

Nano-sclerometry measurements of superhard materials and diamond hardness using scanning force microscope with the ultrahard fullerite C₆₀ tip

V. Blank and M. Popov

*Research Center for Superhard Materials, Troitsk, Moscow reg., 142092, Russia and
Institute of Spectroscopy of the Russian Academy of Sciences, Troitsk, Moscow reg.,
142092, Russia*

N. Lvova

*Institute of Spectroscopy of the Russian Academy of Sciences, Troitsk, Moscow reg.,
142092, Russia*

K. Gogolinsky

High Technology Electronics, Zelenograd, Moscow K-681, P.O. Box 6, 103681, Russia

V. Reshetov

Moscow Physical Engineering Institute. Moscow, 115409, Russia

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The new procedure for the hardness measurements of superhard materials including diamond using the scanning force microscope with the ultrahard fullerite (CM) tip was developed. It is shown that diamond is plastically deformed under the indentation by the ultrahard fullerite indenter at room temperature. Now the correct measurements of diamond hardness have become possible. The hardness values measured are 137 ± 6 and 167 ± 5 GPa for the diamond faces (100) and (111), respectively.

I. INTRODUCTION

Recently a study of mechanical properties of materials on a submicron length scale has become of interest to many investigators. In particular, the problem of the submicron hardness tests exists for thin films and fibers, for the nanophase, and for composite materials. The procedure of these tests was developed in recent years. The measurements are performed using the special hardness testers at the submicro- and nanometer scales which are suitable for measuring hardness against penetration depth.¹⁻⁶ In addition, an indentation size is controlled with scanning or transmission electron microscopy, or scanning force microscopy (SFM). Performing of the direct hardness measurements using the SFM is possible without any additional equipment.⁷

Plasticity of brittle materials and a possibility of a crack-free indentation on the submicron length scale¹ make the procedure of the submicron hardness measurements available for superhard materials, especially for diamond, whereas earlier the plasticity of diamond at room temperature as well as results of the hardness measurements were doubtful.⁸

An extra opportunity for carrying out these tests appears with use of ultrahard fullerite C₆₀ as the indenter material. The synthesis conditions of this material and investigation of its structure by x-ray powder diffractometry and Raman scattering were described in Refs. 9 and 10. Theoretical prediction of anomalously high mechanical properties of the fullerite C₆₀ phase,

characterized by the intermolecular distances matching the intermolecular distances of C-C bonds, is given in Ref. 11.

The NanoScan (NS) measurement system based upon the principles of the SFM is used in the present study for hardness measurements of superhard materials and diamond. It was developed by the HTE company (Zelenograd) in partnership with the Moscow Engineering and Physics Institute.

II. NANOSCAN MEASUREMENT SYSTEM

The NanoScan has the following differences from the known ARM.¹²⁻¹³ The sensitive part of the probe is a piezoceramic resonator (PCR) in the form of a bimorph cantilever beam. The cantilever was made similarly to that reported in Ref. 14, but with higher bending stiffness. The effective spring constant of the cantilever was determined from load-displacement dependence of the cantilever and found equal to 10^5 N/m. The PCR is connected to an autogenerator circuit, and they form the completed oscillation system. This system oscillates at a resonant frequency F with a cantilever bending amplitude A ($F = 10$ - 100 kHz, $A = 0.1$ - 10 nm). Contrary to Ref. 14, where an ac force detection is used (dc output signal proportional to the magnitude of ac force is measured), in NS the amplitude and frequency of oscillation are measured and controlled with a feedback system during scanning. As a

result, the surface images can be obtained with the constant value of one of these two parameters (A or F). These modes of measurement are sensitive to viscous and elastic properties of the studied surface.¹⁵ This makes it possible to observe both viscous surfaces and elastic surfaces under a viscous layer (for example, under a contamination layer). This possibility was checked against a sample with known structure that was covered by a layer of oil.

The second important feature of the NS is the vertical displacement system of the tip relative to a surface. The actuating part of this system is bimorph, which bends under the influence of a control voltage. This makes it possible to make a controllable indentation (with applying the bending voltage). The tip for the surface scanning in the NS is simultaneously an indenter for indentation. The maximum bend amplitude is $5\ \mu\text{m}$ and the maximum load on tip is $0.5\ \text{N}$. To provide the measurements of the sclerometry hardness (scratching at constant load on the tip), the XY-scanner moves the sample for the given distance within the scanning range. As a result a scratch is formed on the surface.

So, the design and operational principle of the probe allow use of the cantilever with a stiffness of bending higher than known earlier, achieving a high load during the indentation.

The problems of a hysteresis, nonlinearity, and cross-talk among the x , y , and z deflections in a piezoelectric scanner are important for scanning probe microscopy.^{12, 13} We studied this phenomenon for NS using samples with a periodic structure of the known geometrical sizes.¹⁶ Distortion of geometrical sizes of the image details does not exceed 10% for the NS. Creep of the piezoelectric material is avoided by pauses about 10 s under indentation and between indentation and the scanning.

However, it is necessary to note that the indentations are made in the same area of the scanning window and the scanning will be carried out in an identical mode (window of scanning, number of lines, speed of scanning, etc.). Hence, the geometrical distortions are always constant in the experiments and the instrumental error of the indentation size measurements less than 1%.

III. PLASTICITY OF DIAMOND AT ROOM TEMPERATURE

To study the plasticity of diamond at room temperature for correct measurements of the diamond hardness and to perform a comparison (if the hardness of ultrahard fullerite C_{60} , and diamond, a set of scratches was created on the surface (111) of a natural diamond crystal with any one of the edges of the specimens of ultrahard fullerite and carbonado-type diamond. A relief of the modifying

diamond surface (111) was studied using the NS. The characteristic results of these tests are shown in Fig. 1.

The scratching of the surface (111) of the natural diamond crystal with the carbonado was accompanied by the appearance of numerous cracks [Fig. 1(a)]. That was typical for diamond.⁸

In contrast to this, the diamond surface (111) was deformed as a plastic material [Fig. 1(b)] under the scratching with ultrahard fullerite. It means that the hardness of ultrahard fullerite is enough to create a sufficient pressure in the contact point for the plastic flow of the diamond at room temperature, and the hardness of

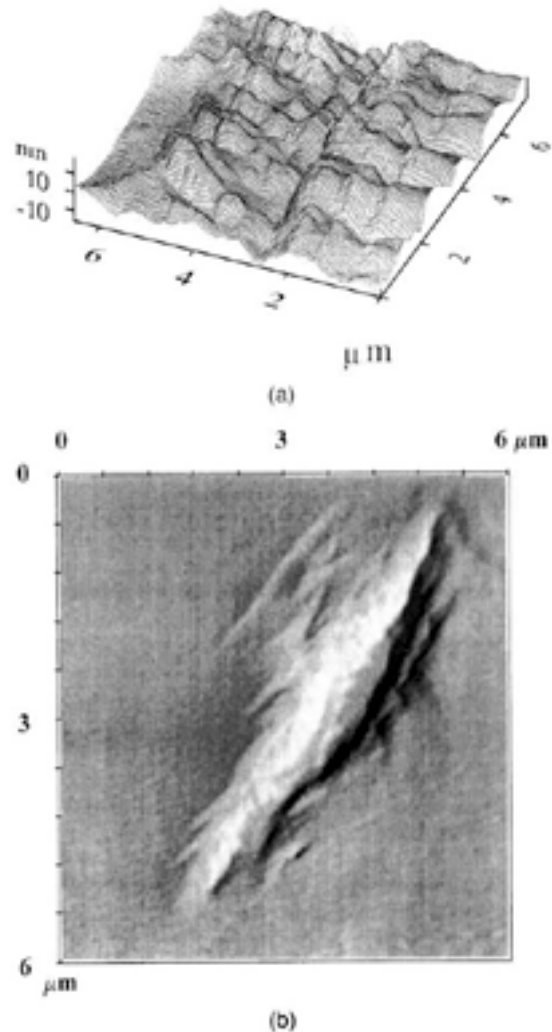


FIG. 1. The NanoScan images of the scratches on the surface (111) of a natural diamond crystal. The scratches were created at room temperature by carbonado-type diamond (a) and ultrahard fullerite (b). Vertical scale is $90\ \text{nm}$ for (b).

and the hardness of ultrahard fullerite exceeds the hardness of diamond.

Results of this experiment provide the opportunity for correct diamond hardness measurements with the ultrahard fullerite indenter.

IV. HARDNESS MEASUREMENTS

The hardness measurements at a submicron scale may be accompanied by a specific kind of error.^{4, 17} To avoid this a new procedure for hardness measurement was developed in the present study.

The method of sclerometry (scratch at a constant indenter load) was used for hardness measurements using the NanoScan. The sclerometry method implies a larger plastic deformation in comparison with the indentation method¹⁸ [that is, a value $e_e/(e_e + e_p)$ for the method of indentation exceeds that for the method of sclerometry; here e_e is the elastic and e_p is the plastic deformation in the volume deformed under the scratching or indentation.

A detailed comparison of the indentation and sclerometry methods is described in Ref. 18. These methods conform well to each other.

According to the sclerometry method the hardness value H is calculated as

$$H = kP/b^2 \quad (1)$$

In this equation k is a coefficient of the tip shape, P is the indenter load, and b is a scratch width.

The shape of the indenter is a very important parameter for the submicron hardness test,¹⁷ but in practice it is difficult to make the indenters with a repeatable geometry. A special procedure was used in this study to perform the indenter calibration.

In accordance with the standard method of the sclerometry, at designated P the scratch width b is measured. During the proposed procedure b is a constant (in this study it was 0.6 μm), P_m is measured and the hardness H_m is proportional to P_m , according to Eq. (1). Thus, it is necessary to perform the tip calibration by reference to a primary standard with the known hardness H_s (to determine the load P_s , under that, the scratch with $b = 0.6 \mu\text{m}$ is created) to measure the hardness of other materials. According to Eq. (1), if the b^2 is constant and the k is constant, we have:

$$H_m/H_s = P_m/P_s \quad \text{and} \quad H_m = H_s (P_m/P_s) \quad (2)$$

The primary standard for this procedure must have mechanical properties close to the properties of the tested material. Sapphire was used in this study as the standard.

To simplify the measurement procedure, a variation and an extrapolation of the parameter b in the range 0.5-0.7 μm according to Eq. (1) are possible.

The scratch was made in the method "indenter edge forward". The time of the indenter loading was 10 s, the scratching time was 2 s, the scratch width was in the range

0.5-0.7 μm , and the scratch length was about 2.5 μm in all experiments.

To avoid possible mistakes, the hardness measurements were performed on the same specimens using both the NS with the new procedure and a standard microhardness tester PMT-3 with the Vickers indenter test (with the exception of cubic BN and diamond). Single crystals were used for the hardness measurements.

Samples were prepared according to the requirements listed in Ref. 18. A surface of the specimens was cleaned with organic solvents. No special methods of final cleaning to remove contaminant molecules were used, because, as mentioned above, the NS makes it possible to observe an elastic surface under a viscous layer.

Data of the hardness tests were obtained as a result of the five to ten measurements for every specimen. The standard error σ of the measurements is practically the same for both test types: an order bigger than the device error (for both testers) and both are listed in Table 1.

The indenter for the sclerometry hardness measurements is simultaneously the tip for the surface scanning in the NS. Ultrahard fullerite C_{60} and natural diamond were used as materials for the tip. Shape does not matter in the new procedure: fragments of these materials with a shape close to a three-sided pyramid with an apex angle about 90° were used for the tip. The size of the tips was about 0.5-1 mm. The tip was fixed on the end of the cantilever with phenyl salicylas.

The results of sclerometry hardness measurements listed in Table 1 harmonize with Eq. (1). The coefficient k of the tip shape was calculated from data of the present study according to Eq. (1) ($k = Hb^2/P$). It belongs in the range 1.5-3.5, depending on a given tip and corresponds to the known values.¹⁸ More than 15 different tips of ultrahard fullerite and diamond were used. For example,

TABLE 1. Results of the hardness tests by the PMT-3 microhardness tester ("Vickers hardness" in the table) and by the NanoScan ("SFM hardness" in the table) are listed in this table: " σ " is the standard error. The SFM hardness is measured by the ultrahard fullerite tip with exceptions marked by *. The last one is measured by the diamond tip.

Material	Vickers hardness.		SFM hardness.	
	Gpa	σ	Gpa	σ
Quartz	11	± 1	11	± 1
Topaz	17	± 1	19	± 1
Garnet	19	± 1	19	± 1
Sapphire	23	+1	23	± 1
Cubic 7r0.	24	± 2	27	± 1
Cubic BN	60	± 3
Type IIa diamond (100)	137	± 6
Type IIa diamond (111)	167	± 5
Type IIa diamond (111)*	231*	± 6

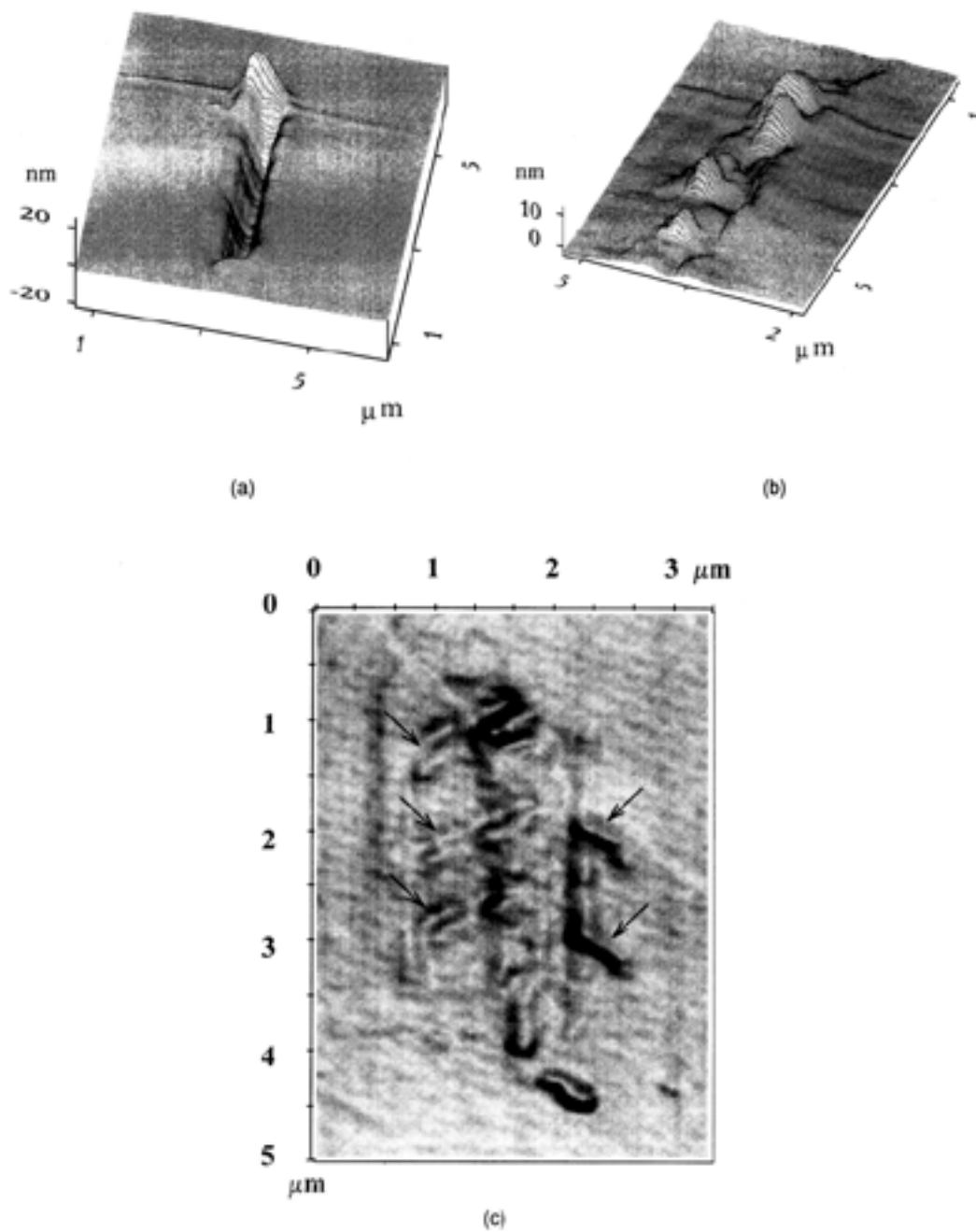


FIG. 2. The NanoScan images of the scratches of the sclerometry tests obtained with the ultrahard fullerite tip on the topaz face (a), (111) diamond face (b), and with the diamond tip on the (111) diamond face (c)/ Cracks are marked by arrows/ Vertical scale is 2 nm for (c).

to create a scratch with $b = 0.6 \mu\text{m}$ the tip load for diamond was 0.02-0.04 N and for sapphire $(2-6) \times 10^{-3}$ N, depending on the coefficient k of the tip shape.

Examination of the tip was performed after each measurement by a second tip calibration. No changes were revealed after scratching of all materials with the exception of diamond. It is possible to perform 3-5 hardness measurements for diamond face (111) by the ultrahard fullerite C_{60} tip with a small correction of coefficient k after each measurement. As for the diamond lip, it cannot be used more than once for this measurement.

V. RESULTS AND DISCUSSION

Each section of the specimen was imaged using the NS both before and after scratching. The size of surface roughness was an order less than the features after scratching.

The results of the hardness tests are listed in Table 1. The hardness measured with use of the NS ("SFM hardness" in Table 1) are in good conformity with that obtained with the microhardness tester ("Vickers hardness") and agrees with literature data.^{8, 18, 19}

In Figs. 2(a)-2(c) the NS images of the scratches of the sclerometry tests obtained with the ultrahard fullerite tip on the topaz face [Fig. 2(a)] and (111) diamond face [Fig. 2(b)], and with the diamond tip on the (111) diamond face [Fig. 2(c)] are represented. The qualitative difference between Fig. 2(b) and 2(c) is analogous with that between Fig. 1 (a) and Fig. 1 (b): the scratching of the (111) diamond face with the diamond tip is accompanied by the appearance of numerous cracks, whereas the scratching of that with the ultrahard fullerite tip caused the plastic deformation of diamond without fracture. As mentioned above, that depends upon the fact that the hardness of ultrahard fullerite exceeds the hardness of diamond.

In Ref. 9 it was reported that the diamond indenter did not produce an indentation on the ultrahard fullerite specimen. The same result was obtained in the sclerometry tests with using NS in the present study. It is a supplementary evidence for high hardness of ultrahard fullerite.

Some disagreement may occur in the comparison of the measurement hardness using the NS at the scale $0.6 \mu\text{m}$ and using the PMT-3 tester at the scale $10 \mu\text{m}$ because of the size dependent hardness effect (the hardness increasing with an indentation size decreasing). That is seen at the deformed volume less than $1 \mu\text{m}$ in size.^{2, 3} The following possible reasons determine the absence of the display of the size effect in the present study: (a) The width of the scratch ($0.5-0.7 \mu\text{m}$) is not small enough to display the size effect, (b) The tip calibration for the NS tests was performed by reference to sapphire. Its hardness was measured using the microhardness tester at the scale $10 \mu\text{m}$. Thus, it is impossible to observe the size effect in

this procedure at least for sapphire. If the rest of the tested materials have the same (or close to that) function of the size effect as sapphire, it is impossible to observe the size effect for these materials, too.

Let us discuss the measurements of the diamond hardness. Several problems exist for the indentation hardness method when a diamond indenter is used. The first is an indentation plasticity for diamond at room temperature (which is doubtful⁸) and cracking in a brittle condition.

Another problem is the indentation size effect. It is seen at the indent size $3-4 \mu\text{m}$ for diamond,¹⁹ as opposed to less than $1 \mu\text{m}$ for other materials.²³ The measured Vickers hardness of the (100) diamond face¹⁹ increases from 114 GPa (indent size $6.3 \mu\text{m}$) to 257 GPa (indent size $0.9 \mu\text{m}$).

The disagreement between the measured hardnesses of the diamond face (111) obtained with the ultrahard fullerite and diamond lips (167 and 231 GPa, respectively) displays the difference between the conditions of the indentation with ultrahard fullerite (that hardness exceeds diamond) and diamond tips: crack-free indentation for the first and the effect of cracking for the last.

Implementation of the ultrahard fullerite indenter for the hardness tests has solved these problems in the present study. Diamond was deformed plastically and we conclude that the measured hardnesses 137 ± 6 and 167 ± 5 GPa for the diamond faces (100) and (111), respectively, are correct.

VI. SUMMARY

The diamond surface (111) was deformed as a plastic material under scratching with the ultrahard fullerite C_{60} indenter. This means that the hardness of the ultrahard fullerite is sufficient to create a large pressure in the contact point for the plastic (low of diamond at room temperature, and it exceeds the hardness of diamond. This establishes the usefulness of the ultra-hard fullerite indenter for the correct measurements of diamond hardness.

A new procedure for the hardness measurements of the superhard materials and diamond using the SFM with the ultrahard fullerite (CM) tip is developed. The measured hardness is 137 ± 6 and 167 ± 5 GPa for the diamond faces (100) and (111), respectively. The new procedure makes it possible to develop correct submicron hardness tests also for thin films and fibers, for the nanophase and the composite materials.

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