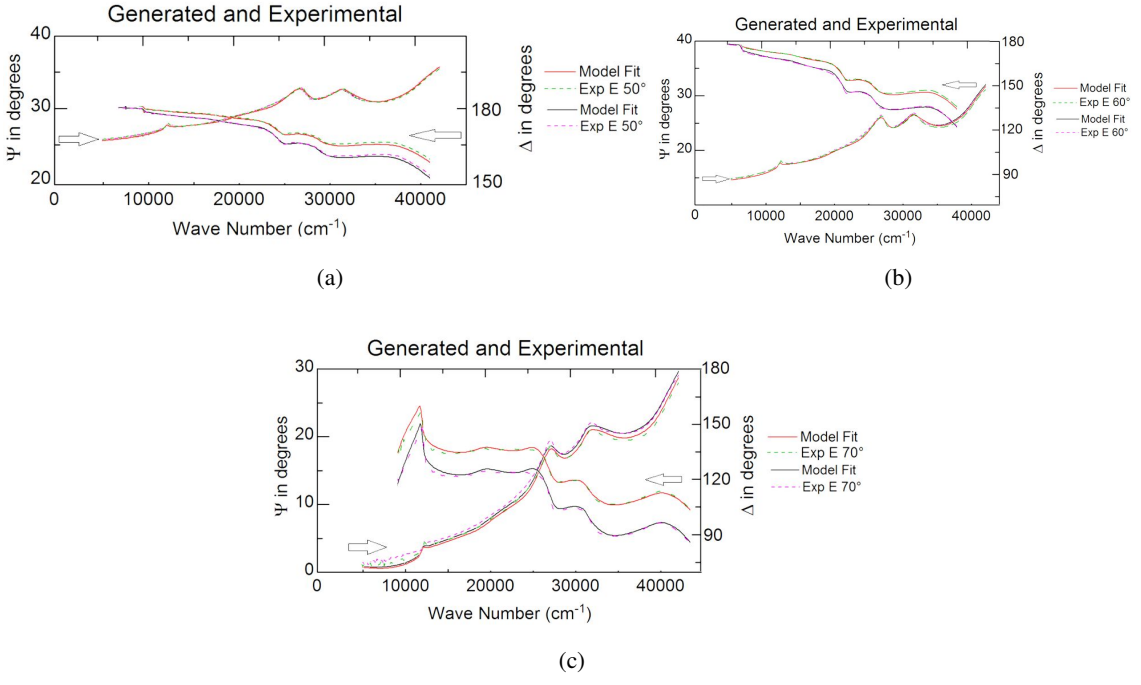
4. Conclusions

We examined the differences in the oxides on Cd- and Te-terminated surfaces of CdTe monocrystals after selective chemical etching. Surface conditions after a short oxidation time were investigated



(a) (b)

Fig. 2. SEM-images: (a) Cd -terminated surface, (b) Te -terminated surface.

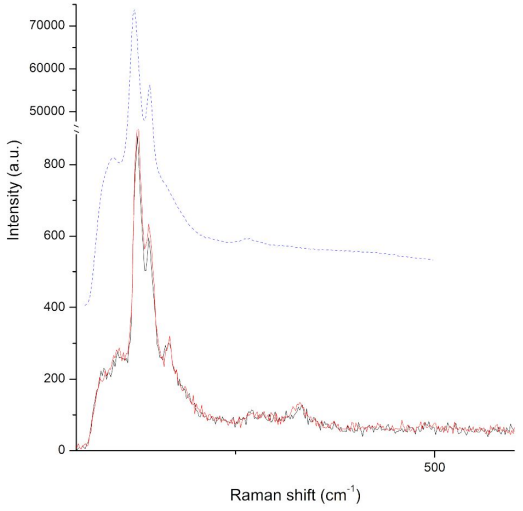


(a) (b)

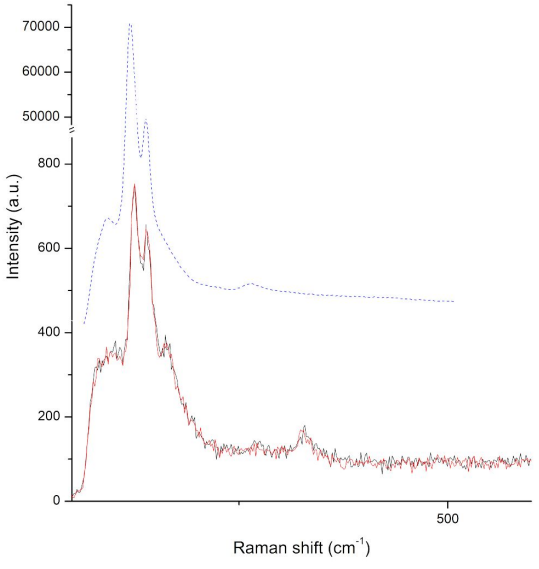
(c)

Fig. 3. Ellipsometric spectra: black lines for Cd-terminated surface; red lines for Te-terminated surface.

by SPM, SEM, Raman spectroscopy and ellipsometry. The results can be very useful in studying the long-term oxidation of CdTe. Measurements of the surface morphology of the oxides occurring over a short time (e.g. 24 h) are valuable for deeper understanding of material degradation and the fabrication of reliable devices. It is important to take into account the exposed face of the crystal after selective etching: here, we examined the differences in morphology and optical properties of the native oxides on Cd- and Te-terminated surfaces of CdTe. All presented results are complementary and consistent. Further work will be connected with the analysis of textures of the oxides on the surfaces



(a)



(b)

Fig. 4. Raman-spectra of (a) Cd-terminated and (b) Te-terminated surfaces.

of CdTe. Numerical characterization of surface micromorphology should provide data for modeling and prediction of oxides growth.

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