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Acta Materialia 61 (2013) 7180-7188



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Time-dependent nanoscale plasticity of ZnO nanorods

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Received 21 July 2013; received in revised form 9 August 2013; accepted 10 August 2013 Available online 14 September 2013

Abstract

External stresses are applied during operation or storage in flexible electronics, which makes understanding time-dependent plastic deformation of nanobuilding blocks more crucial for ensuring the reliability of the devices. Here, we systematically explored the time-dependent nanoscale plasticity of single-crystal ZnO nanorods and its size effects. A series of compression creep tests under different low stresses (in elastic regime) were performed on vertically oriented rods having equivalent diameters in the range of ~ 200 to ~ 2000 nm. It was revealed that creep indeed occurs in the rods even at ambient temperature, and is more pronounced in smaller nanorods. Analyzing the stress exponent and the activation volume suggests that the enhanced plasticity may be controlled by the diffusion creep (through the "space-charge layer" near the surface and/or along the interface between the punch and the top surface of the rod), which is supported by the results from in situ creep tests under electron-beam irradiation and in situ electric measurements. © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: ZnO nanorods; Time-dependent plasticity; Diffusion creep; In situ SEM test

1. Introduction

The advancement of micro- and nanoelectronics has been driven primarily by scaling down the size of elements in order to increase both the computing power and reduce the production cost. In addition, recent progress has been focused on the development of a new type of electronics consisting of components that are composed on flexible and stretchable substrates [1–5]. Organic semiconductors have been considered as candidate materials for the components in flexible devices, but the fabrication of high-performance organic electronics is extremely challenging due to the intrinsically poor carrier mobility. As an alternative, inorganic components that have been carefully engineered to withstand mechanical deformation offer significant

* Corresponding authors. *E-mail addresses:* jijang@hanyang.ac.kr (J.-i. Jang), wipark@hanyang. ac.kr (W.I. Park). potential for flexible and stretchable devices [1]. The assembly of inorganic one-dimensional (1-D) nanostructures, such as nanowires and nanorods, is especially promising due to their ability to accommodate large strain without failure, and the single-crystal nature of the nanostructure also ensures high-quality performance of the device [2]. The inorganic 1-D nanostructures are utilized in several different applications with externally applied stresses, e.g. nanogenerators based on ZnO nanorods [3]. The piezopotential generated in ZnO nanorods upon the application of external stress can also be used to enhance the current flow in electronic devices [4], as well as increasing the efficiency of optoelectronic devices [5].

In accordance with such change in operating environments, achieving mechanical reliability of electronics under non-negligible external stresses can be a significant challenge [6]. The flexible devices can be rolled or bent for storage and transport, which will result in each component of the device being placed under substantial external stresses

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for a relatively long time. In this regard, better understanding of the time-dependent nanomechanical behavior of the nanostructures can be crucial for predicting device failure, and suggesting the optimal conditions to improve the device's lifetime and reliability.

Regardless of its importance, however, there have been no systematic investigations and analysis of the timedependent plastic deformation (often referred to as "creep") of the inorganic 1-D nanostructures. The lack of creep studies of 1-D nanostructures is mainly due to the absence of an established method for the exploration of nanoscale creep behavior. For example, although nanoindentation with a sharp indenter at a constant peak load has been popularly used for analysis of small-scale creep tests, there are difficulties in its precise analysis due to several factors, such as the complex stress distribution underneath the indenter, only a fixed characteristic strain being applied within the plastic regime and the unavoidable indentation size effect [7,8].

Here, we have investigated the nanoscale creep behavior of vertically oriented, single-crystal ZnO nanorods (one of the most important nanomaterials today, exhibiting excellent performance and multifunctionality in a wide range of applications in electrical, optical, sensing and energy harvesting devices [9,10]) through a uniaxial compression creep test that can overcome the difficulties of conventional nanoindentation creep tests [7]. Note that the time-"dependent" plasticity of 1-D ZnO nanorods has not been systematically examined yet, although the time-"independent" (i.e. instantaneous) mechanical behavior of ZnO nanostructures has been investigated through nanoindentation [11,12], bending [13,14] and uniaxial [15,16] tests (see Table S1 of the Supplementary material for a summary of the literature data). In this study, the hydrothermally grown ZnO nanorods were chosen as a test system since a well-organized geometry of nanorods with various diameters and positions can be readily achieved at very low growth temperatures. Moreover, this bottom-up method can eliminate the issues associated with the possible surface damage that can be generated during the nanopillar sample preparation by focused ion beam (FIB) milling [17,18]. By analyzing the room-temperature creep behavior of ZnO nanorods of various sizes, it was revealed that nanoscale creep behavior becomes more pronounced with decreasing nanorod size. Evaluation of the creep stress exponent and the activation volume suggests that the enhanced creep may be controlled by surface and/or interfacial diffusion, which is further supported by the results from in situ creep tests inside a scanning electron microscope (SEM) under electron-beam irradiation and from mechanical-electrical coupled tests.

2. Experimental

Single-crystal ZnO nanorods were synthesized via a hydrothermal method, in which their size and position were controlled using a growth mask patterned by electron beam

lithography [19]. Poly(methyl methacrylate) (PMMA) layers are generally used as the growth mask since they are widely used in electronic photoresists and their glass temperature of 105 °C is higher than the growth temperature of the nanorods. In this case, however, it is inevitable for a necked region to develop at the bottom of the nanorod above the ZnO seed layer, as clearly observed in SEM image of Fig. 1. Formation of this necked region is due to the lateral overgrowth above the circular holes in growing the hexagonal rods [20]. Since the bottom neck leads to severe stress concentrations that result in catastrophic failure during compression testing, it is necessary to avoid its formation. For this purpose, a graphene layer was introduced as a growth mask since this layer, which has an intrinsic strength of ~130 GPa [21], can effectively support the ZnO nanorods for the compression test.

The fabrication procedures of graphene-assisted ZnO nanorods are schematically illustrated in Fig. 1. First, an epitaxial ZnO seed layer was deposited by pulsed laser deposition on (0001) Al₂O₃ substrate. A graphene sheet was then transferred onto the seed layer, followed by spin-coating of a 600-nm-thick PMMA layer onto the



Fig. 1. Schematic illustrations and SEM images showing the process for ZnO nanorod growth and the difference between typical hydrothermal growth and graphene-assisted growth.

graphene. A set of circular (corresponding to the locations for growing ZnO nanorods) and square (for the alignment of indenter probe and ZnO nanorods with optical image) patterns were defined on the PMMA layer by electron beam lithography. By using the patterned PMMA layer as an etching mask, the exposed circular and square regions in graphene were etched with O_2 plasma. The remaining PMMA layer was then eliminated with acetone, and the substrate was placed in an aqueous solution containing 0.025 M zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O;$ Sigma–Aldrich) and 0.025 M hexamethylenetetramine (C₆H₁₂N₄; Sigma-Aldrich) to grow the ZnO nanorods through the hole patterns in graphene. Nanorod growth was typically performed at 70 °C for various times, from \sim 5 h for an equivalent diameter (or diagonal length of the hexagon), d, of 200 nm to ~ 15 h for one of 2000 nm. Consequently, we prepared graphene-assisted ZnO nanorods, wherein the bottom neck is essentially absent due to the thinness of the graphene layer, as seen in Fig. 1. Nanorods with d of ~ 200 , ~ 500 , ~ 800 and ~ 2000 nm were prepared, all with similar aspect ratios in the range of 1.5:1-2.5:1.

Creep experiments were performed using a Nanoindenter-XP (Agilent, Oak Ridge, TN) with an FIB-milled cylindrical diamond flat-punch indenter tip. Prior to the creep segment, a preload was applied to the same stress level as the creep stress in order to minimize the possible effects from the misalignment of the nanorods. During the creep test, the load was increased up to the desired maximum stress level (i.e. 1, 1.5, 2 and 3 GPa) at a fixed loading rate of $(dP/dt)/P = 0.05 \text{ s}^{-1}$, where P is the applied load and t is time, then held for 200 s and finally removed at the same rate as the loading segment (Fig. 2a). From the obtained load (P) vs. displacement (h) curves, the engineering stress (σ) vs. engineering strain (ε) curves were calculated as $\sigma \sim P/A$ and $\varepsilon \sim h/l$, respectively, where A is the initial cross-sectional area, empirically determined at $\sim 1/$ 3 of the rod height from the top for considering the effect of small taper (<1°) using image analysis software (Image-Pro Plus, Media Cybernetics, Silver Springs, MD), and l is the initial rod height (for how to calculate A, see Fig. 3).

The applied creep stress level (which should be in the elastic regime, as in conventional creep tests) was determined by first analyzing the elastic limit through quasi-static compression tests. Abrupt large strain burst was observed during loading (Fig. 2b), which coincided with the brittle fracture of nanorods, and the fracture strength of ~2000 nm ZnO nanorods was calculated to be ~3.17 GPa. This strength value is similar with that obtained by Sung et al. [16], who performed compression tests on FIB-milled ZnO nanopillars having a diameter of ~1000 nm and reported the yield strength to be ~3 GPa. The load-holding time was chosen in consideration of the thermal and instrumental drift [22]. For each testing condition, ~10 tests were conducted to ensure the reproducibility of the results.



Fig. 2. Nanorod creep tests: (a) Schematic illustration of the creep testing sequences (inset images show 17 μ m diameter flat punch tip and 2000 nm diameter nanorods). (b) Representative engineering stress–engineering strain curve for compressed ZnO nanorods with $d = \sim 2000$ nm (inset SEM images were taken before and after the compression test).



Fig. 3. An example of SEM image used for calculating cross-sectional area, A, at ~1/3 of nanorod height from the top: $A = A_{top} + (A_{top} - A_{bottom})/9$, where A_{top} and A_{bottom} are the areas of top and bottom surfaces of ZnO nanorods, respectively, which can be measured through image analysis software.

The morphology of each nanorod was imaged before and after creep testing using a JSM-6330F SEM (JEOL Ltd., Tokyo, Japan), and the microstructural change was observed with a Tecnai F20 transmission electron microscope (TEM; FEI Co., Hillsboro, OR) after cross-sectioning of the rod by dual-beam FIB milling with a Nova 200 (NanoLab, FEI Inc., Hillsboro, OR). Additionally, in situ creep tests were conducted on ZnO nanorods having $d = \sim 200$ and ~ 2000 nm inside a Quanta 250 FEG SEM (FEI Inc., Hillsboro, OR) using a PI 85 picoindenter (Hysitron Inc., Minneapolis, MN). Finally, in situ electric measurements were performed using a Triboindenter (Hysitron Inc., MN), that was equipped with a NanoECR system for applying and measuring electrical signals, with a heavily boron-doped flat-punch diamond indenter.

3. Results

3.1. SEM images

Representative SEM images of the ZnO nanorods as grown by hydrothermal methods and the same-sized nanorods crept at the highest stress adopted in this study (3 GPa) are shown in Fig. 4. It can be clearly seen that the examined nanorods indeed have a hexagonal cross-section, indicating that they are single crystals grown along the [0001] direction. It is noteworthy that, by preparing specimens using bottom-up growth methods, we could exclude any potential influences on the test results from the FIB-milling-induced surface defects. The absence of shearing, bending, barreling and cracking indicates that the shear slips commonly found in single crystalline metals [23,24] have not occurred in the creep tests of the ZnO nanorods at the applied low stresses (within elastic regime). Thus, the creep deformation would be accommodated by the whole body of the pillar.

3.2. Engineering stress-strain

Typical examples of the σ - ε curves (for $d = \sim 200$ nm) obtained from the creep experiments are provided in Fig. 5. The overlapping of the loading curves in a single line indicates that the stress applied at the onset of creep is within the nominal elastic strain regime. An important feature of the figure is that the creep occurs at ambient temperature, and exhibits a displacement of up to ~ 15 nm (for 200 s load-holding) at stresses well below the fracture strength (see the inset of Fig. 5). The creep strain induced during the load-hold segment increases significantly with the applied stress, indicating that the observed creep behavior is not an artifact caused by thermal drift [25,26].

3.3. Creep strain

Fig. 6a provides representative examples of engineering creep strain (ε_{creep}) vs. holding time ($t_{holding}$) plots. The



Fig. 4. Representative SEM images of ZnO nanorods before (a, c, e, and g) and after (b, d, f, and h) the creep test at 3 GPa: (a and b) for 200 nm, (c and d) for 500 nm, (e and f) for 800 nm, (g and h) for 2000 nm. Note the magnification disparity of each image.

curves are mostly parabolic in nature, which is similar to typical high-temperature creep curves of metals and ceramics [27,28], consisting of two regimes in the early stages:



Fig. 5. Representative engineering stress vs. engineering strain curves from uniaxial creep experiments (for $d = \sim 200$ nm). The inset image shows raw load vs. displacement curves.

transient and steady-state creep regimes. It is clear that a large portion of creep strain was produced in the primary creep regime. The two-regime creep behavior also strongly supports our suggestion that the creep is not caused by thermal drift since the thermal drift is expected to induce an approximately linear relation between displacement (and thus engineering strain) and time [25,26].

Two of the most important experimental results are the influences of d and σ on the amount of total creep strain (defined as $\varepsilon_{\text{creep}}$ at $t_{\text{holding}} = 200 \text{ s}$), which are summarized in Fig. 6b. The figure clearly shows that the total creep strain increases not only with increasing σ but also with decreasing d. One may argue that this size effect is possibly a drift-induced artifact because the same amount of thermal-drift-induced displacement will lead to a higher creep strain (i.e. creep displacement divided by rod height) for a nanorod with a smaller height [26]. However, this scenario is not valid in this study since the net value of total creep displacement (creep displacement h_{creep} at t_{hold} - $_{ing} = 200$ s) is also significantly affected by d and σ in the same manner, as provided in the inset of Fig. 6b. Thus, while the absolute values of the total creep strain can be somewhat affected by the thermal drift, the observed size effect is realistic.

3.4. Creep rate

The steady-state creep strain rate is an important quantitative measure of the creep behavior in ceramics as well as



Fig. 6. Results of nanorod creep experiments. (a) Example of creep strain vs. holding time curve (for $\sigma = 1$ GPa); (b) the effects of *d* and σ on the total creep strain (with the inset showing the effects of *d* and σ on the total creep displacement); (c) example of creep strain rate vs. time curve (and strain rate vs. creep strain curves in the inset) for $\sigma = 1$ GPa; (d) the relation between quasi-steady-state creep rate and creep stress.

in metals [27,28]. Here, the creep strain rate $\dot{\varepsilon}_{creep}$ was estimated by fitting the creep curves in Fig. 6a according to Garofalo's mathematical fitting equation. $\varepsilon_{\text{creep}} = \varepsilon_0 + \alpha (1 - e^{-rt}) + \omega t$ (originally suggested for conventional tensile creep analysis), where ε_0 is the instantaneous strain during loading, which is 0 here, and α , ω and r are creep constants (for physical meanings of each parameters, see Ref. [26]). By differentiating the fitted equation with respect to t, the change in $\dot{\varepsilon}_{creep}$ can be obtained as a function of time. Typical examples of the determined strain rate vs. holding time are plotted in Fig. 6c (for $d = \sim 200$ nm), suggesting the possibility of nanorods reaching a steady-state creep condition (hereafter called "quasi-steady-state"). This condition is also observed in $\dot{\varepsilon}_{creep}$ - ε_{creep} curves in the inset of Fig. 6c. Fig. 6d summarizes the variation in quasi-steady-state strain rate $\dot{\epsilon}_{QSS}$ determined from the $\dot{\varepsilon}_{creep}$ value at $t_{holding} = 200$ s. Similar to the trends in Fig. 6b, higher $\dot{\varepsilon}_{OSS}$ values are evident for smaller d and higher σ .

4. Discussion

4.1. Stress exponent, activation volume and creep mechanism

Estimating the dominant creep mechanism is essential for better understanding of the nanoscale creep in the ZnO nanorods. A useful indicator of the creep mechanisms is the creep stress exponent $(n = \partial \log \dot{\epsilon}_{OSS} / \partial \log \sigma)$: n = 1for diffusion creep such as Nabarro-Herring creep (by lattice diffusion) or Coble creep (by grain boundary diffusion), n = 2 for grain boundary sliding, and n = 3 or 5 for dislocation creep in ceramics [27,28]. These creep mechanisms were originally developed for monoatomic crystals and are directly applicable to pure metals, but can be successfully extended to ceramics if the ambipolar diffusions of cations and anions are considered [28–32]. The stress exponent n can be calculated from the slope of $log(\dot{\epsilon}_{OSS})$ and $\log(\sigma)$, as shown in Fig. 6d. Linear fittings of the average points lead to $n \sim 1$ for all d (1.03 for $d = \sim 200$ nm, 1.14 for $d = \sim 500$ nm, 0.96 for $d = \sim 800$ nm and 1.18 for $d = \sim 2000$ nm), indicating that the diffusion creep is the predominant mechanism regardless of the nanorod sizes.

Another important clue for the creep mechanism can be gained by analyzing the activation volume of the event, V^* , which can be estimated with von Mises relation as $V^* = kT(\ln \dot{\epsilon}_{QSS}/\ln \tau) = \sqrt{3}nkT/\sigma$, where k is the Boltzmann constant, T is the temperature, and τ and σ are the applied shear and normal stress acting on V^* , respectively. The V^* was found to increase from ~0.00253 to ~0.00760 nm³ with decreasing σ from 3 to 1 GPa (see Table 1). While the V^* in metals is generally expressed as a fraction of the Burgers vector, b^3 (i.e. ~1 b^3 for diffusion and ~100–1000 b^3 for dislocation movement [33,34]), it may be possible to describe V^* in ceramics with ionic bonding as a fraction of the ionic volume [35]. We calculated the volume of Zn and O ions, V_{Zn} and V_O , with the radius of the Zn ion (0.074 nm) and of the O ion (0.140 nm) [36],

Table 1		
Averaged	activation volumes under different stress	levels

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σ (GPa)	$V^{*} (nm^{3})$	V^*/V_{Zn}	$V^*/V_{\rm O}$	
1.000	0.00760	4.476	0.661	
1.500	0.00507	2.984	0.441	
2.000	0.00380	2.238	0.331	
3.000	0.00253	1.492	0.220	

and expressed V^* again as 0.22–0.66 $V_{\rm O}$ and 1.49–4.45 $V_{\rm Zn}$ (Table 1), which is indicative of the creep deformation occurring via motion of individual ions.

It is generally accepted that the diffusion creep rather than the dislocation creep is the most common creep mechanism in ceramics [29–32]. There are two possible reasons for the enhanced role of diffusion creep in ceramics, which is also possibly applicable to the present study on ZnO nanorods. First, relatively high Peierls stress in ceramics leads to difficulty in enabling dislocation motion [31,32]. In this study, ZnO nanorods fractured during uniaxial compression without showing any plastic flow (Fig. 2b). A second possibility is associated with the existence of the so-called "space-charge layer" near the surface of ceramics. This layer comes from the destruction of electric neutrality in the vicinity of the surface due to the significantly lower formation energy and/or migration barrier of specific ionic defects (e.g. Zn interstitial in ZnO [37]) near the surface than within the lattice [30,38]. Therefore, diffusion of the ionic species can be enhanced within this layer, giving it an "effective" surface thickness, t_{surf} [30,38,39]. A similar defect-accumulated space-charge layer has been also observed near the grain boundaries, which are considered as excellent diffusion paths [40]. This implies that the nanorods with a higher volume fraction of this layer (whose typical t_{surf} is ~10-~100 nm [41-43]) may exhibit stronger diffusion activities. This is discussed further below.

As well as at high temperatures [44], active diffusion in ZnO at low temperatures has been previously reported. ZnO varistors exhibited degradation in their performance at relatively low operating temperature (<373 K) due to diffusion of ionized point defects [37,45]. In ZnO having intrinsic n-type characteristics [9], the zinc interstitials rather than the oxygen vacancies have been considered as the predominant migrating species [37], which is supported by density functional theory calculations [46,47]; for example, the threshold temperature for the migration of Zn interstitial was calculated to be 90-120 K by Erhart and Albe [46] and as 219 K by Janotti and Van de Walle [47]. In the present study, the room-temperature diffusion of Zn interstitials becomes more likely due to the additional driving force by external stress, which was not considered in the previous reports [46,47].

Another important possible contributor to the axial displacement is the occurrence of mass removal of Zn and O ions at the top (and/or bottom) surface of the nanorod. In this regard, a simple model that could be consistent with the observation is diffusive flow along the interface between the diamond punch and the top surface of the nanorod. Wang et al. [48] performed nanoindentation creep tests with a Berkovich tip on nanocrystalline Cu and suggested that, in the shallow-depth regime of $h_{\text{creep}} < 12$ nm (which is very close to the range of measured h_{creep} in present study, although the testing method is different), atoms can move easily along the tip–sample interface. A similar diffusion scenario could be also valid in this study and could explain that the creep rate is enhanced as the applied stress increases and the contact interface area (that is, the cross-sectional area of the nanorod) decreases (Fig. 6).

4.2. Indirect evidence for diffusion creep

While the determined n and V^* values suggest that the predominant mechanism of the room-temperature creep in the ZnO nanorods is diffusion creep, it is almost impossible to confirm this through direct experimental observation. We thus attempted to prove it indirectly through in situ SEM tests. It is reasonable to assume that, if creep were to occur by diffusion (especially surface diffusion), electron-beam (e-beam) irradiation on the surface during creep tests may result in greatly enhanced creep rates while the *n* remains at ~ 1 , which is indicative of diffusion creep. A similar phenomenon of enhanced atomic diffusion by ebeam irradiation has been reported in previous studies. For instance, Hague and Saif [49], who carried out in situ SEM tensile tests on nanocrystalline Al thin films, observed ebeam-induced acceleration of diffusion-based stress relaxation. Such e-beam-assisted acceleration in mass transport has also been reported for brittle ceramic nanostructures [50].

In the present study, in situ SEM creep tests were performed on ZnO nanorods with $d = \sim 200$ and 2000 nm, as shown in Fig. 7a. The total amounts of creep strain were significantly increased in the in situ creep tests compared to the results from the normal nanorod creep tests (Fig. 7b), implying that creep is indeed accelerated by e-beam irradiation. Fig. 7c compares the measured quasi-steady-state strain rates obtained under e-beam irradiation with those without irradiation. As expected, the e-beam irradiation increased the creep rates measurably while the calculated stress exponent remained at ~1 (1.16 and 1.04 for the 200 and 2000 nm diameter nanorods, respectively), which could be indirect evidence of diffusion creep.

Since electric properties can be affected by mechanical deformation [4], measurement of their changes can provide another indirect clue for analyzing creep behavior. Fig. 8 shows the result of the in situ electric measurement test, in which current (*I*) vs. voltage (*V*) sweep curves were recorded at maximum load (P_{max}) during preloading and second loading (indicated by arrows in the inset of Fig. 8). It is reported that dislocations, by themselves, scatter conduction electrons and decrease electron mobility in ionic materials [51]. As the current increases after the creep test within the voltage range from -10 to 10 V, we can



Fig. 7. In situ creep tests. (a) Image showing the in situ creep experimental setup, and the effects of electron beam irradiation on (b) the total creep amount and (c) the strain rate and stress exponent. Inset images in (a) are representative SEM images of ZnO nanorods ($d = \sim 2000$ nm) taken before and after the in situ creep test at 3 GPa.

exclude the possibility of "dislocation creep", which leads to the opposite trend to that in Fig. 8 [51,52]. Further study of this mechanical–electrical coupled behavior is currently underway, and will be treated in detail in a separate publication.

On the other hand, the exclusion of dislocation creep in this study was partly supported by the cross-sectional TEM observation of the nanorods. The images taken before the creep tests exhibit very low dislocation density, which was



Fig. 8. Typical examples of I-V sweep curves recorded at P_{max} of preloading and second loading on ZnO nanorods having d of ~2000 nm. The inset image shows a schematic illustration of the testing sequences (arrows indicate where I-V sweep curves were measured).

not increased detectably by creep experiments (see Fig. S1 of the Supplementary material).

4.3. Size effects of creep behavior

As shown in Fig. 6a–d, the nanoscale creep behavior of the single-crystal ZnO nanorods shows clear size dependency, i.e. the creep strain and strain rate increase with reduction in nanorod size for a given creep mechanism (surface diffusion). Analyses of the size effects on the creep of ceramics in previous studies were mostly limited to the influence of "grain size" [53] and cannot be directly applied to single crystals. Therefore, the size effect of ZnO nanorods in the present study must be understood in a different way, that is, in terms of the increased contribution of the surface in a smaller sample.

Free surface is a very effective diffusion path. The diffusivity of "short-circuit diffusion" along the surface is often approximated as [54] $D_{\text{surf}} \approx 7 \times 10^{-6} \exp(-9.3 \times 10^{-23} T_m/kT)$ (in m² s⁻¹), where k is Boltzmann's constant and T_{m} is the absolute melting temperature. By putting $T_{\text{m}} = 2248 \text{ K}$ [9] and T = 298 K, D_{surf} of ZnO can be estimate to be ~5.92 × 10⁻²⁸ m² s⁻¹. The lattice diffusivity, D_{lattice} , of interstitial Zn in the temperature range of 485– 994 K was investigated by Wuensch and Tuller [55], who found that $D_{\text{lattice}} \approx D_0 \exp(-Q/kT)$ with diffusion coefficient $D_0 \sim 7.26 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and activation energy $Q \sim 2.88 \times 10^{-19} \text{ J}$ atom⁻¹. From this relation, one can estimate $D_{\text{lattice}} \sim 2.56 \times 10^{-40} \text{ m}^2 \text{ s}^{-1}$ at T = 298 K, leading to a ratio of $D_{\text{surf}}/D_{\text{lattice}}$ of >10¹². Note that somewhat different D_0 and Q values are available in the literature, hence $D_{\text{surf}}/D_{\text{lattice}}$ can have a wide range of values: ~10¹²-10⁴³ for Zn diffusion and ~10¹⁵-10⁸⁶ for O diffusion (a summary is provided in Table S2 of Supplementary material).

This large ratio of $D_{\text{surf}}/D_{\text{lattice}}$ suggests that the surfaceto-volume ratio (SVR) may strongly influence the creep characteristics of the nanorods. By assuming a perfect

Tab	le 2

The effect of nanorod size on the surface-to-volume ratio and the volume fraction of the effective surface diffusion path.

<i>d</i> (nm)	$SVR (nm^{-1})$	$SVR \times t_{surf}$
2000	0.00281	0.041
800	0.00702	0.102
500	0.01124	0.163
200	0.02809	0.407

hexagonal prism geometry for nanorods, the SVRs can be calculated as 2.81×10^{-3} , 7.02×10^{-3} , 1.12×10^{-2} and 2.81×10^{-2} nm⁻¹ for $d = \sim 2000$, 800, 500 and 200 nm, respectively. In addition, as discussed earlier, the "space-charge layer" in the vicinity of surface may play an important role in the size effect. Reported values of the layer thickness from the surface, t_{surf} , in ZnO nanostructures are in a wide range (such as 4.4 nm [13], 60 nm [41], 0–25 nm [42] and 14.5 nm [43]). Since the conductivity is closely related to the migration of charged ions in ionic crystals, the $t_{surf} = 14.5$ nm obtained from the surface conductivity in Ref. [43] is adopted here to calculate the ratio of the surface layer volume to the total nanorod volume by SVR $\times t_{surf}$, which can be a measure of contribution of surface diffusion to total creep deformation, including lattice diffusion creep. The calculated values are summarized in Table 2. For $d = \sim 200$ nm, the volume of the surface layer (having high diffusivity) is $\sim 40\%$ of the total volume, which is 10 times larger than that for $d = \sim 2000$ nm ($\sim 4\%$).

5. Summary and conclusions

In summary, nanoscale creep of ZnO at room temperature was systematically explored using compression creep experiments performed on nanorods with diameters of 200, 500, 800 and 2000 nm at low stresses well below the elastic limit. It was revealed that creep indeed occurs at ambient temperatures, and at the stresses within the elastic regime. The post-mortem SEM images suggest that the creep deformation is uniform in nature. The total creep strain and the quasi-steady-state creep strain are significantly affected by both the applied stress and the nanorod size. The creep strain was increased significantly with either an increase in the creep stress or a decrease in the nanorod size. Estimations of the creep stress exponent and the activation volume for the creep suggest that the room-temperature creep of the nanorods at low stresses within the elastic regime may be dominated by diffusion-controlled mechanisms such as surface diffusion of Zn interstitials. This diffusion creep mechanism was also supported by (i) in situ SEM creep tests, in which e-beam irradiation affects only the creep amount, not the mechanism; and (ii) in situ electric measurements, in which conductance was found to be enhanced by the creep. More pronounced creep plasticity for smaller nanorods is rationalized in consideration of the increased contributions of faster diffusion along the free surface for nanorods with large surface area to volume

ratios. As the surface-to-volume ratio increases, the activation energy for diffusion creep decreases, which results in increased diffusion creep strain in the nanorods. In addition, there is a possibility that the mass removal at the top surface of the nanorod (by the interfacial diffusion between the punch and the top surface) plays an important role in the axial creep displacement.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2010-0025526), and in part by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea Government Ministry of Trade, Industry and Energy (No. 20114010203020).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.actamat.2013.08.022.

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