Plastic deformation in nanocrystalline TiN at ultra-low stress: an *in situ* nanoindentation study

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Abstract

It is well adopted that a majority of ceramic materials have low ductility and the plastic yielding in crystalline ceramics occurs succeeding elastic deformation. Here by using *in situ* nanoindentation we show, however, that in nanocrystalline TiN, massive non-elastic events, such as grain rotation and grain boundary (GB) sliding, occur at ultra-low stresses (< 1 GPa), well below the yielding strength of the material (6~8 GPa). Furthermore, by performing *in situ* nanoindentations on TiN with different average grain sizes of 110 nm, 35 nm and 20 nm, we observed a prominent grain size effect: that is specimens with smaller average grain sizes possess greater plastic deformation than the ones with larger grains. This *in situ* nanoindentation study thus provides new perspectives on understanding plasticity of hard nanocrystalline ceramics at room temperature.

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1. Introduction

Nanostructured ceramic materials have attracted extensive interests owing to their unique electrical and magnetic properties, high strength and excellent thermal stability [1-3]. However, the applications of nanostructured ceramics are often limited by their poor ductility, which may lead to substantial device failure [4-5]. Therefore, significant efforts have been focused on improving ductility in nanostructured ceramics [6-8]. Although large plastic deformation of nanostructured ceramics has been reported in α -Al₂O₃, tetragonal ZrO₂ and MgO at elevated temperatures [9], the ductility of nanostructured ceramics at room temperature remain limited because of suppressed dislocation activities [10]. Initial work by Karch *et al.* suggests that ceramics may exhibit considerable ductility at room temperature if the grain size of a polycrystalline ceramic falls within nanoscale where the grain boundary (GB) sliding and grain rotation start to carry plastic deformation [11]. Such grain activities have been reported to enable large plastic strain in a variety of nanoceramics [12-16]. However, there is still a lack of direct experimental evidence for these mechanisms in nanoceramics, especially for the ceramics with grain sizes of 50 nm or less [17].

In situ nanoindentation in transmission electron microscope (TEM) provides great opportunities to investigate the deformation processes in real time [18]. A hand-full of prior work on *in situ* nanoindentation is available mainly for nanostructured metals [19-24]. For example, Shan *et al.* reported *in situ* observations of GB mediated plasticity, such as stress induced grain coarsening in nanocrystalline (nc) Ni films [23]. In contrast, prior reports of *in situ*

nanoindentation on nanostructured ceramics are rare [25-27]. Lee *et al.* reported direct observations of grain rotation and GB sliding assisted by the distribution of hard and soft grains in multi-phase bulk ceramic nanocomposites at room temperature [26].

As one of the transition metal nitrides with most technological interests, titanium nitride (TiN) possesses superior hardness, high electrical conductivity and excellent thermal stability [28]. TiN has a NaCl crystal structure. It can be easily synthesized on Si substrate with microstructure ranging from nc to epitaxial films. It has been extensively employed in a wide range of applications such as wear-resistant coatings [29], electrical contacts [30], and diffusion barriers [31, 32]. Thus understanding the fundamental deformation mechanism of nc TiN is of great interest [33-35]. However prior works mainly focus on *ex situ* studies which are difficult to make direct correlations between deformation mechanisms and grain size [36, 37]. Post-indentation TEM analysis of the indented regions suggested that the deformation could primarily occur by densification of grains and shear sliding along GBs [38, 39]. *In situ* nanoindentation experiments by Minor *et al.* were conducted on epitaxial TiN thin film, wherein the limited plasticity was attributed to the migration of dislocations [40]. There is still a lack of direct *in situ* nanoindentation study to explore grain size effects on the deformation mechanism of TiN thin films in poly- and nc regimes.

In this study, *in situ* nanoindentation experiments have been conducted at room temperature (RT) on nc TiN thin films with well controlled grain sizes. The microstructural evolutions of films during deformations have been captured along with the quantitative force-displacement (F-D) measurements in real time. Grain activities have firstly been observed in TiN thin films at RT. The grain-size dependent deformation mechanisms have been explored based on detailed microstructure analyses from *in situ* videos and the corresponding F-D measurements.

2. Experimental procedures

TiN thin films were deposited on Si (100) substrates using a pulsed laser deposition (PLD) system with a KrF excimer laser (Lambda Physik Compex Pro 205, $\lambda=248$ nm). The laser beam was focused to obtain an energy density of approximately 4.5 J/cm^2 at a 45° angle of incidence. The hot-pressed stoichiometric TiN target was obtained from CERAC Inc. Three depositions were conducted with a repetition rate of 5 Hz and the duration of 40 min at a base pressure of about 1×10^{-6} Torr. The grain size was tailored by controlling substrate temperature at 700°C , 300°C and room temperature (RT), respectively. No post-annealing was performed. The microstructures of as-deposited films were characterized by X-ray diffraction (XRD) (PANalytical Empyrean 2 X-ray diffractometer with Cu K_α radiation operating at 45kV and 40mA). Both plan-view and cross-sectional TEM samples were prepared by manual grinding, polishing, dimpling and a final ion milling process (PIPS 691 precision ion polishing system). The plan-view samples were firstly thinned from the backside of substrates and then ion polished from both film and substrate sides. Therefore, the thin areas of plan-view samples were mainly from the middle portion of the films. TEM and selected-area electron diffraction (SAED) analyses were conducted using a JEOL 2010 analytical microscope with a point-to-point resolution of 0.23 nm.

In situ nanoindentation experiments were conducted using an *in situ* nanoindentation holder manufactured by NanoFactory Inc. The indenter was equipped with a wedge shape diamond tip in order to avoid the slip between tip and sample surfaces. The contact surface of the indenter is flat and thus the indentation contact area is in rectangular shape. *In situ* movies and images were recorded during the loading and unloading processes using a built-in CCD camera in the microscope. During the indentation experiments, the indenter tip was fixed while the

samples were controlled by a piezoelectric actuator to move toward the tip with a precision movement as fine as 0.1 nm/step. A maximum indentation depth of 50 nm was used for cross-section samples to avoid substrate effect. During the loading process, a constant loading rate of 0.5nm/s and a holding time of 10 ns were used. For plan-view specimens, a maximum indentation depth of 100 nm was used with a constant loading rate of 1 nm/s and a holding time of 10 ns.

3. Results and Discussion

3.1 Microstructure of TiN Thin Films

Fig. 1 compares the XRD θ - 2θ scans of TiN thin films on Si (100) substrates deposited at 700 °C, 300 °C and RT, respectively. The TiN film deposited at 700 °C shows a strong peak at $\sim 42.5^\circ$, which corresponds to TiN (200) (Fig. 1(a)). This indicates that cubic TiN has grown highly textured along the (100) orientation. For films deposited at 300 °C (Fig. 1(b)), both TiN (111) and (200) peaks appear, indicating that the film is polycrystalline. For the film deposited at RT, only a weak TiN (111) peak has been observed (Fig. 1(c)), implying the formation of slightly (111) textured film. The XRD results suggest a decrease of texturing quality and grain size of the TiN films with decreasing deposition temperature.

The microstructures of the TiN thin films deposited at different temperatures were further examined by both plan-view and cross-sectional TEM (Fig. 2). Based on the bright field cross-section TEM images shown in Fig. 2(a1), (b1) and (c1), the thicknesses of TiN films deposited at 700 °C, 300 °C and RT were measured to be approximately 500, 360 and 300 nm, respectively. It is also shown that all the TiN films contain columnar grains. The corresponding SAED patterns shown as insets were taken from the Si $\langle 110 \rangle$ zone axis. The cross-sectional and plan-view dark field images in Fig. 2 indicate a clear decrease of grain size (both length and diameter)

with decreasing deposition temperature. Note that, the cross-sectional dark field images were generated from the out-of-plane direction of the samples, i.e. TiN (001) for the 700 °C deposited sample and TiN (111) for 300 °C and RT deposited samples. The plan-view dark field image of the 700 °C deposited sample was generated from TiN (001), while the images of the 300 °C and RT deposited samples were generated using TiN (111) diffraction ring in the SAED patterns. Fig. 2(a2) shows that the 700 °C deposited TiN sample contains columnar grains with the length same as the film thickness (~500 nm). The corresponding SAED pattern shows a clear cube-on-cube epitaxy of TiN on Si (100). The average diameter of the grains was estimated to be ~110 nm (Fig. 2(a4)) based on the plan-view dark field TEM images in Fig. 2(a3). The TiN film deposited at 300 °C has a nc structure with an average columnar grain length of ~175 nm and diameter of ~ 35 nm, as shown in Fig. 2(b2), (b3) and (b4). The SAED rings in Fig. 2(b1) confirm nc structure while the discontinuity of the rings suggests a (111) texture of the TiN film. The RT deposited TiN film contains nc grains with an average length of ~80 nm, as shown in Fig. 2(c1) and (c2). The average grain diameter is estimated to be ~20 nm (see Fig. 2(c3) and (c4)). The corresponding SAED pattern shows more continuous rings compared with the SAED pattern in Fig. 2(b1). It indicates a degradation of {111} texture, which is consistent with the XRD analyses. The reduction in texturing quality and grain size of the TiN films with decreasing deposition temperature is primarily attributed to the reduced adatom mobility on substrate surfaces at lower substrate temperatures. The deposition temperature and the corresponding average grain size for TiN specimens are summarized in Table I. Because the aspect ratios of the columnar grains (average length/diameter) are in comparable range for all three specimens, the average diameters of the grains are used to represent the average grain size and index the

specimens (e.g., TiN20 film represents the TiN thin film with an average grain diameter of 20 nm).

Table I. The deposition temperature of TiN thin films and the corresponding average grain size.

Deposition T (°C)	Avg. grain length (nm)	Avg. grain diameter (nm)	length/diameter	Specimen index
700	500	110	4.5	TiN110
300	175	35	5	TiN35
25 (RT)	80	20	4	TiN20

3.2 *In situ* Nanoindentation on Cross-sectional TiN Films

Fig. 3 presents the snapshots of *in situ* nanoindentation movie of the TiN110 film (deposited at 700 °C). The recorded movie can be found in the supplementary information (supplementary Movie 1). During nanoindentation process, the brightness and contrast of the specimen changes with the applied stress. However, by tracing the boundaries of grains in this movie, no significant grain activities were observed. As an example, the boundaries of two grains, A and B, were marked out by dashed lines in Fig. 3(a)-(d). The diameter of the columnar grain A and B is about 130 nm and 100 nm, respectively, which is comparable with the average grain size of this sample. By comparing the boundaries at different movie frames, no obvious position change or boundary evolution was found during the entire process, indicating that grain A and B didn't experience significant rotation or sliding during nanoindentation. The observed brightness and contrast variation could be related to the global deformation induced strain contrast rather than the local grain activities. After unloading, at 99.88 s (Fig. 3(d)), the sample was almost fully retracted to its original position (Fig. 3(a)) without significant change in contrast, implying a near elastic deformation of the specimen.

To better interpret the mechanical property of the films, stress-displacement (S-D) plot was calculated based on the force-displacement (F-D) plot recorded during this nanoindentation process. The instantaneous stress in the specimen, σ , can be estimated based on the force and the indentation geometries:

$$\sigma = \frac{F}{A}, \quad (1)$$

where F is the force (load), which is the direct measurement of the indentation system. A is the projected contact area. The nanoindentation tip in Fig. 3 shows a flat contact area with the film. Thus the projected contact area, A , can be calculated by:

$$A \approx td, \quad (2)$$

where t is the TEM foil thickness and d is the tip-sample contact length. Previous reports suggested that the thickness of TEM foils made by ion milling are typically ~30 nm or thicker [41, 42]. An estimation based on the CBED (convergent beam electron diffraction) method in the foil area. Such measurement yielded an estimated foil thickness of ~30 nm or thicker.

Fig. 3(e) shows the calculated S-D plot (using $d = 328.6$ nm and $t = 30$ nm). Different indentation stages corresponding to Fig. 3(a)-(d) were labeled. It is obvious that the TiN110 film did not exhibit any prominent plastic behavior during the indentation process.

In contrast plastic deformation was observed in the TiN35 film at an indentation depth of around 30 nm, as shown in Fig. 4(a) (calculated by using $d = 407$ nm, $t = 30$ nm). The loading curve showed an initial constant slope (~0.010 GPa/nm) up to 30 nm of indentation depth, and then gradually transitioned to a new slope of ~0.014 GPa/nm, indicating the existence of non-elastic deformation. The unloading curve is linear. Based on the stress value in the S-D plot, the plastic deformation happened far below the yield stress of TiN, ~ 6-8 GPa [28, 43]. To explore the mechanism of the plastic deformation in this specimen at such a low stress, a series of video

frames were analyzed in Fig. 4(b)-(f). Obvious grain activities were observed in the rectangular area. There are two columnar grains in this area, both with diameters of ~ 40 nm. Before indentation, they had a head-to-head contact and formed a 26° interaxial angle, as indicated by the two dashed lines in Fig. 4(b). Fig. 4(c) was captured right before the onset of the plastic deformation. By tracing the rotation angle of the dashed lines, the top grain tilted $\sim 4^\circ$ clockwise, while the bottom grain remains its original position, resulting in an interaxial angle of 22° between the two grains. Fig. 4(d) indicates the further plastic deformation when the top grain continued to tilt by 6° clockwise, which is 50% larger than the tilting angle during elastic deformation. At the maximum load (Fig. 4(e)), the top grain had tilted another 7° clockwise, resulting in an angle of 9° between the bottom and top. During the unloading process, the top grain rotated counterclockwise. However, after complete retraction (Fig. 4(f)), the top grain still remained a 4° clockwise tilt compared with its original position, suggesting the retention of residual plastic deformation of the film. *In situ* video (see Movie 2 in the supplementary information) and the corresponding S-D plot indicate that for the TiN35 film, local grain activities have occurred at a relatively low stress. Instead of the rotation and sliding of a large amount of the grains in the specimen, the applied stress only caused the bending/tilting of a small amount of grains. The bending/tilting of grains could be caused by both sample solid deformation and GB sliding. Therefore, as observed in the video, the grain bending/tilting activities contributed to both elastic and plastic deformation. However, the magnitude of bending/tilting is greater during plastic deformation.

Comparison of the above two sets of indentation experiments reveals that non-elastic grain activities are more obvious and frequent in the TiN35 film than those in the TiN110 film. Thus one may expect that the TiN20 film could have more significant grain activities. Fig. 5(a)

shows an S-D plot (calculated using $d = 320$ nm, $t = 30$ nm) of the nanoindentation on TiN20 film. The loading curve indicates an obvious plastic deformation under lower stress at an indentation depth less than 40 nm, followed by a more elastic deformation at higher stress. In the plastic deformation regime, the loading curve gradually curves upwards and finally reaches a relatively stable slope.

A series of movie frames were selected and carefully analyzed to reveal the deformation mechanism in the TiN20 specimen (see Movie 3 in the supplementary information). Among the snapshots, Fig. 5(c) was selected from the plastic deformation region, while Fig. 5(d) was selected from the beginning of the more elastic regime. Significant grain activities were observed in these snapshots. In particular, square box 1 and 2 were selected and the grain activities in each area were identified by tracing and comparing the GBs in each snapshot. Enlarged images of each area were shown as inset in each snapshot. Area 1 was on the left of the tip-specimen contact center, while area 2 was on the right side. As shown in Fig. 5(b), grain A and B in area 1, and grain C and D in area 2, were selected for analysis. Among these grains, grain D is identified as a reference grain since it remained stationary during the entire indentation process. Grains A and B have a comparable grain size of about 10 nm. They started to rotate at the very beginning of the loading process. From 0 to 23.13 s, grain A rotated $\sim 3^\circ$ counterclockwise, while grain B rotated $\sim 2^\circ$ clockwise. During subsequent deformation, both grain A and B rotated in clockwise direction. From 23.13s to 36.87 s, grain A and B rotated by 6° and 7° , respectively. By comparing Fig. 5(b) and 5(d), the shape of both grain A and B were significantly altered, which could be related with in-plane grain rotation induced contrast change. From 36.87s to 50.03s (maximum load), grains A and B further rotated 5° and 3° , respectively, along with continuous shape change. The shapes and positions of grains before indentation and at the maximum load

were overlapped and compared in Fig. 5(g). It is revealed that the nanograins experienced not only rotation and shape change, but also position shift. At the maximum load, grain B shifted 5.3 nm upwards. The comparison between the beginning and end of the indentation is shown in Fig. 5(h). After indentation, grain A remained with 6° clockwise rotation and 3.8 nm upward shift, while grain B remained with 2° clockwise rotation and 3 nm upward shift. The shapes of both grains were fully recovered after indentation. Grain C in area 2 also experienced rotation and sliding during indentation, while grain D showed no obvious activities in the entire process. As shown in Fig. 5(g), at the point of maximum load, grain C rotated 6° counterclockwise compared to the beginning. The right side boundary of grain C slid 3.6 nm towards grain D and led to the growth of the grain. After indentation (Fig. 5(h)), grain C retained 6° clockwise rotation and 4.5 nm shift. The detailed evolutions of all these 4 grains were summarized in Table II, where negative angle represents counterclockwise rotation. Overall, the observed grain activities include grain rotation, GB migration and grain shift. The rotation directions and shift distances for each grain are random, which indicates that the observed grain shape and position changes in the movie were caused by local grain activities instead of a global deformation of the whole specimen. The result of retained rotation and shift of grains after indentation is consistent with the plastic deformation observed in the S-D plot. It indicates that the plastic deformation of this sample is mainly attributed by these local grain activities.

Table II. Summary of grain activities of grain A-D in Fig. 5 during nanoindentation process

	00.00s– 23.13s	23.13s – 36.87s	36.87s – 50.03s	00.00s – 99.93s
A	-3°	+6°, shape changed	+5°	+6°, position changed
B	+2°	+7°, shape changed	+3°	+2°, position changed
C	-8°	0°	+14°, shape changed	+6°, position changed

D	0°	0°	0°	no changes
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In the S-D plots shown above, most of the samples didn't fully recover to displacement "0" after unloading. The unreversed distance indicated certain amount of residual plastic deformation in the sample. For the plots shown in Fig. 3(e), 4(a) and 5(a), the unreversed distances are 3, 6, and 11.7 nm, respectively, marked in red in the plots. The plasticity of the TiN films with different grain sizes was characterized by the unreversed distances in the S-D plots. Several *in situ* nanoindentations were conducted on each TiN sample at different areas. The statistics of the unreversed distances are shown in Fig. 6. In general, the TiN samples with smaller grain size show larger unreversed distance, which suggests an increase of plasticity with decreasing grain size of nc TiN films.

3.3 *In situ* Nanoindentation on Plan-View TiN Samples

In order to investigate the in-plane grain behaviors of the columnar shape grains in TiN thin films, *in situ* nanoindentation experiments were conducted on the plan-view TEM samples, as shown in Fig. 7 and Fig. 8. Dark field image mode was used to show a clear view of GB activities. To investigate more grain activities, the indent depth was increased to 100 nm for this set of experiments. Fig. 7 shows the selected video frames recorded during *in situ* indentation on the plan-view TiN35 specimen (see Movie 4 in the supplemental information). Instead of columnar shape, the grains in the plan-view TEM samples generally show equiaxed morphology. The frames show prominent variations in contrast and morphology of grains. From 0 to 25 s, grain A became darker but remained the same shape, while the shape of grain B changed since the contrast of both right and left corners of the grain became darker. From 25 s to 50.07 s, the shape of grain A changed while the top portion of the grain became brighter. Meanwhile, grain B

appeared smaller because the outer portion of the grain turned into dark contrast. After the complete loading-unloading cycle (Fig. 7(d)), both grain A and B recovered close to their original shape and contrast. During this loading-unloading experiment, grain A and B only experienced slow and partial changes in morphology/contrast, consistent with the observations during *in situ* nanoindentation of the cross-section TEM sample.

In comparison, *in situ* nanoindentation conducted on the plan-view TiN20 specimen (see Fig. 8 and Movie 5 in the supplemental information) showed a much more rapid and severe change of the shape and contrast of grains. Several typical grains A, B and C were selected for investigation. During loading process, two new grains, D and E, appeared on top of grain C at 6.57 s (Fig. 8(b)). From 6.57 s to 34.37 s, grains A, B, D, and E all lost their contrast, while grain C remained visible but became smaller. At 34.37 s (Fig. 8(c)), a new grain F appeared at the left of grain C. By 50.07 s (Fig. 8(d)), grain C gradually moved towards grain F and finally showed uniform contrast at the maximum load. During unloading process (Fig. 8(e)), grain C and F were separated. Then grain F gradually returned to its original dark contrast. After indentation (Fig. 8(f)), grain D and E still remained visible, while grain A and B were different from their original shapes and contrast. This series of snapshots implies that the plan-view TiN20 specimen experienced ampler grain activities and therefore more severe plastic deformation compared to the TiN35 sample.

Overall, the observations in the plan-view TEM samples are consistent with the results in the cross-section samples. This indicates similar behaviors of columnar grains in both in-plane and out-of-plane directions and thus confirms the deformation mechanisms in the three-dimensional TiN thin films.

3.4 Discussion

In bulk metallic and ceramic materials in micron size range, it is well accepted that plastic deformation occurs after elastic deformation, and the onset of plastic deformation (accompanied by dislocation dominated activities) typically signals the occurrence of yielding. However, we found that the S-D plots for TiN35 and TiN20 show strong evidences of plastic deformations at a relatively low indentation stress (< 1 GPa), much lower than the yield strength of films ($\sim 6-8$ GPa). In general, dislocation activities in nc ceramic materials are very limited at such a low stress at RT [36]. Previous reports suggested that the plastic deformation of nc TiN thin films could be related with the formation of nanocracks [39, 44] and the shear sliding along columnar GBs [45, 46]. In our experiments, no obvious nano-cracks or columnar shear cracks were observed during all the indentation processes. Instead, massive grain activities, including grain bending, rotation, and GB sliding etc., occurred during deformations of nc TiN. Thus we believe that, the plasticity of TiN films in this study could mainly be attributed to grain activities. Furthermore, the *in situ* nanoindentation results showed an obvious grain size effect on the grain activities, i.e. more grain activities in the samples with smaller grain sizes. For TiN110 film, the applied stress mainly induces global deformation of the specimen instead of grain activities. Hence there is a lack of plastic deformation. For TiN35 film with an intermediate grain size (~ 35 nm), the grains are small enough for the stress to induce a certain amount of grain activities, which account for the observed limited plastic deformation. In contrast, for the TiN20 films with a much smaller average grain size (~ 20 nm), the stress induces massive grain activities, which lead to significant plastic deformation. In the conventional ex-situ nanoindentation studies, the inversed Hall-Petch effect has been reported in TiN [28] and many other nitride materials [47] when the grain size decreased to below 50 nm. Our *in situ* nanoindentation results provided

direct evidences that these material softening effects could mainly be related with the enhanced grain activities with decreasing grain size.

According to the S-D plots for TiN35 and TiN20, it is interesting to note that when the grain size is small enough, the grain activities could occur at a stress much lower than the yield strength of the films. Previous studies revealed that the GB sliding rate ($\dot{\epsilon}$) is related with the applied stress σ , the absolute temperature (T), and the grain size of the material (d) [48, 49]. It could be theoretically estimated by the following equation:

$$\dot{\epsilon} = \frac{cDG\mathbf{b}}{kT} \left(\frac{\mathbf{b}}{d}\right)^m \left(\frac{\sigma}{G}\right)^n$$

where c is a constant, D is the diffusion coefficient, G is the shear modulus of the material at the testing temperature, $\mathbf{b}$ is the Burgers vector, k is Boltzmann's constant, m and n are the exponent constants [48]. This equation indicates that the GB sliding rate is proportional to the applied stress and not limited by the material yield strength. Therefore, GB sliding may even occur at ultra-low stress, but with a relatively low sliding rate, which explains the plastic deformation observed under low stress (below 1 GPa) during *in situ* nanoindentations on nanocrystalline TiN.

Further analysis on the S-D plots for TiN35 and TiN20 shows that these nc TiN films experienced more obvious plastic deformations at lower stress but less plastic deformations at higher stress, i.e., more unreversed grain activities occurred at the early stages of the nanoindentations. This could be related to the grain boundary characteristics in the early stage of the deformation. Previous reports suggested that high angle GBs have larger diffusion coefficient and thus a higher sliding rate than the low angle GBs [50, 51]. It was also reported that nc TiN thin films with high angle GBs could contain large residual stress [52]. Therefore, in the early stage of deformation, high angle GBs in nc TiN films could start to slide under low stress and at a relatively high rate, and form lower angle GBs. The residual stress in the film could also assist

this process and get released. As GB angles decrease and the stress releases, the GB sliding rate reduces. Thus at the later stage of deformation, the grain activities become slower even with increasing stress.

4. Conclusions

In situ nanoindentation experiments were conducted at RT on TiN thin films with the average grain size ranging from 110 nm to 20 nm. The deformation mechanisms of TiN films exhibited significant grain size dependence. The TiN 110 film showed nearly elastic deformation. In comparison, films with smaller grain size show abundant non-elastic deformation, manifested as grain rotation and grain boundary sliding, at ultra-low stress (< 1 GPa), well before the stress necessary for plastic yielding. This *in situ* study reveals the real time deformation mechanisms as a function of grain size, which is critical for understanding the mechanical properties of nc ceramic materials.

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Table and figure captions

Table I. The deposition temperature of TiN thin films and the corresponding average grain size.

Table II. Summary of grain activities of grain A-D in Fig. 5 during nanoindentation process

Fig. 1. The XRD profiles of TiN thin films on Si (100) substrates deposited at (a) 700 °C, (b) 300 °C and (c) RT.

Fig. 2. TEM images and grain size characterization of TiN thin films on Si (100) substrates deposited at (a) 700 °C, (b) 300 °C and (c) RT. The cross-section TEM images of each specimen are shown in (a1), (b1) and (c1). Insets are the corresponding selected area electron diffraction (SAED) patterns. (a2-c2) and (a3-c3) are the cross-section and plan-view dark field TEM images of the films. The statistics of grain diameter distribution presented in (a4-c4) show the average grain diameter of 110, 35 and 20 nm for films deposited at 700 °C, 300 °C and RT, respectively.

Fig. 3. A series of *in situ* TEM snap shots captured during nanoindentation on TiN110 thin film with a maximum indentation depth of 50 nm: (a) before indentation, (b) during loading, (c) at the maximum load, and (d) after unloading. (f) The stress-displacement plot of this indentation process shows nearly elastic deformation of the film with 110 nm grain size, with a small irreversible deformation of 3 nm.

Fig. 4. Response of the TiN35 thin film to *in situ* nanoindentation. (a) Stress-displacement plot shows prominent inelastic deformation when the indentation depth reaches ~ 30 nm. A series of video frames recorded during loading-unloading process: (b) right before indentation, (c) in the non-elastic deformation region during loading, (d) in the elastic region during loading, (e) at the maximum load, and (f) after indentation. The bending of a columnar grain during indentation is traced as shown in the dashed rectangle box.

Fig. 5. Plastic deformation of TiN20 thin film revealed during *in situ* nanoindentation. (a) Stress-displacement plot shows significant non-linear deformation behavior. Sequential video frames during loading-unloading process: (b) before indentation, (c) in the plastic region during loading, (d) in the elastic region during loading, (e) at the maximum load, and (f) after indentation. Insets show the magnified images of the square box 1 and 2. Comparisons of grain A, B and C (g) before indentation and at the maximum load, and (h) before and after indentation reveal several plastic deformation events, including grain rotation and GB sliding. Grain D barely changed and is used as a reference for the comparison.

Fig. 6. The irreversible deformation measured by numerous *in situ* nanoindentations tests on the TiN films. The statistics show greater irreversible deformation, an indication of more plasticity, in the TiN films with smaller average grain size.

Fig. 7. A series of movie frames during indentation on the plan-view sample of TiN35 film: (a) before indentation, (b) during loading, (c) at maximum load, and (d) after unloading. The maximum indentation depth is 100 nm. The movie was recorded in the dark field image mode to show a clear view of grain activities.

Fig. 8. A series of movie frames during indentation on the plan-view TEM sample of TiN₂₀ film: (a) before indentation, (b)-(c) during loading, (d) at maximum load, (e) during unloading, and (f) after unloading. The maximum indentation depth is 100 nm. The movie was recorded in the dark field image mode to show a clear view of grain activities.

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Plasticity of TiN films with different grain size

Fig 7

Fig 8