Deformation behavior during nanoindentation of epitaxial ZnO thin films on sapphire substrate

R. Navamathavan a,⁎, Kyoung-Kook Kim a, Dae-Kue Hwang a, Seong-Ju Park a, Tae Geol Lee b, Gwang-Seok Kim b, Jun-Hee Hahn b

a Nanophotonic Semiconductor Laboratory, Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, South Korea
b Chemical Metrology and Materials Evaluation Division, Korea Research Institute of Standards and Science, Yuseong, Daejon 305-600, South Korea

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Abstract

Nanoindentation studies were carried out on epitaxial ZnO thin films on (0001) sapphire substrates grown by radio frequency magnetron sputtering. A single discontinuity (‘pop-in’) in the load–displacement curve was observed at a specific depth (13–16 nm) irrespective of the film thickness. The physical mechanism responsible for the ‘pop-in’ event in these epitaxial films may be due to the nucleation, propagation and interaction behavior of the glissile threading dislocations during mechanical deformation. Indentation well below the critical depth was found to be plastic deformation behavior (residual impression of 4 nm).

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1. Introduction

Recently, epitaxial ZnO thin film has rapidly emerged as a promising analogue to GaN because of its large band gap of 3.37 eV and large exciton binding energy of 60 meV [1,2]. A successful fabrication of optoelectronic devices based on epitaxial ZnO thin film requires an understanding of the mechanical properties of this material as well as its optical and electrical properties. The former are of special concern since heteroepitaxy using typical substrates (e.g., sapphire) involves high lattice mismatch. Nanoindentation has emerged as the most important probe, both in basic research and industrial applications for investigating the mechanical properties of dimensions ranging from few nanometers to few microns.

Studies on the mechanical deformation of ZnO bulk single crystal have already been reported by Kucheyev et al. [3] and Bradby et al. [4]. Multiple discontinuities in load–displacement curves obtained by using a spherical indenter were observed and attributed to the initiation of the slip [3]. Further, nanoindentation studies of nanocrystalline ZnO and ZnO epitaxial whiskers have been reported [5,6]. A recent study reported that the absence of ‘pop-in’ events in ZnO epitaxial layers grown on a- and c-axis sapphire, were due to the strain compensation site present in the material [7]. The purpose of this article is to give the deformation behavior of epitaxial ZnO thin films during nanoindentation. We also discuss how the defect structure becomes responsible for the ‘pop-in’ event in epitaxial films and correlate it with bulk ZnO single crystal.

2. Experimental

The epitaxial ZnO thin films were grown on (0001) sapphire substrates using a horizontal-axis type rf magnetron sputtering technique. In order to study the effects of thickness, films with the thickness of 0.4, 0.6, 0.8 and 1.0 μm were prepared with rf power of 120 W (growth rate, 1 μm/h) at a growth temperature of 750 °C. The grown films were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), Rutherford backscattering spectroscopy, photoluminescence...
and X-ray diffraction techniques. These results revealed that the epitaxial ZnO thin films have good crystalline characteristics. A detailed description of the growth and structural characterization was provided elsewhere [8,9]. High quality bulk single-crystal ZnO samples used in this study were commercially purchased from Cermet Inc.

Indentations were made using Nanoindenter XP (MTS) with a dynamic contact module (DCM) head. The indenter tip in the nanoindentation system is a Berkovich diamond tip with a tip radius of approximately 80 nm. The nanoindentation system was fully calibrated using fused silica as a standard sample before the measurements. The measurements were carried out by loading to the maximum load; then unloading to 95% and holding for 20 s for the thermal drift correction of the sample; and then complete unloading. The deformation loading and unloading was controlled by strain rate and load, respectively. All indentations were made at a depth less than 10% of the total film thickness in order to avoid the influence of the substrate effect on ZnO films.

3. Results and discussion

Fig. 1 shows the load–displacement curve of the epitaxial ZnO thin film with 0.8 μm thickness. The maximum indentation depth is 55 nm, which is corresponding to the applied load of 0.58 mN. This curve exhibits a single discontinuity (also referred as ‘pop-in’) at an indentation depth of 14 nm during loading. The shape of the load–displacement curve is related to the tip geometry, plastic flow behavior and the elastic properties of the material. Interestingly, all other films irrespective of their thickness showed this ‘pop-in’ phenomenon consistently at similar depths (namely 13–16 nm). Further, we observed only a single ‘pop-in’ event, no other ‘pop-in’ even when the indentation depth was increased even up to 125 nm and no ‘pop-in’ was observed during the unloading phase. This is in contrast with the results of ZnO epitaxial films reported earlier by Coleman et al. [7]. The origin of this discrepancy is not clear at present. Perhaps, our nanoindentation study used the Berkovich indenter rather than the spherical indenter. One likely explanation for the ‘pop-in’ event in the case of the heteroepitaxial films can be attributed to the defects invariably present inside these films. The in-plane epitaxial relationship of the ZnO thin film on α-Al2O3 (0001) substrates was found to be ZnO [1010] || α-Al2O3 [1120], indicating a 30° rotation of the ZnO unit cell with respect to the α-Al2O3 (0001) substrate [8]. The large lattice mismatch between the ZnO film and sapphire substrate (mismatch \( \approx 18.3\% \)) resulted in a high density of threading dislocations in the epitaxial ZnO film [10]. This critical depth for the occurrence of first ‘pop-in’ in the ZnO epitaxial thin film is lower than that of epitaxial GaN thin films on sapphire substrates (‘pop-in’ depth 23–26 nm) as we studied earlier [11]. The mechanism responsible for the ‘pop-in’ event in these epitaxial films may be due to the nucleation, propagation and interaction behavior of the glissile threading dislocations that existed in the film during the mechanical deformation. Glissile dislocations will move under the application of a force and their Burgers vector is in the direction of the slip. Therefore, glissile dislocation can move with the applied force. We believe further that the existence of the high density of threading dislocation (10^{10} \text{ cm}^{-2}) in the ZnO films could be the possible reason for the occurrence of shallow depth ‘pop-in’ event during the loading process. There is no indication of the formation of micro cracks or other phases, so local deformation seems to proceed exclusively by the activation threading dislocations in the film. In addition, the amplitude-mode AFM image on the...
residual indentation impression revealed no micro cracks even after the indentation beyond the critical depth (Fig. 2). Therefore, the origin of the ‘pop-in’ is due to the dislocation based phenomenon. However, it is obvious that more work is required to better understand the physical mechanism of the deformation behavior of these epitaxial films. Moreover, we performed the deformation studies on (0001) bulk ZnO single crystal with the same experimental conditions as that of thin film. Fig. 3 shows the load–displacement curve bulk ZnO single crystal illustrating a ‘pop-in’ event at a depth of 16 nm (for the critical load of 0.07 mN) as that of epitaxial ZnO films. We made 36 indentations on the bulk crystal, out of that 16 tests showed ‘pop-in’ event (≈45% of the tests show ‘pop-in’ in bulk crystal). No other ‘pop-in’ event was observed even when the indentation depth increased up to 300 nm and the results are reproducible. Previous indentation studies on bulk ZnO crystals showed that there are multiple ‘pop-in’ events at relatively deeper depths using the spherical indenter tip corresponding to large applied load [3]. However, our present investigation clearly illustrates the critical depth of the ‘pop-in’ event with Berkovich tip in the shallow depth of the sample (at a depth less than 20 nm). This may be due to the dislocation density of bulk ZnO single crystals, which has a relatively low dislocation density (10^4–10^9 cm^{-2}, no threading dislocation) [12] compared to that of epitaxial ZnO film (10^9 cm^{-2}) [13].

Fig. 4 shows the load–displacement data with the maximum indentation depth of 10 nm for ZnO thin film (0.8 μm). Slow loading (strain rate controlled, 0.1 s^{-1}) and unloading (load rate controlled, 5 μN/s) was maintained to observe the deformation behavior of the thin films at low loads. Fig. 4 shows some plastic deformation behavior (residual impression is about 4 nm) even well before the ‘pop-in’ event took place. This indicates that some dislocations are generated even before the ‘pop-in’, which differs from the results of another study on AlGaN thin film that flexed elastically and recovered completely with loads below the critical values [14]. For the AlGaN thin film, the ‘pop-in’ event was attributed to the dislocation nucleation [14]. This behavioral difference between ZnO and AlGaN systems indicate that our ‘pop-in’ is not due to dislocation nucleation.

4. Conclusions

The deformation behavior of epitaxial ZnO thin films grown on sapphire substrates has been studied by nanoindentation. A single discontinuity (‘pop-in’) in the load–displacement curve of all samples was observed at the depth of 13 to 16 nm. The physical mechanism responsible for the ‘pop-in’ events in these epitaxial films may be due to the nucleation, propagation and interaction behavior of the glissile threading dislocations during the mechanical deformation. In addition, for indentation depths below the critical depth conducive to the ‘pop-in’ event, plastic deformation behavior (residual impression of 4 nm) was observed, which indicates that some dislocations were generated even before the ‘pop-in’ event.

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References