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Enhanced hardness in B-doped ZnO thin films on fused quartz substrates by pulsed-laser deposition

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Abstract

B-doped ZnO thin films have been fabricated on fused quartz substrates using boron–ZnO mosaic target by pulsed-laser deposition technique, and the mechanical properties have been studied by nanoindentation continuous stiffness measurement technique and transmission electron microscope (TEM). Nanoindentation measurement revealed that the hardness of B-doped ZnO films, 9.32 ± 0.90 to 12.10 ± 1.00 GPa, is much greater than that of undoped ZnO films and very close to that of traditional semiconductor Si. The mean transmittance (%) is larger than 81% in the visible range (380–780 nm) for all the films, and the Hall effect measurement showed that the carrier density is around 2×10^{20} cm^{-3} and the resistivity lower than 3×10^{-3} Ω cm. TEM characteristics show undoped thin films have more amorphous area between grains while the B-doped ZnO films have thin grain boundaries. We suggest that the grain boundaries act as the strain compensation sites and the decrease in thickness of grain boundaries enhances the hardness of the B-doped ZnO films.

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Keywords: Nanoindentation; Hardness; ZnO thin film; B-doped; TEM

1. Introduction

ZnO has recently attracted great attentions due to its potential applications in the opto-electronic devices [1–4]. It is well known that material's mechanical property is one of the most important effect factors in the fabrication of the opto-electronic devices because of the unavoidable extensive handling. Poor mechanical performance may severely limit their potential applications since very soft materials may not be compatible with current semiconductor processing [5]. However, up to the present, nearly all studies on the mechanical properties of the undoped ZnO thin films and single crystals showed that ZnO was a comparatively ‘‘soft’’ material with a relatively low hardness of only 5–7 GPa (compared to ∼12 GPa for Si and ∼15 GPa for GaN) [5,6–11]. In this paper, we have prepared B-doped ZnO thin films and reported the hardness from 9.32 ± 0.93 to 12.10 ± 1.20 GPa. Transmission electron microscope (TEM) characteristics provide insight into the nature of this enhanced hardness.

2. Experimental

The thin films were grown on fused quartz substrates by pulsed-laser deposition using a boron and ZnO mosaic target (1/4 area for high purity of 99.99% boron sheet in a shape of sector on a 99.99% ZnO target) under a pure oxygen background at different substrate temperatures of 350, 450 and 550 °C, respectively. In order to avoid B to react with the ambient oxygen, we applied a low oxygen pressure of 2×10^{-3} Pa in the film deposition process. A KrF excimer laser (248 nm, 15 ns), operating at a repetition rate of 4 Hz, was used to ablate

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the mosaic target, and the on-target laser energy density was 2 J/cm^2. The film thickness was fixed at 500 nm. Our experimental conditions are consisted with other technique reported in Ref. [12]. X-ray diffraction (XRD) showed our films are single-phased with preferred *c*-axis orientation. The crystalline structure of the as-grown films was characterized by TEM. The amount of doped boron was detected by inductively coupled plasma spectrometer (ICP) which gave 0.8%, 1.50% and 4.00% atomic ratio of zinc to boron at 350, 450 and 550 °C, respectively. The stoichiometric difference resulted from the different growth rates. The deposition rate of boron is almost stable with the deposition temperature [13], while that of ZnO decreased considerably with increasing substrate temperatures for Zn cation possessing high vapor pressure [14–16]. The hardness and elastic modulus were performed by a MTS XP Nanoindenter system equipped with the continuous stiffness measurement (CSM) option [17–19]. Ten indents with a space of 50 μm were made on each sample and the precision of the indentation measurement was better than 10%. The results were an average of the 10 measurement indentations. The maximum indentation depth was about 200 nm with a surface approach velocity of 10 nm s^{-1}, and the displacement resolution was less than 0.01 nm in XP mode. Frequency of 45 Hz was used to avoid the sensitivity to thermal drift, and the loading resolution was 50 nN.

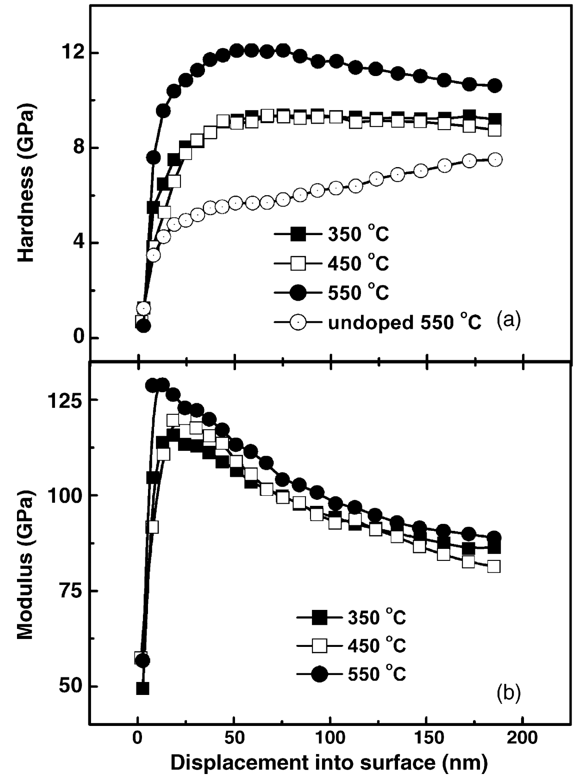

Fig. 2. (a) Hardness and (b) modulus as a function of displacement into surface for B-doped and undoped ZnO films prepared at different temperatures.

3. Results and discussion

As displayed in Fig. 1, the mean transmittance (%) is large than 81% in the visible range (380–780 nm) for all the films, which is normalized to that of the bare substrates. In addition, the Hall effect we measured showed that the carrier density is around 2×10^{20} cm^{-3} and the resistivity lower than 3×10^{-3} Ω cm in all cases. These results show our B-doped ZnO films are transparent and conductive and can meet the demands of the manufacture of device such as ultraviolet light emitting diodes and lasers.

Fig. 2 presents the hardness and modulus as a function of displacement into surface for B-doped and undoped ZnO thin films. The hardness values of B-doped ZnO thin films are 9.32 ± 0.90, 9.35 ± 0.94 and 12.10 ± 1.00 GPa at a contact depth of 60 nm at 350, 450 and 550 °C, respectively, much greater than that of undoped ZnO film. Li and Bhushan [18] suggested that a substrate effect on the hardness emerges when the contact depth exceeds 20% of film thickness. In our case, the film thickness is 500 nm, indicating the data is rational. In addition, the modulus of 103.5 ± 5.0, 105.5 ± 5.1 and 114.4 ± 5.2 GPa can be observed, which are much smaller than that for expitaxial layer but close to that for single crystal [8].

Shown in Fig. 3 are force–displacement curves for the B-doped thin films at 350, 450 and 550 °C. They are continuous, and no pop-in event is found. This is different from the behavior observed for the bulk material, which shows multiple pop-in

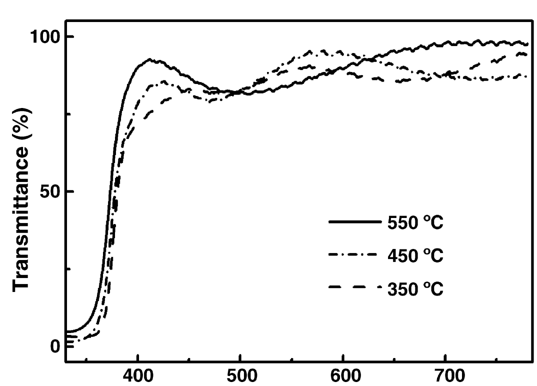

Fig. 1. Transmittance (%) spectra of B-doped ZnO thin films on fused quartz substrates at different temperatures.

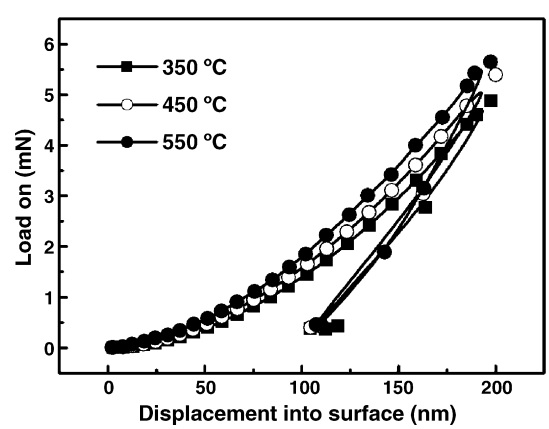

Fig. 3. Load–unload curves of B-doped ZnO film on fused quartz deposited at 350, 450 and 550 °C, respectively.

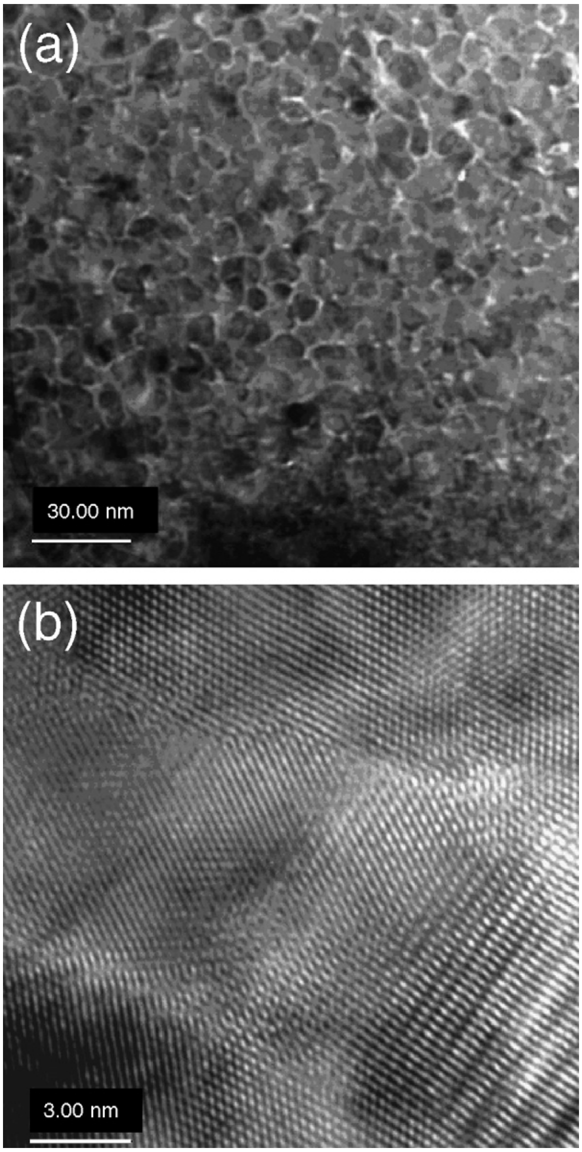

Fig. 4. (a) Low resolution and (b) high resolution TEM images of B-doped ZnO thin film deposited at 550 °C.

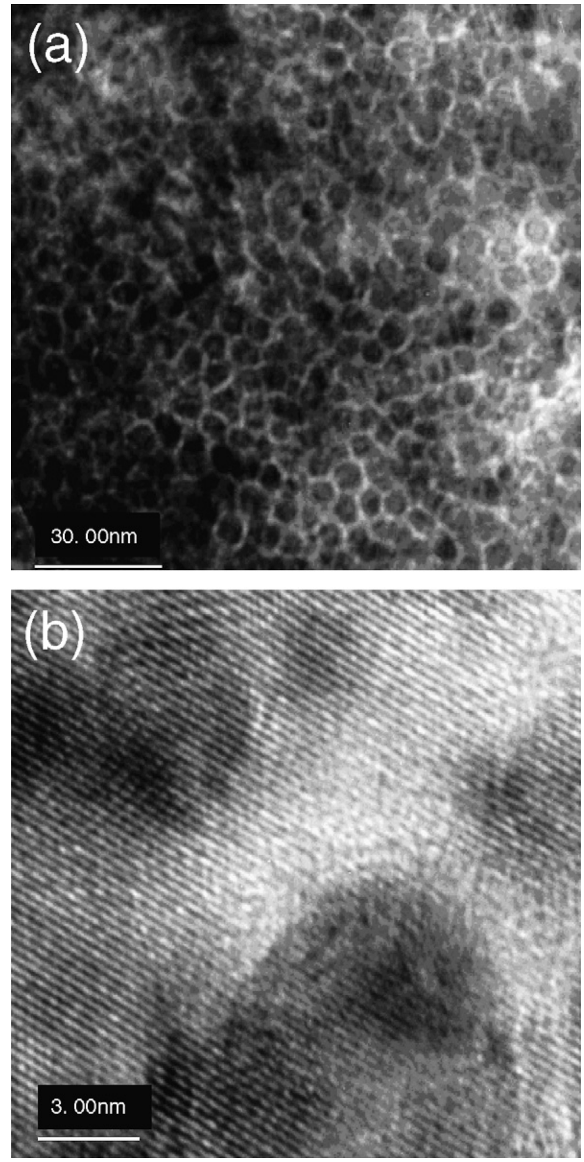

Fig. 5. (a) Low resolution and (b) high resolution TEM images of undoped ZnO thin film deposited at 550 °C.

events [8,9]. Our B-doped ZnO films are single phase with grain size of about 5–10 nm (Fig. 4), and those grain boundaries will act as strain compensation sites which are responsible for the absence of pop-in events as suggested by Coleman et al. [8].

We now turn to discuss the enhancement of hardness of ZnO thin films by B-doping. In simple metals and ionic substances, the bonding is delocalized, and hardness is determined by extrinsic factors such as impurities, precipitates, grain boundaries, and the like [20]. Fig. 4(a) and (b) exhibits the TEM images of B-doped ZnO film at 550 °C with different resolution, and a clear-cut structure with decreased-thickness grain boundaries is present. We suggest that such grain boundaries act as the strain compensation site like the threading dislocations in epitaxial layer under indent region [8]. When the indent gives a load on the films, these tight linked grains will uniformly absorb and propagate the pressure produced by this load without threading dislocations because of arbitrary arrangement of the grain boundaries, and return to indent with compressive stress. Such compressive stress can be larger than that of epitaxial layers presented by suddenly engendered threading dislocations. To confirm our proposal, the structural comparison is made between B-doped and undoped ZnO thin films under same fabricated condition at 550 °C. As shown in Fig. 5(a) and (b), amorphous grain boundaries indicate the low crystalline of the undoped films. Based on the data in Fig. 2(a), the undoped film has a hardness of only 5.68 ± 0.50 GPa. Therefore, the B-doping can decrease the thickness of the grain boundaries, eventually bring on improvement of hardness.

4. Conclusion

In summary, the mechanical properties of B-doped ZnO thin films have been investigated by nanoindentation and TEM. One can obtain a larger hardness of 12.10 ± 1.2 GPa in the B-doped

ZnO films deposited at 550 °C, which is close to that of the traditional semiconductor. Different from that in undoped ZnO films, the grains in B-doped ZnO films are tight linked with the narrow boundaries, which play a significant role in the enhanced hardness.

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