Journal of Alloys and Compounds 590 (2014) 153–156

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Berkovich nanoindentation-induced dislocation energetics and pop-in effects in ZnSe thin films

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ARTICLE INFO

Article history:
Received 16 November 2013
Received in revised form 11 December 2013
Accepted 11 December 2013
Available online 18 December 2013

Keywords:
ZnSe thin film
Nanoindentation
Pop-in
Transmission electron microscopy

ABSTRACT

The Berkovich nanoindentation-induced characteristic "pop-in" phenomena observed in ZnSe thin films are investigated in this study. The ZnSe thin films are grown on the GaAs(001) substrates by using the molecular beam epitaxy (MBE) system. No evidence of nanoindentation-induced phase transformation was revealed in ZnSe thin film by the cross-sectional transmission electron microscopy (XTEM) and selected area diffraction (SAD) analyses. Furthermore, as displayed in the SAD results, the distortion of diffraction spots did indicate severe deformation of indented ZnSe thin films resulting from the nanoindentation load. Based on this scenario, an energetic estimation of dislocation nucleation is made.

1. Introduction

Nanoindentation is a widely recognized method to investigate the fundamental mechanical properties of various nano-scale structured materials [1–3] and thin films [4–10], such as the hardness and Young's modulus. This method has many other potential applications in various fields, e.g., investigation of phase transformation [11,12] and fracture behaviors of materials [13,14]. The difference between the elastic and plastic deformation behaviors enables the analysis of the mechanical responses. The initial segment of the load–displacement curve resulting from nanoindentation is usually the manifestation of the elastic behavior, whereas the onset of plastic deformation is generally associated with a displacement discontinuity, *i.e.* the characteristic "pop-in" event, during the loading process [15–17]. Analysis of each part of the curves provides prominent information about the mechanical behaviors of the material under investigation.

Previous nanoindentation study on ZnSe single crystals by Grillo et al. [18] concluded that no obvious pop-in event could be discerned in the load–displacement curves. However, since the onset of nanoscale plasticity and mechanical properties are strongly influenced by various factors, such as crystal orientation [19], temperature [20] and the tip geometry of indenter [21] during nanoindentation measurements, the interplays between the observed pop-in event and the onset of micro/nanoscale plasticity in ZnSe thin films remain to be clarified. In this study, the characteristic pop-in behaviors and mechanical deformation mechanisms of ZnSe thin films derived from nanoindentation with a Berkovich indenter were extensively investigated in conjunction with the observations of cross-sectional transmission electron microscopy (XTEM). We note that the use of the Berkovich indenter not only reflects the more realistic situations might be encountered in real applications but also will result in much higher local pressure with similar load, and hence, will be helpful in clarifying the issue of indentation-induced structural deformation. In particular, based on the classical dislocation theory [22], the number of dislocation loops formed in the first pop-in event can be estimated, which in turn may shed some light on the understanding of deformation behaviors and mechanisms of ZnSe thin films at the nanometer-scale.

2. Experimental details

Experimentally, the ZnSe thin films were grown on the semi-insulating GaAs(001) substrates by means of molecular beam epitaxy (Veeco EPI 620 MBE). Knudsen cells were used to evaporate Zn and Se sources. The fluxes of Zn and Se were calibrated using a movable linear flux gauge under the substrate holder. The substrates were mounted on the substrate holder using indium. Following desorption of native oxide, the substrate temperature was reduced to 320 °C to grow the ZnSe thin films. All ZnSe thin films investigated in this study were about 600 nm thick.

Nanoindentation tests were performed on a MTS NanoXP® Nanoindenter system (MTS Cooperation, Nano Instruments Innovation Center, Oak Ridge, TN, USA) with a diamond pyramid-shaped Berkovich-type indenter tip. The radius of curvature of the tip is 50 nm. The cyclic nanoindentation tests were performed in a sequence described as followings. We first apply the indentation loading to the set maximum load and unloading by 90%. Then, reload the indenter to the maximum load and unload it by 90% again. At this stage, the indenter was hold for 5 s at 10% of the maximum load for thermal drift correction. After that, the indenter was completely unloaded and, thus, finished a cyclic nanoindentation test for a certain targeted maximum load.

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0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.12.103

The typical load–displacement curves comprise with four cyclic tests at maximum loads of 1.2, 2.4, 5.0 and 10 mN are clearly shown in Fig. 1 (ten nanoindentation tests are plotted). The thermal drift was kept below ±0.05 nm/s for all indentations considered in this work. The same loading/unloading rate of 10 mN/s was used. At least 10 indents were performed at an indentation load of 10 mN in order to obtain good statistics and, the nanoindentations were sufficiently spaced to prevent from mutual interactions. In addition, the hardness and Young's modulus of ZnSe thin films were measured by a continuous stiffness measurements (CSM) technique [23] with a constant nominal strain rate of 0.05 s^{-1}. The hardness and Young's modulus of ZnSe thin films, obtained from the load–displacement curves by using the analytic method developed by Oliver and Pharr [24], are 2.0 ± 0.1 GPa and 72.6 ± 0.5 GPa, respectively.

The cross-sectional transmission electron microscopy (XTEM) samples near the indented regions were prepared by means of a dual-beam focused ion beam (FIB, Nova 220) station with the Ga ions being accelerated at a voltage of 30 keV. Prior to milling, a layer of 1 μm-thick Pt was deposited on the ZnSe surface to prevent from damages introduced by the FIB processes. In addition, the XTEM lamella specimen was examined in a JEOL 2010F TEM (JEOL Ltd., Tokyo, Japan) operating at 200 kV with a point-to-point resolution of 2.3 nm and a lattice resolution of 0.10 nm.

3. Results and discussion

The typical load–displacement curves with a maximum indentation load of 10 mN are displayed in Fig. 1. The enlargement of the load–displacement curves in the inset of Fig. 1 clearly exhibits a series of bursts, known as the characteristic "pop-in" phenomena, occurring at a similar critical load (P_{cr}) of about 0.13–0.17 mN. Such characteristic "pop-in" event has been reported in numerous materials [25] and corresponds well to the sudden decrease in the hardness of indented materials [26]. The occurrence of characteristic "pop-in" event has been linked to the abrupt plastic flow generated by the high-density of dislocation nucleation and propagation [17,27], the formation of cracking [14,28] or the phase transformation [12]. In particular, the reverse discontinuity during unloading curve, the so-called "pop-out" event, commonly observed in Si and has been attributed to pressure-induced phase transformation [12], which is not observed here. As revealed by the SEM photograph shown in Fig. 2, the substantial pile-up along the edges of the residual indented pyramid is observed. Therefore, the cause of the pop-in event may have been complicated by the involvement of the Berkovich indentation-induced pile-up phenomenon on the surface of ZnSe thin film. Nevertheless, if the dislocation nucleation and subsequent propagation are indeed the primary mechanisms for the observed pop-in, it should prevail underneath the indented surface. It is also interesting to check if there is any pressure-induced phase transformation involved.

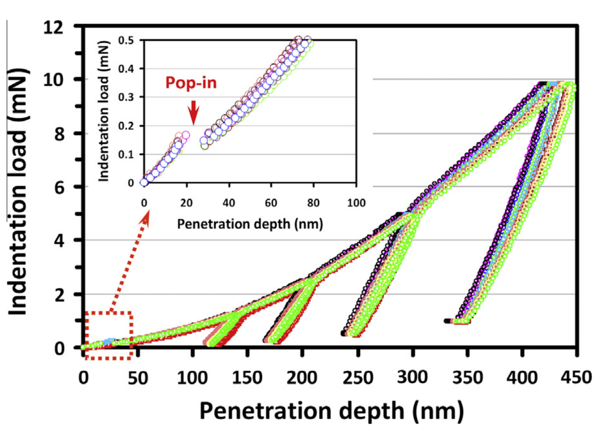

Fig. 1. The typical load–displacement curves obtained at an indentation load of 10 mN for ZnSe thin film. The inset: the magnified characteristic "pop-in" phenomena are observed.

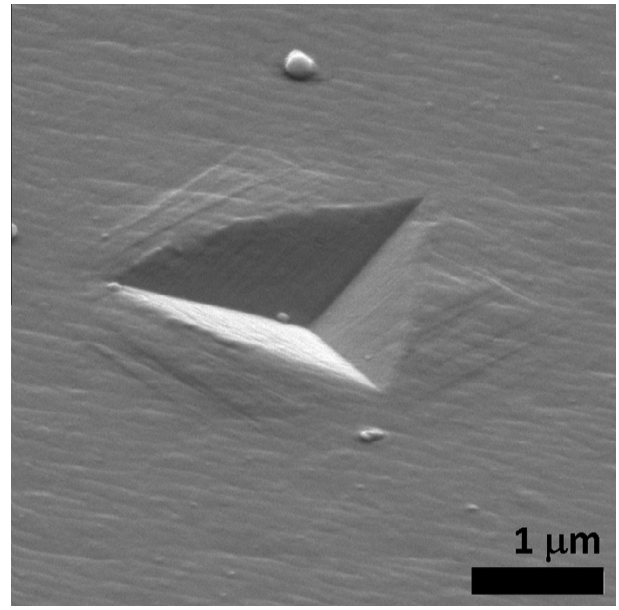

Fig. 2. SEM micrograph on an "indented" ZnSe thin film showing the pile-up event along the edges of the Berkovich indent after an indentation load of 10 mN.

According to the previous studies [29,30], ZnSe transformed from the low-pressure zinc blende phase into a site-ordered NaCl phase at a pressure around 13 GPa. Subsequently, a very slow continuous transition from NaCl → Cmcm structure has been observed at 30 GPa [31]. These values are, however, significantly higher than the apparent room-temperature hardness obtained for the present ZnSe thin films. Furthermore, the SEM image displayed in Fig. 2 does not reveal any characteristic of the pressure-induced metallization, either. We suspect that, in the thin film–substrate system, the indentation load applied to thin film may have been partly absorbed by the substrate and distributed over a much larger area. Consequently, the local stress concentration beneath the indenter is significantly reduced to values insufficient for phase transformation to occur. As will be presented below, the XTEM observations should shed some light to clarify some of the issues concerning the nanoindentation-induced phase transformation in ZnSe thin films.

Fig. 3 shows a bright-field XTEM image of ZnSe film after subjecting to an indentation load of 10 mN. It can be found that, although the deformation-induced strain directly underneath the indent is quite severe, there is neither any cracks in the entire film cross-section nor delamination in the vicinity of film/substrate interface. As suggested from the rather uniformly distributed heavily strained features, the nanoindentation-induced deformation seems to extend over the entire film, presumably due to the excellent interface coherency between the ZnSe thin film and GaAs substrate. It is also interesting to note that there is no deformation at the interface of ZnSe thin film and GaAs substrate other than the bending contours, indicating that this indentation load is insufficient to initiate measurable deformation in the GaAs substrate, thus no nanoindentation-induced slip bands should be expected. The local compressive plastic strain evidently results in accumulation of high-density of dislocations in ZnSe thin film beneath the indentation region. Furthermore, the selected area diffraction (SAD) analysis of the deformed area shown in Fig. 3 does not reveal any halo rings or diffraction spots from other phases. Consequently, it is plausible to state that ZnSe thin film did not undergo the amorphization or phase transformation in the present Berkovich nanoindentation scheme.