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Spectroscopic, microscopic, and internal stress analysis in cadmium telluride grown by close-space sublimation

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ABSTRACT

High quality materials with excellent ordered structure are needed for developing photovoltaic and infrared devices. With this end in mind, the results of our research prove the importance of a detailed, comprehensive spectroscopic and microscopic analysis in assessing cadmium telluride (CdTe) characteristics. The goal of this work is to examine not only material crystallinity and morphology, but also induced stress in the deposit material. A uniform, selective growth of polycrystalline CdTe by close-space sublimation on patterned Si(111) and Si(211) substrates is demonstrated by scanning electron microscopy images. Besides good crystallinity of the samples, as revealed by both Raman scattering and Fourier transform infrared absorption investigations, the far-infrared transmission data also show the presence of surface optical phonon modes, which is direct evidence of confinement in such a material. The qualitative identification of the induced stress was achieved by performing confocal Raman mapping microscopy on sample surfaces and by monitoring the existence of the rock-salt and zinc-blende structural phases of CdTe, which were associated with strained and unstrained morphologies, respectively. Although the induced stress in the material is still largely due to the high lattice mismatch between CdTe and the Si substrate, the current results provide a direct visualization of its partial release through the relaxation effect at crystallite boundaries and of preferential growth directions of less strain. Our study, thus offers significant value for improvement of material properties, by targeting the needed adjustments in the growth processes.

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1. Introduction

The benefit of strong quantum confinement effects in chalcogenide narrow-gap semiconductors such as cadmium telluride (CdTe) makes them valuable candidates for potential applications to solar energy conversion and infrared devices [1–5]. Despite the fact that they have been studied extensively, there are still obstacles to the full use of their characteristics, generally because of the lack of success in fabricating defect-free large areas of these materials (*i.e.*, without voids and cracks in thin film single crystals, and without twinning in polycrystalline materials). In so far as deposition substrates for the development of infrared devices are concerned, the transparency of silicon (Si) in this spectral region, its inexpensive commercial availability with predefined crystallographic growth directions, and its straightforward use in signal processing, makes it most suitable. However, the significant mismatch of about 20% between the lattice constants of 5.43 Å for Si and 6.48 Å for CdTe, still remains the main impediment to growing high quality CdTe on such a substrate, emphasizing the importance of finding ways to reduce the induced interfacial stress [1–6]. Alternative substrates, insertion of buffer layers, and material doping have been investigated as possible solutions to this problem [2,3,6]. For example, one of the most commonly used interfacial buffer layers, ZnTe, has a lattice mismatch of 12.3% with Si and of 7% with CdTe [2]. Thus, through gradual stress relieve, improvement in the morphology of the material is achievable. Reduction of dislocation density in CdTe has also been observed for different preferential orientations of Si substrates [7–10]. For instance, CdTe grown on Si(211) misoriented 5° towards the [111] crystallographic direction resulted in a decrease of twin formation along the CdTe(211) orientation [10].

The goal of this work is to explore, by detailed spectroscopic and microscopic analyses, if the growth of polycrystalline CdTe on patterned Si(111) and Si(211) substrates results in fewer defects and, consequently, enhancement of material properties. Not only we seek to elucidate if the reported surface energy differences between Si(111) and Si(211), with the former having the lowest energy [11], has an effect on the average dimension of CdTe grains, but also if the induced interfacial stress is minimized in the currently employed selective growth method, with crystallite formation directly on top of 1 μm diameter Si pillars and no incorporation of an additional buffer layer.

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Infrared (IR) absorption and Raman spectroscopies, which are the main techniques employed in the current analysis, have proven useful in monitoring material morphology, as well as in revealing potential size-confinement phenomena [12–21]. Material crystallinity was usually evaluated by comparison of phonon modes measured in microcrystallites with corresponding modes in the bulk material, such as acoustical phonon modes (*e.g.*, transverse acoustical (TA) and longitudinal acoustical (LA) modes), optical phonon modes (*e.g.*, transverse optical (TO) and longitudinal optical (LO) modes), and their overtones and combinations [12,16,17,19]. Broadening and shifting of the TO and LO lines due to phononic mode mixing and size-confinement effects in small crystallites, and the appearance of surface optical (SO) modes forbidden in the bulk configuration, were reported [13,14,20–22]. It has also been shown that with increasing pressure, CdTe undergoes a structural phase transition from a cubic (zinc-blende) phase under normal conditions to a rock-salt structure under pressure [23,24]. Considering these facts, we present here a confocal Raman mapping investigation, which allows a direct visualization of the local distribution of these phases in the grown CdTe. Consequently, a qualitative estimation of the induced stress in the material can be obtained by comparing the presence of the CdTe rock-salt phase (*i.e.*, strained phase) with that of an unstrained, zinc-blende structure. This information is essential if strain reduction in the material through different growth approaches is sought, and cannot be obtained from other imaging techniques such as scanning electron microscopy (SEM). Thus, the current results demonstrate Raman versatility beyond that of its standard employment in spectral analysis, as previously reported [12–17]. Complementary analysis of material morphology and crystallinity by SEM and IR absorption measurements are presented and discussed, too. We also consider and investigate the potential existence of size-confinement phenomena in the far-IR spectral region.

2. Experimental details

The CdTe polycrystalline samples for this study were selectively grown using close-space sublimation (CSS) on top of 1 μm diameter pillars of patterned Si(111) and Si(211) substrates of 1 cm × 1 cm dimensions. The photolithography process was performed by coating the wafers with negative photoresist and exposing them for 17 s to ultraviolet light. A MJB3 mask aligner with a 2 μm window was used. The Si substrates were isotropically dry etched using sulfur hexafluoride (SF_6) gas in an Oxford Plasma laboratory etcher, to result in 1 μm diameter pillars with 700 nm to 1 μm heights. To eliminate surface contaminants, the patterned substrates were cleaned by immersion in a piranha solution consisting of H_2O:NH_4OH:H_2O_2 with a ratio of 5:1:1 for 10 min. at a temperature of 130 °C. Prior to each deposition, the native Si oxide layer was removed using a buffered oxide etch (BOE) solution for 10 s and the likely thin oxide layer formation at the surface of the CdTe(111) single crystal source (Keystone Crystal Co.) was eliminated by annealed the source for 30 min at 600 °C. Also, the reactor chamber was purged with helium to reduce the potential oxygen contamination. During the 5 min. deposition, the temperatures of the source and the substrate were kept constant at 550 °C and 450 °C, respectively. They were monitored with Eurotherm thermocouple controllers that were attached to graphite blocks located above the substrate and below the source.

The SEM images were acquired with a Hitachi S4800 scanning electron microscope at an accelerating voltage set to 20 kV. An alpha 300R WITec system equipped with a 532 nm frequency-doubled Nd:YAG laser and a 100× objective lens was used for performing the confocal Raman measurements, which were collected at ambient conditions. In addition to the WITec Control software that controls the piezoelectric stage for sample scanning, and which is normally employed for data acquisition, the Cluster Analysis K-Means of the WITec Project Plus software was employed in the analysis of structural phase separation data. The far-IR transmission measurements were acquired in vacuum, at room temperature, with a Bruker IFS 66v FT-IR spectrometer equipped with a Ge-coated mylar beamsplitter and a deuterated triglycine sulfate (DTGS) detector. For each IR spectrum, data accumulation was performed for 256 scans at a resolution of 4 cm^{-1}.

3. Results and discussion

Representative SEM and confocal Raman images of samples grown on Si(111) substrates are presented in Fig. 1(a) and (b), respectively. A uniform pattern of CdTe crystallites with sizes varying between 2.3 μm and 4.8 μm and with clearly defined grain boundaries is revealed by the SEM image in Fig. 1(a). Subgrains can be observed in this image, along with grains with smooth, flat surfaces that demonstrate the high quality of the grown material.

On the basis that with increasing pressure CdTe undergoes a phase transition from zinc-blende to rock-salt [23,24], together with the fact that the first order LO Raman scattering mode while allowed by symmetry in the former structure, is forbidden in the latter, we performed confocal Raman mapping for detecting and monitoring the potential co-existence of these phases. The Cluster Analysis K-Means software and appropriate filters for the Raman signatures of the two CdTe morphologies, such as the LO band centered around 170 cm^{-1} for the zinc-blende structure and the 2LO feature at 329 cm^{-1} for the rock-salt phase, were considered in obtaining the Raman mapping image shown in Fig. 1(b). Two pseudo-colors were assigned to these phases, namely yellow for the rock-salt phase and brown for zinc-blende. Besides a dominant yellow color, which shows that, generally, the material is under the expected induced stress, there is a slight presence of unstrained CdTe structure (*i.e.*, brown color) at every crystallite boundary. Since in the current patterned growth process part of each CdTe crystallite will be located outside the pillar top in the 2 μm separation between pillars, we associate the observed partial release of the stress and the existence of unstrained structure, potentially, to the contribution of the grain relaxation effect at its boundary.

Corroborative spectral results are provided in Fig. 1(c), where the integrated Raman spectrum of this confocal image and the standard Raman spectrum of a free standing polycrystalline CdTe film are presented. While a well defined Raman vibration attributed to the LO mode is seen in the film spectrum, suggesting its zinc-blende morphology, the 2LO band is the strongest CdTe feature in the integrated Raman spectrum. This observation is in agreement with our affirmation regarding the dominance of a strained rock-salt structure in the deposited material. On the other hand, the very low intensity of the LO Raman peak in the integrated Raman spectrum also confirms the scarceness of the unstrained phase. The position of the LO peak for the polycrystalline CdTe at about 170 cm^{-1} is shifted by approximately 22 cm^{-1} with respect to the reported value for bulk CdTe [16–18]. Comparable large shifts of this Raman line were observed and interpreted in terms of strong spatial confinement of phonons in low-dimensional CdTe [12–21]. Other combinations of phonon lines such as the LO + LA at 214 cm^{-1} and the LO + TO at 267 cm^{-1} could also be seen in both Raman spectra [16–18].

At a glance, similar behavior with an overall presence of a strained structure is depicted in the confocal Raman image of a sample grown on Si(211), which is presented in Fig. 2(a). A closer look at this image also reveals a slight increase in the average size of the crystallites, implying that indeed the substrate orientation might have an influence on the dimensions of the grains. However, given that an intrinsic grain size variation is expected, this observation could be rather conditional. More importantly, a preferential direction for the release of the stress is observed in this image, which is implied by the uneven thickness of the unstrained phase at the crystallite boundaries (*i.e.*, brown pseudo-color) and the elongation of strained phase images that define the grain shapes. Since the material will favor growth in a direction with less induced strain, this information is valuable for improving the fabrication procedure through appropriate orientation of the mask or

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