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A Nanoindentation Method for Measuring the Young Modulus of Superhard Materials Using a NanoScan Scanning Probe Microscope

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Abstract—A new method for measuring the Young modulus using a NanoScan scanning probe microscope is proposed. This method is based on measurements of the oscillation frequency of a probe that is in contact with the surface as a function of the probe–surface separation, and allows the Young modulus to be determined on a scale of a few hundreds of nanometers for many objects, including superhard materials. The error of the Young-modulus measurements does not exceed 10%. The results obtained with this method agree well with the data obtained using the standard nanoindentation technique within the accuracy of measurements. The proposed method is actually nondestructive, since the probe penetration depth into the surface does not exceed several nanometers and the diameter of the contact area is about several tens of nanometers. Thus, it ensures correct measurements of the elastic properties of thin films and separate components in complex multiphase structures.

INTRODUCTION

The Young modulus is one of the basic characteristics of solids. The materials whose Young moduli exceed 500 GPa are considered to be superhard. As a rule, it is rather difficult to measure the elastic characteristics of such materials with an ultrahigh spatial resolution.

To measure the Young modulus with a submicrometer spatial resolution, several methods are currently used: acoustic, optical, and contact. Of these, the contact method is the only direct measurement method. It is based on the mechanical interaction of an indenter with the surface of a material. The advantage of this technique consists in the possibility of determining the direct elastic reaction of the surface layer to an external mechanical action, which allows the Young modulus to be measured with a nanometer spatial resolution.

The instruments and techniques of today that are based on this mechanical contact and make use of the methods of scanning probe microscopy, allow the Young modulus to be measured for a limited number of materials in a narrow range of its absolute values [1–10]. This is the result of both the design features of standard probes and comparatively soft tip materials. It is impossible to measure the Young modulus of objects whose high elasticity is their main index of quality using such instruments. This problem is especially serious in studies of multiphase structures, since the measured value of the Young modulus of separate components does not coincide with the value obtained in macroscopic measurements.

This work proposes a method for measuring the Young modulus using a NanoScan scanning probe microscope (SPM). This method is based on measurements of the oscillation frequency of a probe that is in contact with the surface as a function of the probe–surface separation, and allows the Young modulus to be determined on a scale of several hundreds of nanometers for many objects, including superhard materials.

NANOSCAN SCANNING PROBE MICROSCOPE

NanoScan is intended for investigating mechanical properties of surfaces and measuring the hardness of superhard materials and thin films (coatings) [11]. This instrument has been used successfully in research for a number of years [12–14].

The peculiarities of the principle of the probe's operation and the use of an elastic element (a cantilever) with a high bending stiffness ($k_0 \sim 10^4\text{--}10^5$ N/m) make it possible to obtain an image of the surface topography and the map of the distribution of elastic properties in open air, and to measure the hardness of materials with fairly high indices of mechanical properties.

When conducting measurements with a NanoScan SPM, samples are preliminarily ground and polished to a roughness level of ~ 10 nm. The natural resonance frequency f_0 of probe oscillations is 12 kHz. A trihedral diamond pyramid with a vertex angle of $\sim 60^\circ$ serves as the tip. The radius of the tip end is ~ 100 nm. The values of the tip's Young modulus and Poisson ratio used in

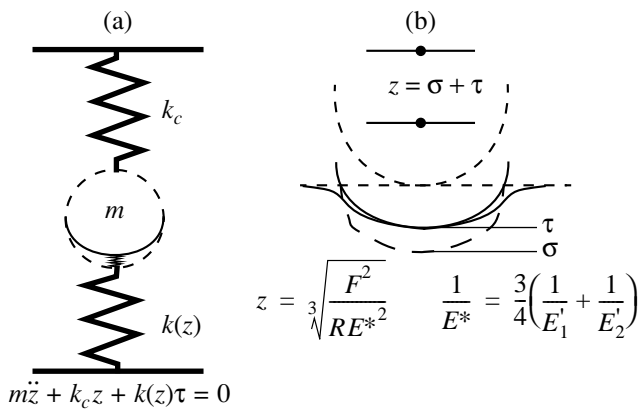


Fig. 1. (a) Mechanical model of the probe and (b) a model of the contact between the tip end and a surface in measurements of the loading curves using the NanoScan SPM. The notation is given in the text.

calculations are $E = 1140$ GPa and $\nu = 0.07$, respectively.

THEORETICAL MODEL

To interpret the obtained data and justify the qualitative measurements of the Young modulus, we considered a model of the interaction between the SPM tip and the material surface.

A mechanical model of the probe in contact with a surface can be represented in the form of a load oscillating under the action of two springs (Fig. 1a). The stiffnesses of these springs are determined, on the one hand, by the bending stiffness of the cantilever and, on the other hand, by the elastic properties of the investigated material. The effect of the surface at the point of the contact is regarded as an additional elasticity depending on the strain value.

The contact between the tip and the surface is described using the Herz model (Fig. 1b). As a result of our analysis, the following dependence of the change in the probe-oscillation frequency on the tip–surface separation was obtained:

$$\Delta f = \frac{f_0 \sqrt{R}}{k_c} E_1' \left(\frac{E_2'}{E_1' + E_2'} \right)^2 \sqrt{z}. \quad (1)$$

Here, f_0 is the natural resonance frequency of the probe; R is the radius of the tip end; k_c is the constant of the cantilever bending stiffness; z is the distance between the tip and the surface; and $E_{1,2}' = E_{1,2}/(1 - \nu_{1,2}^2)$, where $E_{1,2}$ and $\nu_{1,2}$ are the Young moduli and Poisson ratios for the tip and the material under study, respectively.

Like the majority of contact methods, the proposed method allows the value of $E' = E/(1 - \nu^2)$ to be measured. Since the Poisson ratio for the overwhelming majority of materials belongs to the range of 0 to 0.5, it

is precisely the Young modulus that dominates in the E' value. In the case of hard and superhard materials characterized by high elasticity moduli and small Poisson ratios, the difference between E' and E values is within 5%. Based on the assumed value of the Poisson ratio for the material under study and using a tabulated value, we can introduce a correction for refining the measured value of the Young modulus.

The model used to describe the interaction takes into account the strain of the SPM tip during measurements, thus allowing one to determine the Young modulus for superhard materials when the elasticity moduli of the sample under study and the tip are comparable.

EXPERIMENTAL DATA

The essence of the proposed method is as follows. A probe with a tip fixed at its end oscillates in the direction normal to the sample surface. Simultaneously with the oscillatory motion, the base of the probe moves to the surface. At a certain moment, the tip touches the surface, after which the tip–sample interaction occurs in a tapping mode. As the probe is pressed further, a moment comes at which, the oscillations in the tip–surface system proceed in a strictly contact mode with no detachment. In this case, the oscillation parameters depend on the characteristics of the probe and tip and also on the elastic properties of the material under study. After calibrating the probe and tip on samples with known values of the modulus of elasticity, it is possible to measure the absolute values of this quantity.

The loading curves measured for 12 samples are listed in the table. The samples were selected so that the values of their elasticity moduli spanned the range of interest for investigations of very hard nanomaterials, whose Young modulus lies in the range $E = 100$ – 1100 GPa.

The results of measurements obtained by the nanoindentation method using the CSM Instruments Nano-Hardness Tester instrument were taken as reference values of the modulus of elasticity. For hard alloys based on tungsten carbide and diamond, tabulated values are used.

A general view of the loading curves obtained with the NanoScan system is shown in Fig. 2. Four segments can be distinguished on this curves. In segment 1, the tip oscillates without contact with the surface, and, therefore, the oscillation frequency is independent of the distance. Segment 2 corresponds to contact between the tip and the viscous layer adsorbed on the sample surface in open air. Segment 3 corresponds to direct interaction with the atoms at the surface. This segment has two parts. The amplitude of the tip oscillations is still rather large immediately after the contact, and the probe base is far from the surface; therefore, the interaction in the segment 3' occurs in the tapping mode. As the loading increases, the amplitude decreases and the probe base approaches the surface to within a rather

Young modulus of materials measured by a CSM Instruments Nano-Hardness Tester at an indentation depth of ~30 nm using the NanoScan SPM

No.	Material	E , GPa	
		CSM Instruments	NanoScan SPM
1	SiO ₂ · CaO (glass)	86	74
2	SiO ₂ (100) (quartz)	106	129
3	LiNbO ₃ (0001) (lithium niobate)	215	222
4	Gd ₃ Ga ₅ O ₁₂ (110) (gadolinium gallium garnet)	270	261
5	Y ₃ Al ₅ O ₁₂ (100) (yttrium aluminum garnet)	277	284
6	ZrO ₂ (100) (zircon)	280	319
7	Y ₃ Al ₅ O ₁₂ (111) (yttrium aluminum garnet)	322	330
8	Al ₂ O ₃ (sapphire)	370	375
9	SiC (001) (silicon α -carbide)	446	404
10	WC + 8% Co (tungsten carbide)	650 (tabulated value for WC)	631
11	WC + 6% Co (EF) (tungsten carbide (extra fine))	650 (tabulated value for WC)	631
12	C (diamond, type II A)	1140 (tabulated value)	–

short distance. At a certain moment, the tip and surface begin to oscillate without separation, i.e., in a strict contact mode. Segment 3", in which the latter process takes place, is considered to be the working part of the curve and serves for determining the elastic properties of the material under study. Segment 4 corresponds to a damping of the probe oscillations and/or a plastic deformation.

DISCUSSION

Figure 3 shows the measured curves for all model samples on a common scale. In accordance with the proposed model, the segment of the quadratic dependence with the greatest approximation to a straight line was chosen as the working segment. The slope of the working segment with respect to the z axis is determined by the elasticity of the material. More elastic materials have larger slopes.

Using the method developed, the Young modulus values were calculated for each of the model samples (see the table). Using these data, we plotted a curve (Fig. 4) of the dependence of the measured value on the reference value. As is seen, the results obtained by the different methods coincide within the experimental accuracy.

The accuracy of the elastic-modulus measurements is determined by the error in calculating the slope of the working segment, which in turn depends on the reproducibility of the loading curves. The reproducibility of measurements increases proportionally to the quality of the prepared surface of the sample under study. According to numerous experiments, the error of the elasticity-modulus measurements does not exceed 10%.

The interaction between the tip and sample surface at which we can correctly speak of measuring the latter's elastic properties must occur without a plastic deformation. Therefore, this technique may be inapplicable to quite soft materials. However, repeated scanning in the indentation region revealed no plastic deformation for all of the model samples.

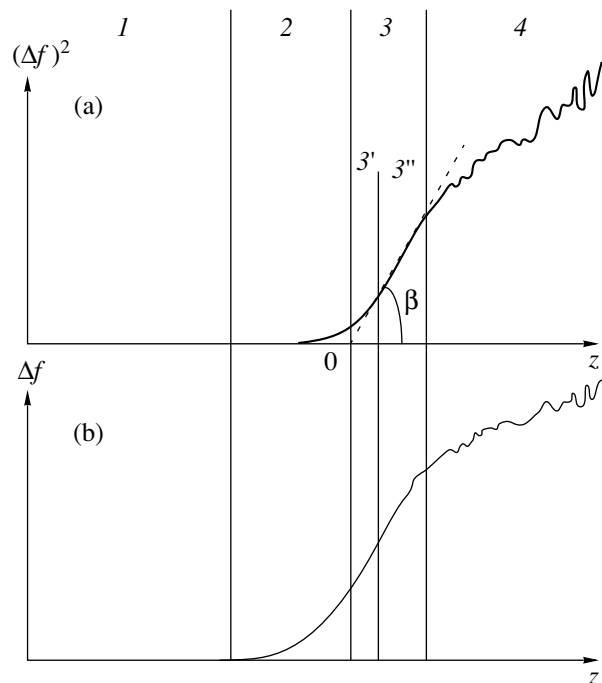


Fig. 2. General view of the loading curve. Numbers 1–4 designate characteristic segments of the curve (see the text).

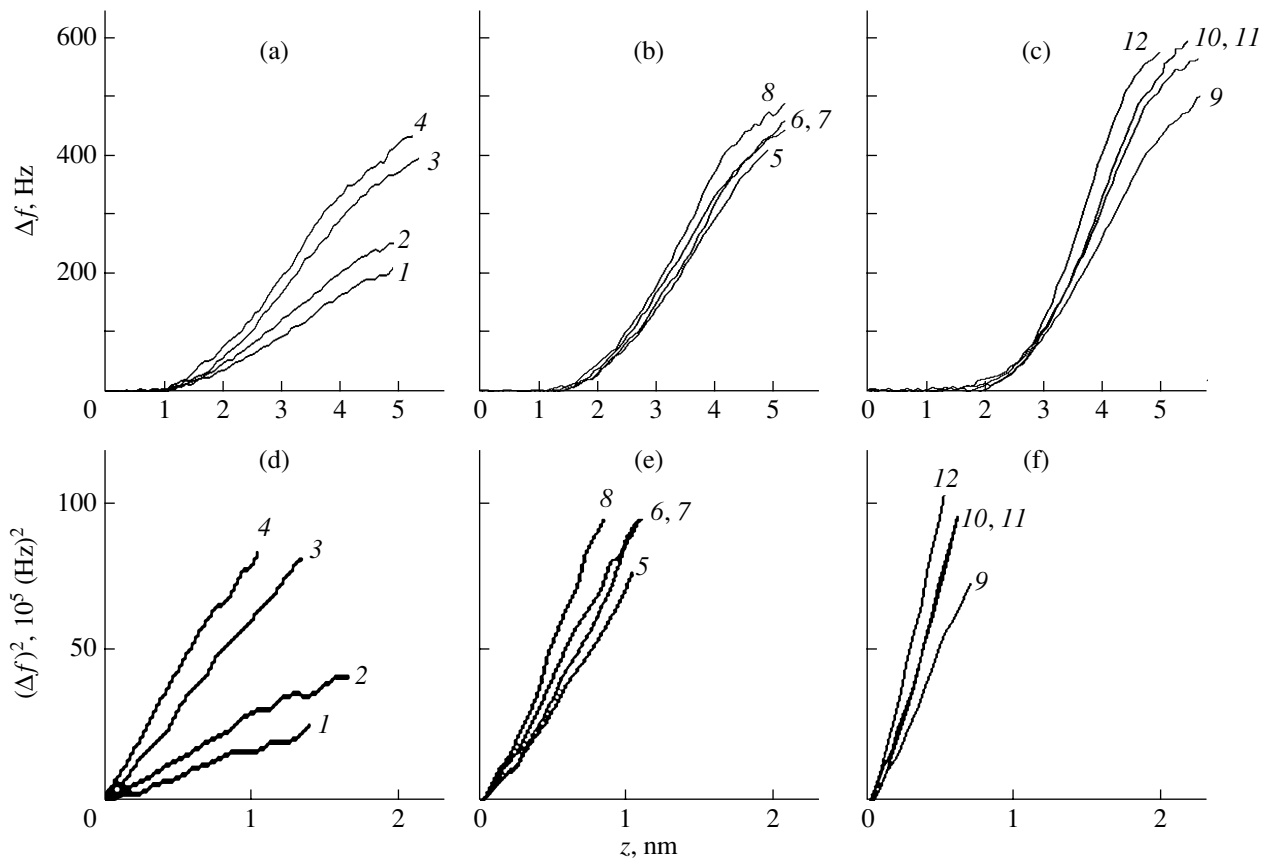


Fig. 3. Experimental dependences for model samples: (a, b, c) dependences of the frequency shift on the tip–surface separation and (d, e, f) working segments of the dependences of the square of the frequency shift on the tip–surface separation. The notations of the curves corresponds to the numbers of samples in the table.

The maximum modulus of elasticity that can be measured using this method is determined by the form of the dependence for the frequency shift and is limited by the modulus of elasticity of the tip used in measurements of the loading curves.

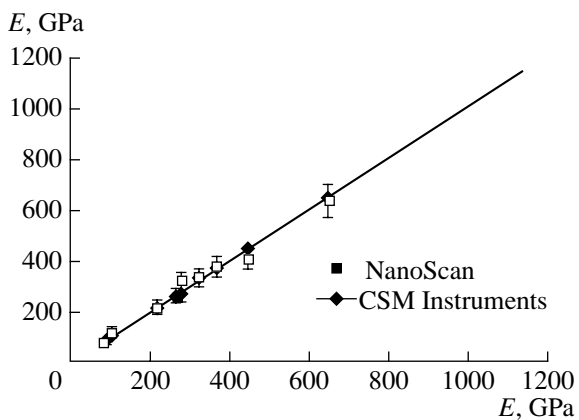


Fig. 4. Values of the modulus of elasticity measured by the nanoindentation method (CSM Instruments Nano-Hardness Tester) and obtained using the method developed (NanoScan SPM).

CONCLUSIONS

The technique developed makes it possible to perform correct measurements of the Young modulus of materials over a wide range of magnitudes. The error of measurements is 10%. The comparison with the data obtained using the standard nanoindentation technique shows that the experimental results coincide within the accuracy of measurements.

This technique was applied to new superhard materials for measuring the slopes of the loading curves whose values exceed the corresponding values for the tip material. This allows us to presume that this method is applicable to materials with Young moduli higher than that of the tip material.

The range of the measured values of the Young modulus can also be extended by using a tip manufactured of C_{60} ultrahard fullerite. Such a tip was successfully used in measurements of diamond hardness by the sclerometry technique (the application of scratches) using the NanoScan SPM [16].

The proposed method is actually nondestructive, since the tip penetration depth into the surface does not exceed several nanometers and the diameter of the contact area is within several tens of nanometers. There-

fore, this technique ensures correct measurements of the elastic properties of thin films and separate components in complex multiphase structures.

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