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Mechanical deformation of single-crystal ZnO

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The deformation behavior of bulk ZnO single crystals is studied by a combination of spherical nanoindentation and atomic force microscopy. Results show that ZnO exhibits plastic deformation for relatively low loads ($\gtrsim$4–13 mN with an ~4.2 μm radius spherical indenter). Interestingly, the elastic–plastic deformation transition threshold depends on the loading rate, with faster loading resulting, on average, in larger threshold values. Multiple discontinuities (so called "pop-in" events) in force–displacement curves are observed during indentation loading. No discontinuities are observed on unloading. Slip is identified as the major mode of plastic deformation in ZnO, and pop-in events are attributed to the initiation of slip. An analysis of partial load–unload data reveals values of the hardness and Young's modulus of 5.0 ± 0.1 and 111.2 ± 4.7 GPa, respectively, for a plastic penetration depth of 300 nm. Physical processes determining deformation behavior of ZnO are discussed. *© 2002 American Institute of Physics.* [DOI: 10.1063/1.1448175]

For the past several decades, ZnO has been a subject of intensive research driven by important technological applications of this material. In particular, polycrystalline ZnO has been widely used in the fabrication of nonlinear electrical devices known as varistors.[1] More recently, significant research interest has been attracted by single-crystal ZnO as a potential material for short-wavelength optoelectronics. A successful fabrication of (opto)electronic devices based on ZnO crystals requires an understanding of several important properties of this material, one of which is mechanical deformation behavior. Hence, studies of processes controlling contact damage, wear, and cracking of ZnO are not only physically interesting but also of significant technological importance.

The mechanical properties of ZnO (usually polycrystalline sintered ceramics) have previously been studied using conventional Vickers microhardness testing (see, for example, Refs. 2 and 3). Depth-sensitive nanoindentation, a more powerful technique for studying deformation behavior, has been used in Refs. 4 and 5 to examine ZnO polycrystalline ceramics. We are not aware of any previous nanoindentation studies of single-crystal ZnO. Hence, in this letter, we report on the main features of the deformation behavior of bulk single-crystal ZnO during nanoindentation. We also discuss how these features correlate with indentation-produced defect structures revealed by atomic force microscopy (AFM).

High quality single-crystal bulk wurtzite ZnO samples used in this study were purchased from Cermet Inc. As specified by the grower, the samples were (0001) oriented, O face polished, and with an etch pit density of $<4\times10^4$ cm^{-2}. Our Rutherford backscattering/channeling spectrometry study confirmed that the samples were high quality single crystals. The samples were subjected to indentation using an ANU UMIS-2000 nanoindentation system with an ~4.2 μm radius diamond spherical indenter. The shape of the indenter tip was characterized by scanning electron microscopy. The indentation system and indenter tip were carefully calibrated by indenting fused silica. A series of both partial and continuous load–unload indents was carried out. All indents were performed at room temperature. The partial load–unload data were analyzed using the method of Field and Swain[6] to extract the hardness and elastic modulus as a function of indenter penetration. After indentation, samples were examined by tapping-mode AFM to check for evidence of slip, cracking, and pileup/sink-in.[7] The AFM study was performed under ambient conditions with a Nanoscope III scanning probe microscope using commercial single-beam Si cantilevers with force constants of 30–120 N m^{-1}.

A typical continuous load–unload force–displacement curve of ZnO is shown in Fig. 1. This figure clearly illustrates that multiple discontinuities (or "pop-in" events) in

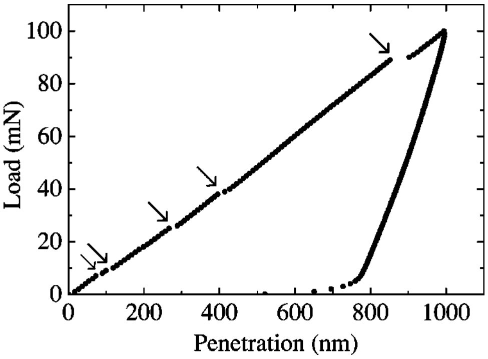

FIG. 1. Typical continuous load–unload curve of single-crystal ZnO. The maximum load is 100 mN. Arrows denote pop-in events.

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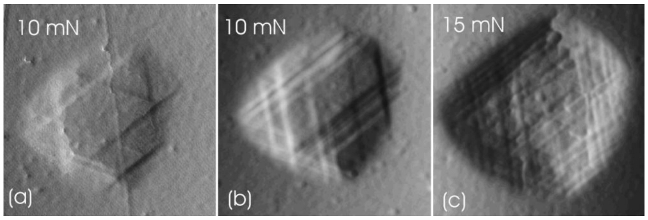

FIG. 2. Amplitude-mode AFM images illustrating that slip occurred during indentation of ZnO at maximum loads of 10 mN [(a) and (b)] and 15 mN (c). Horizontal field width is 2.5 μm for all images (a), (b), and (c). The near-vertical line in (a) is a surface scratch.

the force–displacement curves occur during loading. No discontinuities have been observed on unloading. Results show that the critical load for the first pop-in, which corresponds to the elastic–plastic threshold, varies in the range of ~4–13 mN. An analysis of nanoindentation data also reveals that the larger the load required for the first pop-in to occur, the larger the length of indenter excursion during the pop-in event. As a result, the maximum penetration of the indenter is essentially independent of the number of pop-in events during loading. Interestingly, results also show that the elastic–plastic threshold depends on the loading rate (varied in this study from ~0.5 to ~1.8 mN/s), with faster loading resulting, on average, in a larger value of the elastic–plastic threshold. Details of the influence of the loading rate on the deformation behavior of ZnO will be reported elsewhere.

Figure 2 illustrates typical amplitude-mode AFM images of residual impressions produced by indentation to maximum loads of 10 mN [Figs. 2(a) and 2(b)] and 15 mN [Fig. 2(c)]. All indents shown in this figure were loaded above the elastic–plastic threshold. The cross-hatched relief of the slip observed in the AFM images from Fig. 2 reflects the slip planes of the wurtzite lattice structure of ZnO that intersect the surface. Note that the contact diameters at maximum loads of 10 and 15 mN are ~1.7 and ~2.0 μm, respectively. Hence, the size of the regions with the steps observed by AFM is close to the contact diameter at the maximum load.

Figure 2 clearly illustrates the evolution and the statistical nature of slip in ZnO during loading. Indeed, Figs. 2(a) and 2(b) show that, for low loads when only a few pop-in events occur, identical loading conditions may result in a different number of slip bands on the sample surface, indicating the statistical nature of slip nucleation. In addition, a comparison of Figs. 2(a) and 2(b) with Fig. 2(c) shows that the number of slip bands increases with increasing loading.

Shown in Fig. 3 are the curves of the average contact pressure [or (Meyer) hardness] H [Fig. 3(a)] and Young's modulus E [Fig. 3(b)] as a function of indenter penetration below the circle of contact, as determined from partial load–unload data. The hardness value of ZnO is 5.0 ± 0.1 GPa at a plastic penetration depth of 300 nm. In addition, Fig. 3(b) shows that the Young's modulus remains essentially constant over the indenter penetration depth, with $E = 111.2 \pm 4.7$ GPa. Previous indentation studies of (mostly polycrystalline) ZnO have reported a rather wide range of H (~1.5–12 GPa) and E (~40–120 GPa) values, depending on the method used to make ZnO ceramics examined.[2–5] Hence, the values of H and E determined in the present study are within the range of the values reported previously, but, in our case of single-crystal ZnO, the results are very reproducible.

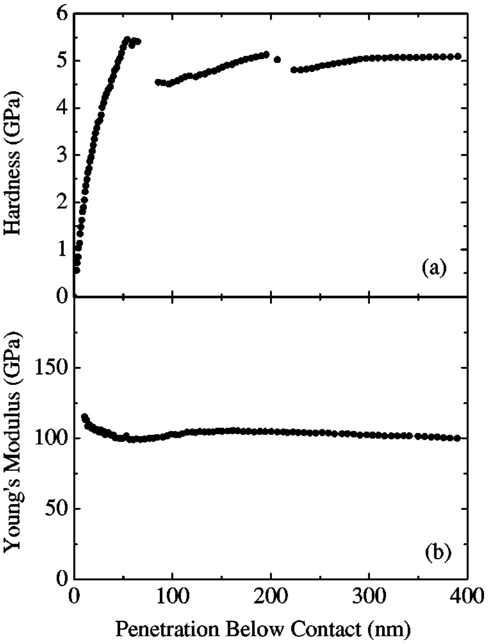

FIG. 3. Curves of (a) the hardness and (b) Young's modulus of ZnO as a function of indenter penetration below the circle of contact, as determined from partial load–unload data.

It is well known that accurate determination of H and E from nanoindentation data requires a low level of pileup and sink-in.[6,7] AFM imaging of residual impressions in ZnO reveals negligible pileup and sink-in during relatively low load indentation ($\leqslant$100 mN) used to identify the values of H and E. However, AFM shows that large load indentation with a maximum load of 200 mN (which results in a maximum indenter penetration depth of ~2 μm) results in pronounced pileup around the impression. No cracking has been observed by AFM for the loads used in this study ($\leqslant$200 mN). The presence of such pileup for large loads is expected given that, as shown above, ZnO is a relatively soft material.

The above AFM results (see Fig. 2) clearly show that slip is the major mode of plastic deformation in ZnO and strongly suggest that slip is responsible for the pop-in events observed during loading. Indeed, pop-in events often result in overloading effects, as revealed in H measurements [see Fig. 3(a)], and are indicative of important physical processes occurring during deformation, such as the initiation of slip and/or pressure-induced phase transformations (see, for example, Refs. 8 and 9). Previous nanoindentation studies have shown that such an overloading behavior is typical for a number of compound semiconductors studied (such as GaAs, InP, and GaN), where plastic deformation involves slip via the punching out of dislocations (see, for example, Refs. 10–13). It is important to note that previous transmission electron microscopy and Raman spectroscopy studies have revealed no evidence for pressure-induced phase transformations in compound semiconductors during spherical indentation at room temperature.[10–13] In such cases, slip has been identified as the only physical mechanism responsible for plastic deformation under indentation conditions similar to those used in the present study. Hence, a comparison of indentation results for ZnO with data known for other compound semiconductors strongly supports an argument that slip is the sole mechanism for plastic deformation of ZnO during room-temperature spherical indentation. However, additional experimental studies are highly desirable since, at this stage, deformation-induced phase transformations cannot be completely ruled out.

Another intriguing feature of ZnO deformation is the *multiple pop-in* behavior observed in Fig. 1. It should be noted that a similar loading behavior with multiple pop-in events (though much less pronounced) has previously been observed in indentation studies of sapphire[8] and GaN.[12] It is interesting that these three materials (sapphire, GaN, and ZnO), where multiple pop-in events occur, have a hexagonal lattice structure, while semiconductors with a cubic structure (such as Si, GaAs, and InP) exhibit a behavior with a single pop-in event on loading.[10–13] This suggests that particular features of the hexagonal lattice structure may play an important role determining the nucleation, propagation, and interaction behavior of dislocations during mechanical deformation, resulting in multiple pop-in events.

We propose the following scenario to explain this multiple pop-in effect. Above the elastic–plastic threshold, ZnO deforms plastically via slip initiating at the region of maximum shear stress under the indenter and involving the punching out of dislocations. These dislocations will tend to follow directions of easy slip, as determined by the crystallography, and may be pinned as a result of interactions between slip bands. Thus, with increasing loading, the further propagation of indentation-produced dislocations will be impeded. In this case, further plastic deformation must involve the nucleation of additional slip bands, resulting in the multiple pop-in events, as experimentally observed. However, it is clear that more work is needed to better understand the physical mechanisms of the deformation behavior of hexagonal crystals.[14]

Finally, it is interesting to note that the deformation behavior of ZnO is similar to the behavior of another important material for short-wavelength optoelectronics applications—GaN.[11] However, results of this study show that ZnO is significantly softer than GaN [$H_{\mathrm{GaN}} = 15.5 \pm 0.9$ GPa and $E_{\mathrm{GaN}} = 210 \pm 23$ GPa (see Ref. 11)]. Hence, large load indentation of GaN results in large-scale lateral elevation of the material around the impression with negligible pileup,[11] which is in contrast to the situation in the case of large load indentation of ZnO discussed above. The lower value of H of ZnO as compared to that of GaN is, in fact, expected, given a lower melting point ($T^{\mathrm{melt}}_{\mathrm{GaN}} \approx 2500\,^\circ\mathrm{C}$ and $T^{\mathrm{melt}}_{\mathrm{ZnO}} = 1975\,^\circ\mathrm{C}$) and larger ionicity [0.616 for ZnO and 0.500 for GaN (Ref. 15)] of ZnO. Indeed, the activation energy for dislocation propagation during slip may be expected to scale with the melting point.[16] Furthermore, the more ionic nature of chemical bonding is expected to facilitate the nucleation and propagation of dislocations via the ease of bond-angle distortion compared with purely covalent bonding.[16]

In conclusion, the deformation behavior of single-crystal bulk ZnO has been studied by nanoindentation in combination with AFM. Multiple discontinuities have clearly been observed during loading when the maximum load is above the elastic–plastic threshold. The elastic–plastic threshold has been found to be dependent on the loading rate, with faster loading resulting, on average, in larger threshold values. Slip, initiation of which appears to cause pop-in events, has been shown to be the major mode of plastic deformation in ZnO. Finally, results of this study may have technological implications for the estimation of contact damage in ZnO-based devices.

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[14] An influence of the lattice structure on dislocation propagation discussed here can be examined in indentation studies of crystals with different orientations. Indeed, pressure-induced propagation of dislocations during slip is expected to be different for different crystallographic directions, and this effect deserves additional studies. Note that, in all studies where multiple pop-in events were observed, crystals of (0001) orientation were used.

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