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Experimental Analysis of the Elastic–Plastic Transition During Nanoindentation of Single Crystal Alpha-Silicon Nitride

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The elastic-to-plastic transition in single crystal α-silicon nitride was experimentally characterized through a series of nanoindentation experiments using a spherical indenter. The experimental results provide a quantitative description of the critical shear strengths for the transition, as well as estimates of the shear modulus and nanohardness of the material.

I. Introduction

Silicon nitride (Si_3N_4) is an important ceramic material due to its unique mechanical, thermal, and electronic properties including high strength with low density, excellent resistance to thermo-mechanical-loading, good oxidation and corrosion resistance, and wide bandgap. For these reasons, it has attracted great interest for a wider range of applications, especially in the aerospace and micro-/nano-electronics industries. Polycrystalline silicon nitride is typically based on two well-known hexagonal polymorphs, α-Si_3N_4 (space group *P31c*) and β-Si_3N_4 (space group $P6_3/m$), although other polymorphs (c-Si_3N_4 and δ-Si_3N_4) have been also reported. However, experimental characterization of the mechanical properties of the single crystal α form of silicon nitride has been limited to conventional hardness measurement,[1–3] mainly due to the difficulties in producing appropriate single crystal samples large enough for mechanical testing. In particular, the single crystals' yielding behavior, which can be critical from a design perspective, has never been experimentally measured, although *ab initio* studies[4,5] have predicted the theoretical strength of the single crystals.

From this motivation, this work was undertaken to experimentally explore the elastic–plastic transition (i.e., yielding) in α-Si_3N_4 single crystal through a series of spherical nanoindentation experiments and analysis of 'pop-in' behavior in a way suggested by Page *et al*.[6] The purpose of this note is to report these results and the elastic modulus E and hardness H measured by nanoindentation testing.

II. Experimental Procedure

All measurements were performed on a small disk of ~3 mm in diameter and ~2 mm in thickness of an α-Si_3N_4 single crystal synthesized at Union Carbide Coating Services (Cleveland, OH). The crystal was produced by a chemical-vapor-deposition using $HSiCl_3$, NH_3, and H_2 gases reacted in a chamber at a pressure of about 70 Pa and a temperature of 1573–1773 K. Details of the crystal growth procedures and fundamental information about the produced crystal are described elsewhere.[2,3] Laue back-reflection analysis confirmed that the sample was an α-Si_3N_4 single crystal with a flat testing surface normal to the [11$\bar{2}$0] direction. Nanoindentation experiments were restricted to this surface due to the limited volume of prepared sample. Although we could not fully evaluate the dependency of crystallographic orientation, insight can be gained from previous studies[2,3] in which Knoop and Vickers hardness tests were carried out on several different surfaces of a sample produced by the same methods. The studies[2,3] revealed that both the hardness and indentation fracture toughness were almost independent of orientation "within statistical variations," i.e., no greater than one standard deviation. This suggests that these mechanical properties are essentially close to isotropic at room temperature. These results are qualitatively consistent with those in an earlier study of an α-Si_3N_4 single crystal by Nihara and Hirai,[1] in which the hardness showed only a small variation with changing orientation.

Nanoindentation experiments were conducted using a Nanoindenter-XP (formerly MTS—now Agilent, Oak Ridge, TN) system with a spherical indenter. The indenter radius R was found to be 1.5 μm, which was determined from Hertzian contact analysis[6,7] of indentations made on an electropolished tungsten single crystal whose elastic constants were independently measured by ultrasonic techniques. The detailed procedure is well described elsewhere.[8] With this indenter, load-controlled experiments were carried out at a various loading rates in the range 0.05–10 mN/s to various peak loads in the range 1–50 mN. For measurement of hardness and elastic modulus, some tests were also performed with a three-sided-pyramidal Berkovich indenter. In all experiments, thermal drift was maintained below 0.05 nm/s.

III. Results and Discussion

Figure 1a shows a representative nanoindentation load-displacement (P–h) curve obtained at a relatively low load, P_{max} = 30 mN. The loading part of the curve is completely reversed upon unloading, indicating that the deformation is perfectly elastic. This elastic P–h behavior can be described by Hertzian contact theory using[6,7]:

$$P = \frac{4}{3} E_r \sqrt{R} \cdot h^{\frac{3}{2}} \tag{1}$$

where the reduced modulus, E_r, is given by

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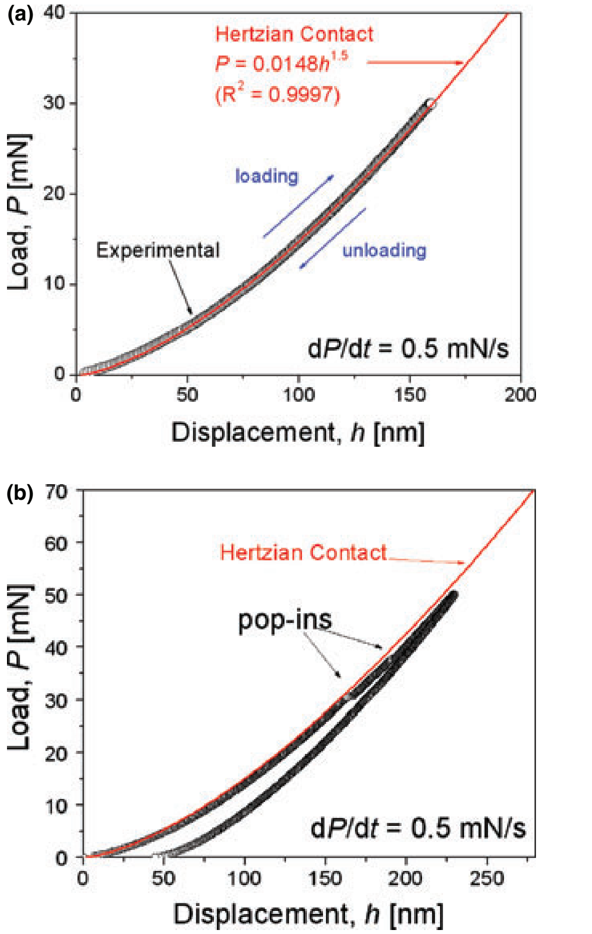

Fig. 1. Nanoindentation load-displacement curves showing (a) perfectly elastic behaviors below the first pop-in load; and (b) pop-in during loading and permanent deformation after unloading.

$$\frac{E_s}{1-\nu_s^2} = \left(\frac{1}{E_r} - \frac{1-\nu_i^2}{E_i}\right)^{-1} \tag{2}$$

In this expression, E is the elastic modulus and ν is Poisson's ratio, with the subscripts s and i indicating the sample and the indenter. The reduced modulus, E_r, accounts for the fact that elastic deformations occur in both the indenter and the sample. For the diamond tip employed in the studies, E_i = 1141 GPa and ν_i = 0.07.[9] By fitting the loading part of the P–h curve to Eq. (1) and applying a typical Poisson's ratio for polycrystalline Si_3N_4 (ν_s = 0.24) [10] in Eq. (2), E_s was calculated as 365 ± 2 GPa. For comparison purposes, we also estimated the E_s by nanoindentation with a Berkovich indenter according to Oliver-Pharr method.[9] To avoid issues related to the precise area function, a large indentation load of 700 mN (that is the maximum load of the used instrument) was utilized. The estimated values from the Berkovich indentations were E_s = 364 ± 5 GPa, which is essentially the same as that measured by spherical indentation, and H = 34.5 ± 2 GPa. Thus, the shear modulus, $G = E/2(1+\nu)$, is approximately 147 GPa assuming E = 365 GPa. Interestingly, the G and H obtained here are higher than the predicted values of defect-free α-Si_3N_4 single crystals estimated in an *ab initio* study by Ogata *et al.*,[4] G = 132 GPa and H = 23 GPa.

Figure 1(b) shows a P–h curve recorded at somewhat higher load, P_{max} = 50 mN. A sudden displacement excursion or "pop-in" was observed during the loading sequence, and upon unloading, the displacement was not fully recovered, thus suggesting that the pop-in corresponds to the elastic–plastic transition, i.e., yielding and the onset of plasticity, as reported previously (for example, see Refs. 6,8,11–14).

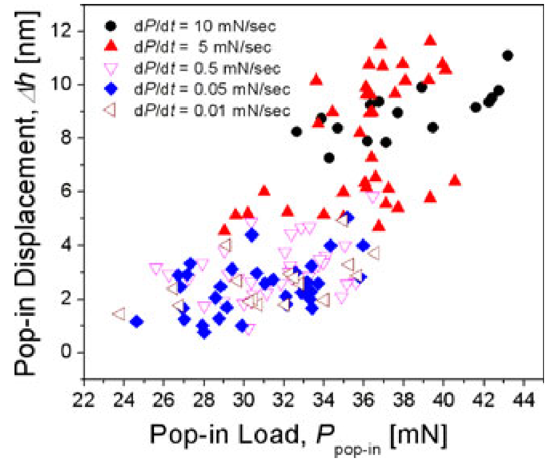

Fig. 2. The relationship between the load at the first pop-in and the resulting displacement excursion during the pop-in.

Figure 2 illustrates the correlation between the first pop-in load and the amount of the indenter displacement during the pop-in event. It is clear that the higher pop-in load, the larger pop-in displacement, as has been observed by others.[13] The behavior suggests that, at the pop-in event, the indenter displacement jumps from purely elastic Hertzian contact to a P–h curve more representative of elastic–plastic contact, and that, for a given R, the physical nature of the elastic–plastic transition does not vary with the load level or loading rate.

As the first pop-in event is caused by the elastic–plastic transition, the maximum shear stress at pop-in represents the critical shear yield strength. For Hertzian contact, the maximum shear stress occurs at a distance approximately half the contact radius directly below contact on the axis of symmetry. The magnitude of this shear stress is given by[6,7]:

$$\tau_{max} = 0.31p_0 = 0.31\left(\frac{3}{2}p_m\right) = 0.31\left(\frac{6E_r^2}{\pi^3R^2}P\right)^{\frac{1}{3}} \tag{3}$$

where p_0 and p_m are the maximum and mean pressure of the contact, respectively. As shown in Fig. 3, the calculated τ_{max} at pop-in points is distributed over the range 17–21 GPa. These values are of the order of the theoretical shear strength of a defect-free material, which is often estimated as $G/2\pi$ or $G/10$.[15] For G = 147 GPa, the theoretical strength should

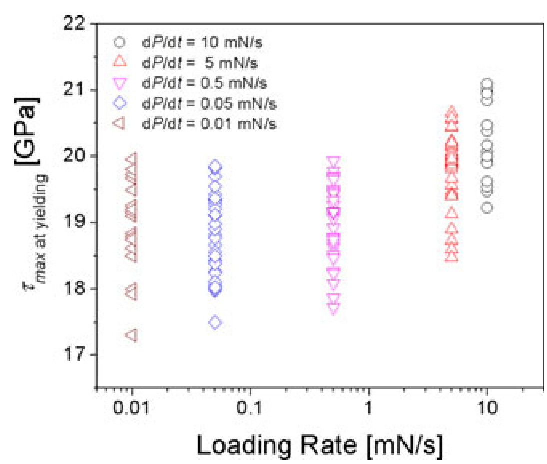

Fig. 3. Variation in the maximum shear stress for the elastic-to-plastic transition as a function of loading rates.

thus be in the range 15–23 GPa, consistent with the experimental measurements. This suggests that the pop-in is indeed associated with the homogeneous nucleation of dislocations rather than the activation of pre-existing dislocations.

As shown in Fig. 3, higher loading rates generally produce higher pop-in loads and thus higher critical shear strengths, in a manner consistent with previous observations[13,14]; if loading rate is higher, the probability of reaching a critical thermal fluctuation (to overcome the activation energy barrier) at a certain stress is lower, and higher stress is required. Thus, the pop-in event results from a stress-assisted thermally activated process, most commonly thought to be associated with homogeneous nucleation of dislocations[16,17] in a dislocation-free region of the crystal.

IV. Summary

The elastic-to-plastic transition in single crystal α-silicon nitride was experimentally characterized through a series of nanoindentation experiments using a spherical indenter. The experimental results show that the critical shear strengths for the transition are in the 17–21 GPa, depending on loading rate. Other properties were measured using a Berkovich indenter, giving $E = \sim 365$ GPa, $G = \sim 147$ GPa, and $H = \sim 35$ GPa, all of which are higher than values predicted by *ab initio* calculations.

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