Investigation of Specificity of Mechanical Properties of Hard Materials on Nanoscale with Use of SPM- Nanohardness Tester

N.A. Lvova, V.D. Blank, K.V. Gogolinskiy, V.F. Kulibaba
Technological Institute for Superhard and Novel Carbon Materials (TISNCM), Troitsk, Moscow Region, Russian Federation
natalvova@rambler.ru

Abstract. Specifisities of deformation on nanoscale of hard brittle materials with the hardness exceeding 10 GPa by means of scanning probe microscope – nanohardness tester "NanoScan" are investigated. It is found, that pile-up is forming at scratching of sample surface with use of diamond indenter. Height of this pile-up depends on hardness and elastic modulus of the material. Definition of the contact area without taking into account height of pile-up leads to an overestimation of hardness values. At scratching of silicon carbide surface a transition from plastic flow to fracture is found out. The results received allowed to estimate fracture toughness $K_{IC}$ for silicon carbide.

Introduction

Mechanical properties are of great importance for characterization of hard and superhard materials such as minerals, ceramics, and glasses. Hard and superhard materials concern to substances with covalent bonding. Large lattice resistance to movement of dislocations in these materials is the reason of their brittleness at a room temperature [1]. In practice measurement of microhardness of brittle hard materials by standard methods of indentations and sclerometry (scratching at a constant indenter load) is accompanied by formation of system of cracks on a surface or near to it. However, reduction of scale of indentation and scratching up to a submicronic level does possible to observe essentially plastic flow without formation of cracks [2].

According to the quantitative analysis of this effect lead Lawn and Fuller [3], transition from plastic flow to fracture occurs at increase in the indentation size up to size $a$, given by

$$a = \left( \frac{K_{IC}}{H} \right)^2 \frac{\pi^3}{12} \tan^2 \theta$$

where $H$ is hardness, $K_{IC}$ is fracture toughness of the material, $\theta$ is indenter half angle. Before such transition was observed at scratching of surface of glasses [2] and silicon [4], the width of the scratch was about some microns.

For measurements of mechanical characteristics on submicronic and nanoscale nanoindentation is usually used. Oliver-Pharr method is standard for definition $H$ and $E$ on a "load-penetration depth" curve. However in case of pile-up formation this method may gives the underestimated value of the contact area, that leads to an overestimation of $H$ and $E$ values.
Experimental method of measurement of mechanical characteristics is nanoindentation and nanoscratching by means of atomic-force microscope (AFM) [5]. Indentation with use of AFM has advantage in comparison with conventional nanoindentation, because a direct supervision of a residual indent and groove is possible. The purpose of the present work is to research mechanisms and laws of pile-up formation, and also influence of pile-up on measurement of mechanical characteristics of hard and superhard materials with use of scanning probe microscope (SPM). Besides especial interest represents an opportunity of observation of transition from plastic flow to fracture of traditionally brittle hard materials at nanoindentation and nanoscratching.

Experiments

The NanoScan (NS) measuring system based upon principles of SPM, is used in the present study. The NS developed in TISNCM, is an effective tool for studying mechanical properties of hard and superhard materials on submicronic and nanoscale [6]. The NS differs from other similar devices with high stiffness of a probe (~10^4 N/m), representing piezoceramic resonator in the form of a bimorph cantilever beam. The tip for surface scanning is simultaneously the indenter for scratching and indentation. Diamond trihedral pyramids close to Berkovich pyramid, synthesized in TISNCM are used as tips. Work of the probe in a resonant mode allows to control tip-surface contact on change of amplitude and frequency of the probe oscillations. Such mode allows not only to receive the information about topography of surface scanned, but also to estimate the elastic modulus in various points of the surface during scanning (to build a map of the elastic modulus). The construction of the probe gives possibility to put indenter load up to 100 mN, that enables to measure hardness of hard and superhard materials by indentation and sclerometry method.

In NS measurement system the original method of elastic modulus measurement by means of approach curves is applied [7]. This method allows to measure elastic modulus on scale less than 100 nm for a wide range of objects. The method is based on dependence of frequency of the probe oscillations which is being in contact to the surface, on penetration of the tip into the surface at loading. Application of NS for materials with hardness 1-100 GPa and the elastic modulus 10-1000 GPa is most effective.

The technique of measurement of hardness by means of NS consists in the following: in SPM mode the surface of the sample is investigated and the site with a minimal inclination and a roughness gets out. On the chosen site the same tip does a scratch or indent with the designated indenter load. Then the same site is scanned in SPM mode again. The received image is used for definition of character of deformations and the width of the scratch. Microhardness of various materials, obtained by sclerometry and indentation methods, have close values in that case when the tip at scratching plastically deforms the material. It corresponds to a case “indenter edge forward” scratching. Thus deformation has a character of a plastic expression from the groove, similar to expression at Vickers test. However, the plastic part of the total deformation at scratching is more, than at indentation [8]. Thus hardness $H$ is defined as:

$$H = kP / b^2$$

where $k$ - factor of the form of indenter, $P$ - load on indenter, $b$ - width of the residual scratch [3]. The shape of the indenter is a very important parameter for submicrometre hardness tests, but in practice it is difficult to make indenters having a repeatable geometry. So an individual indenter calibration on reference materials with known hardness is required. For this purpose process of measurement of hardness on the reference sample is carried out at different loadings and, accordingly, different values of scratch width. Then if the scratch width on the sample tested $b_s$ is close to that on standard sample $b_S$, hardness $H_s$ of the sample tested according to the formula (1) is defined as
where \( P_x \) and \( P_s \) - load on the indenter at scratching the sample and the standard with known hardness \( H_s \) correspondingly. The reference sample should be homogeneous on volume and isotropic as much as possible, with a smooth surface. It is necessary to measure hardness of the reference sample by the standard certified devices preliminary. As it was mentioned earlier, Vickers hardness test is the most close to the method described. Thus, conversion from micro- to nanohardness is possible.

In addition hardness of the samples investigated was controlled by means of standard microhardness tester, and also of commercial "NanoHardness Tester" (dynamic nanoindentation method).

**Results and discussion**

Monocrystals of hard and superhard materials were chosen as samples in this study. Surfaces of samples were prepared by careful mechanical polishing. Nanocratching of samples was carried out under the scheme "by an edge forward" and it was not accompanied by formation of radial cracks. Thus formation of pile-up on both sides of the scratch was observed. Distances \( S_1, S_2 \) and \( S_3 \) (Figure 1) were used as width of the scratch and indent in different works [4,9,10]. Therefore it was important to find out what of these distances should be considered at definition of hardness by a sclerometry method on nanoscale. Glass was chosen as the test sample. Results of measurements were shown that hardness measured in view of distance \( S_1 \) is equivalent to microhardness. The choice of distances \( S_2 \) and \( S_3 \) leads to the underestimated or overestimated values.

It is known, that there is an elastic recovery of depth of the scratch after removal of loading [11], thus the distance between tops of pile-up (\( S_1 \)) does not vary. Therefore in case of an estimation of width of scratch on distance \( S_2 \) the mistake in definition of hardness arises owing to a various degree of elastic recovery at different materials. The mistake in determining \( H \) at definition of width of scratch as \( S_3 \) arises owing to a difference in a configuration of pile-up for various substances. At increase in loading and, consequently, width of scratche up to 1,5 \( \mu m \) a mistake in measurement of the width increases, connected with outcrops of dislocations in the pile-up area (Figure 2).

In work [5] a significant difference in hardness values obtained by Oliver-Pharr procedure and from direct measurement of the size of the indent by means of AFM for fused silica and silicon was observed. A conclusion has been drawn that Berkovich and Vickers indenters are blunt and, therefore, not suitable for hardness test by nanoindentation method because of
significant elastic recovery of the residual indent. Thus special tips with an included angle of approximately 60° are necessary for nanohardness measurements, especially when depth of penetration does not exceed 50 nanometers. For Berkovich indenter this size is about 140°. In the present work Berkovich indenters with included angles from 120° up to 160° were used for nanoscraping. However, a distinction in the hardness values obtained for indenters with different angles was not marked. It is known, the sclerometry method implies a larger plastic deformation in comparison with the indentation method [8]. So the impression is easier to form by scratching, then by indentation. Thus, an advantage of sclerometry method is an opportunity of using of standard Berkovich pyramids, and also more blunt indenters for nanohardness measurements. It is especially important for hardness tests on thin films and coatings with thickness not exceeding some tens nanometers.

Hardness values were defined not less than on ten scratches, made in various crystallographic directions. Results of hardness measurements for investigated samples are listed in Table 1. Hardness measured by means of NS, coincides with microhardness, whereas dynamic indentation method gives the overestimated values \( H \) (dynamic nanoind.). Therefore microindentation of hard and superhard materials can be substituted for equivalent by results, but less destroying nanosclerometry.

Table 1. Hardness of investigated samples

| Sample | Glass | Quartz | Silicon | ZrO\(_2\) | Ruby | Sapphire | Silicon carbide |
|--------|-------|--------|---------|-----------|------|----------|-----------------|
| \( H \) (NanoScan), GPa | 6.0±0.3 | 12±1 | 12±1 | 18±1 | 22±2 | 21±2 | 32±3 |
| Microhardness, GPa | 6.2±0.3 | 11±1 | 12±1 | 16±2 | 20±2 | 22±2 | 33±3 |
| \( H \) (dynamic nanoind.), GPa | 5.6±0.5 | 10±1 | 12±1 | 21±2 | 33±3 | 30±3 | 45±4 |

Thus for revealing of crystals anisotropy the sclerometry method appears more effective. Hardness measurement by a sclerometry method is influenced by the relation between the direction of the hardness track and the underlying crystal geometry. Anisotropy of hardness is shown only in change of width of the scratch. Indentation with use of Berkovich and Vickers pyramids appears less effective because at presence of anisotropy a print of a pyramid get the deformed form. That complicates measurement of their diagonals and, hence, definition of value of hardness.

Jadret et al. [10] investigated scratching process of elastic-plastic materials in a wide range of physical-mechanical properties from metals up to polymers, width of residual scratch was in range from 1 to 30 µm. It is revealed, that the height of pile-up depends on a ratio of elastic and plastic parts in the total deformation, and this dependence is the general for all materials investigated. Bucaille et al. [11] carried out a numerical study of the behavior of elastic-plastic materials during a scratch test. Simulations were performed with a three-dimensional finite element modeling, the results showed a good correlation with experimental study [10]. According to [11], the value of height of pile-up \( h_a \) to full depth of a scratch \( h \) (Figure 1) depends on a reologic factor \( X = E \cot \theta / \sigma_0 \), where \( E \) – Young’s modulus, \( \sigma_0 \) – yield stress, and \( \theta \) - indenter half angle. For brittle materials \( H = 2\sigma_0 \) [12]. When an interaction of the indenter and surface is elastic – plastic, \( h_a / h \) value is given by following:

\[
\frac{h_a}{h} = 0.25339 \ln X + 0.5017
\]  

(4)

at scratching using Berkovich indenter by "an edge forward" scheme.

Dependence \( h_a / h \) for the materials investigated in our study is represented on Figure 3. Diamond indenter with half angle about 120° was used for the scratching. The result of calculation under (5) is...
represented with a continuous line. The good agreement of data of the present work with (4) for all samples investigated, except for silicon, confirms plastic flow in these materials, thus formations of system of cracks do not occur in all range of the load applied. Similar research was carried out for silicon carbide, included angle of the indenter used was 140°. The height of pile-up around of the scratch approximately corresponded to the size calculated under (4).

However, silicon is exception, because pile-up is not formed at the scratching. At the same time asperities arises at the bottom of the scratch groove, which are absent at the bottom of a scratch on surface of other sample. The mode I fracture toughness $K_{IC}$ determined at indentation of silicon on submicronic scale is about 0.6 MPa $\sqrt{m}$ [13]. According to (1), transition from plastic deformation to fracture in silicon should occur at excess of scratch width of value ~300nm. Therefore asperities observed may be consided as median cracks arising at scratching by pyramidal indenter. Presence of system of median cracks testifies that a critical pressure for them in silicon below, than for radial cracks. Besides at penetration of indenter into the surface of silicon the phase transition induced by contact pressure and accompanied change of density of the material [13] is possible. Such phase transition also can influence nanoscratching of silicon surface.

The study shown, that significant pile-up is formed at scratching of ZrO$_2$, sapphire, ruby and silicon carbide, for which hardness measured by dynamic nanoindentation method with use of "NanoHardness Tester", exceeds values received by nanosclerometry and microindentation methods. According to [10], for the same samples pile-up at nanoindentation should be formed. In that case heigh of pile-up should be included into the penetration depth of indenter. However, penetration depth in Oliver-Pharr procedure is counted from a level of an initial surface. Therefore the projected contact area appears underestimated, that leads to the overestimated value of hardness calculated. Thus, it is possible to explain the difference of hardness values by mistake in definition of the contact area using dynamic nanoindentation.

At scratching of 15R-SiC monocrystal surface a transition from plastic flow to fracture with formation of radial cracks was observed at increase in scratch width till 800 nm, that corresponded to loading 8 mN (Figure 4). Radial and median cracks appeared at scratching under the scheme "indenter edge forward", and under the scheme "indenter face forward". However scratching the sample "face forward" is much more destructive in comparison with scratching "an edge forward" at the same load. At indentation of SiC formation of radial cracks was not observed.
The results received allowed to estimate fracture toughness $K_{IC}$ for silicon carbide. As scratching by the “edge forward” method is similar to impression in Vickers hardness test, we used a model for indentation by Vickers pyramid [12]. Thus $K_{IC}$ is given by

$$K_{IC} = 0.035(L/s)^{1/2}(CE/H)^{2/5}Hs^{1/2}C^{-1}$$

(5)

where $s$ – half of the scratch width, $L$ - length of a radial crack, $C=2$ for brittle materials [12]. The estimation according to this model gives value $K_{IC}$ close to 1MPa$\sqrt{m}$. The literature data is 2.8 MPa$\sqrt{m}$. Underestimated value $K_{IC}$ received in the present work, probably, is connected with features of the sample studied, and also with use of model for indentation, extended to nanoscale. Substitution $H$ and $E$ obtained in the present work to the formula (1) gives value $a \sim 500$ nanometers. That corresponds to the scratch width at which median cracks appear. As radial cracks arise at increase in width of a scratch up to 800 nanometer, it is possible to draw a conclusion, that in given sample SiC critical loading for median cracks is less, than for radial.

**Conclusions**

It was shown that nanoscratching is an effective method of investigation of plastic deformation of brittle hard and superhard materials on nanoscale. Definition of contact width of a residual scratch as a distance between tops of pile-up on sides of the scratch groove allows to avoid mistakes in hardness measurement, connected with elastic recovery, and also with difference in pile-up configuration. Nanohardness measured by sclerometry does not depend on included angle of diamond indenter in the angle range of $120^\circ \pm 160^\circ$. Height of pile-up formed at scratching depends on rheologic factor of material. Observation of transition from plastic flow to fracture with increase in load on indenter gives possibility to study nucleation of nanocracks of various types. Moreover it is possible to determine fracture characteristics on submicronic and nanoscale.

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