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Evaluation of elastic properties of DLC layers using resonant ultrasound spectroscopy and AFM nanoindentation

Tomáš Kocourek [a,b,*], Michal Růžek [c], Michal Landa [c], Miroslav Jelínek [a,b], Jan Mikšovský [a,b], Jaromír Kopeček [a]

[a] Institute of Physics AS CR v.v.i., Na Slovance 2, 182 21 Praha 8, Czech Republic
[b] Czech Technical University in Prague, Faculty of Biomedical Engineering, nám. Sítná 3105, 27201 Kladno, Czech Republic
[c] Institute of Thermomechanics AS CR, Dolejškova 1402/5, 182 00 Praha 8, Czech Republic

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ABSTRACT

Elastic properties of diamond-like carbon (DLC) layers with gradient carbon–silicon interlayer were studied by resonant ultrasound spectroscopy (RUS) and standard nano-indentation technique. The DLC layers were prepared by pulsed laser deposition on SiC/Si substrates. The RUS method is based on modal analysis of the specimen vibration. The resonant frequency shifts caused by the layer are for the evaluation of the dynamic in-plane elastic properties of the deposited DLC. The results were compared with the quasi-statical quantities — Young's modulus and hardness, obtained by nanoindentation using the AFM tip.

1. Introduction

DLC coatings have a great potential in electronics and biomedical applications. Pulsed laser deposition (PLD) is a suitable method for DLC deposition on the substrates of various materials — from polymer to metals. The matching gradient interlayer between the coating and the substrate can improve the adhesion of DLC films. Nondestructive characterization of mechanical properties of DLC is important for the optimization of deposition techniques, determination of the quality of DLC and for the study of residual stresses.

Indentation technique is a usual tool for the investigation of elasticity and hardness of surfaces. This technique in the nanoscale version, using Atomic Force Microscopic tip (AFM), is an established method for the evaluation of Young's modulus and nanohardness of thin films on substrate. The method evaluates the elastic quantity from very localized area in the direction perpendicular to the surface. The scanning of indentation is necessary to measure a greater part of the deposited film to obtain a representative average quantity. The results are strongly influenced by the elasticity of the substrate. This method is quasistatic and so it is difficult to distinguish between the stiffness and relaxation behavior of the tested materials.

Contrariwise, ultrasonic methods represent nondestructive dynamical tests which reveal pure elasticity of the studied materials. Resonant ultrasound spectroscopy (RUS) is one of the most precise methods for the measurement of the elastic properties of different materials [1–5]. Originally, this method was developed for the measurement of bulk elastic properties from the free modal vibrations of a homogenous sample. The method is based on a mathematical model which enables to calculate the natural frequencies of the material specimen for arbitrary elastic constants. The model is called the *forward problem*. A specimen is then submitted to free vibrations in its natural frequencies. Once the measurements of a response give the resonance spectrum of the specimen, the next step consists in the finding of appropriate elastic constants which are inserted into the forward problem to obtain the same resonant frequencies as measured in the spectrum. This procedure is called *inverse problem*. The inverse problem is usually the most complicated part of the measurement because it requires solving the non-linear system of equations. The experimental "errors" of the evaluated constants are determined from the analytical expressions of the gradient and the Hessian of the error function used in the optimization procedure [1]. Recently, the RUS method has been modified for the evaluation of the in-plane elasticity of the thin surface layers [6–9].

In this paper, the modified RUS approach and AFM nanoindentation are applied on the DLC films with the SiC buffer layer.

2. Experimental

2.1. Deposition

DLC films were fabricated by KrF excimer laser ablation from a graphite target. The repetition rate of laser pulses was set to 10 Hz. To

* Corresponding author at: Institute of Physics AS CR v.v.i., Na Slovance 2, 182 21 Praha 8, Czech Republic.
E-mail address: kocourek@fzu.cz (T. Kocourek).

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obtain films of various hardnesses, the energy density of the laser beam on target was adjusted to 4, 6, 8, or 11 J cm^{-2} [10]. The substrates of $4.5\times3.5\times0.3$ mm were cut from the silicon single crystal in the planes (111). To increase the adhesion of DLC to the Si substrate, the 30 nm thin SiC graded buffer layer was fabricated by a combination of PLD and DC magnetron sputtering [10]. No significant effect of the graded buffer layer on the measured Young's modulus and hardness of the DLC films (compared to the direct DLC/Si coating) was observed. The substrate temperature was 20 °C. The distance between the substrate and laser target was 5 cm. The deposition ambient was 0.25 Pa of argon [10].

2.2. Analysis

Thickness and surface roughness were measured by the mechanical profilometer Tencor AlphaStep 500.

Mechanical properties measured by RUS are based on the comparison of the mechanical vibration resonant spectra of a given sample before and after the deposition of the thin film (Fig. 1). Due to the deposition of the layer, resonant frequencies of the sample are shifted. The shifts are dependent on many factors like geometry and properties of the substrate, thickness and density of the film and finally the stiffness of the film. Mathematically, this can be written like [9]:

$$F(Q,\rho,h,\ \ldots) = \Delta\omega$$

where Q is the vector of in-plane layer elastic module, ρ and h are the layer density and thickness and $\Delta\omega$ is the vector of angular frequency shifts. Function F cannot be constructed analytically, however, it can be determined numerically. Moreover, it was shown [9] that this function can be approximated by a linear function:

$$AQ - M\rho h = \Delta\omega$$

where matrix A describes the effect of the film stiffness and matrix M effects of the film mass on frequency shifts $\Delta\omega$. Both effects are multiplied by elastic module Q and surface mass density ρh. Once we know the film density ρ and its thickness h we can readily determine the elastic module Q. The fact that the forward problem is the linear dependence strongly simplifies the inverse procedure and it can be used for reliable error estimation. The inverse procedure is described in detail in Ref. [11]. To fulfill the required free boundary conditions. The novel experimental arrangement was developed (Fig. 2). The sample is posed with one corner on a very thin glass fiber, and the

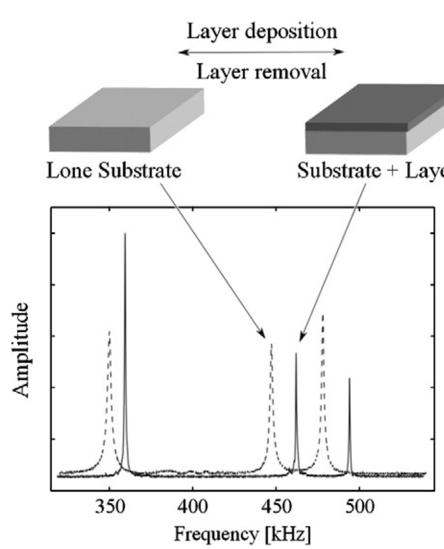

Fig. 1. Principle of the RUS method applied on thin films.

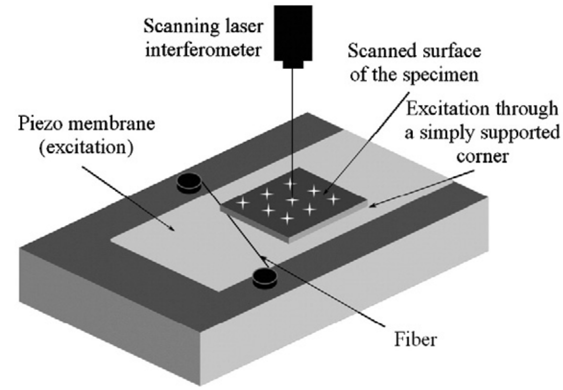

Fig. 2. Schematic experimental configuration.

opposite corner lies on the actuated piezo-membrane glued onto a solid copper block. The burst chirp signal swept from 100 kHz to 3 MHz was used for the excitation of the sample vibration. The dynamical response of the sample is measured by the scanning laser interferometer (Polytec MicroSystem Analyzer MSA-500) in many points of the scanned face. This instrumentation enables the identification of the measured vibration modes and employ them into the inverse procedure. The frequency range is pre-determined by the shape and dimensions of the sample. The observed frequencies are sensitive enough to distinguish the frequency shifts caused by the deposition of a DLC layer thickness of about 300 nm. The number of the analyzed resonant frequencies was up to 25 for each sample. The problem of the optimum number of frequencies used is described in Ref. [11].

The elastic module of all deposited samples was determined independently. The density of all the films was considered to be 3.5 g/cm^3 for all the diamond-like films.

The inverse procedure evaluates the all in-plane elastic properties from the substrate, however with different accuracy. The Young's or shear moduli are expressed in the same order of the precision, but the bulk modulus or Poisson's ratio have much more uncertainty.

AFM nanoindentation was determined using the AFM Solver Next device with the nanoindentation head equipped by a diamond tip of the Berkovich shape. Before the measurement, the calibration of the load line on the fused silica (FS) sample was made. The fused silica sample has the known elasticity modulus. The evaluation of the Young modulus and hardnesses was determined via standard procedures in the software NSViewer (NT-MDT co.).

3. Results and discussion

The thickness of the SiC buffer layers was 30 nm. The thickness of the PLD created DLC layers was in the range from 200 nm to 385 nm, depending on the deposition conditions — see Table 1. The maximum *roughness* of the DLC films was not higher than 1.4 nm.

3.1. XPS measurement

The percentage of the “diamond” sp^3 bonds was determined by X-ray photoelectron spectroscopy (XPS). With increasing laser energy density from 4 Jcm^{-2} to 11 Jcm^{-2} the content of the sp^3 *bonds* was increasing up to 62 at.% [12–14].

3.2. RUS measurement

The diamond layer was supposed to be elastic, isotropic and homogenous material. The linear elasticity is described with two independent elastic constants (e.g. Young's and bulk moduli). However, only one elastic modulus (represented by Young's

Table 1
Properties of DLC layers. Results of analyses of RUS, AFM nanoindentations, XPS, and AlphaStep of the DLC layers in dependence on energy density laser beam on target.

Energy density [J/cm^2]	RUS		AFM nanoindentation			XPS	AlphaStep
	Young modulus [GPa]	Mean Young modulus [GPa]	Young modulus [GPa]	Mean Young modulus [GPa]	Indentation depth [nm]	C sp^3 [%]	Thickness [nm]
4	525.3 ± 88.5	545.8 ± 106.8	378 ± 38	378 ± 38	26 ÷ 57	52	330 ± 10
	557.6 ± 39.4						
	570.6 ± 70.5						
	545.1 ± 224.2		–	–	–		385 ± 10
	548.5 ± 47						
	528.3 ± 39.7						
6	583 ± 118	585.2 ± 57.6	–	–	–	–	375 ± 10
	581.6 ± 94.9						
	590.9 ± 83						
8	641 ± 45.4	623.8 ± 44.4	516 ± 80	516.5 ± 73.8	12 ÷ 52	60	310 ± 10
	639.6 ± 98		517 ± 124		12 ÷ 62		
	590.9 ± 77.7						
11	749 ± 56	730.5 ± 46.3	–	–	–	62	200 ± 10
	712 ± 34						

modulus) of the film plays an important part in the vibrational modes. The second independent elastic modulus (in this case, bulk modulus) is difficult to determine by this method. All results are summarized in Table 1. From the RUS measurements, the dependence of Young's modulus on energy density of the deposition laser is obvious — Fig. 3. The higher energy density results in increase of sp^3 bonds and the creation of the harder diamond-like films.

3.3. AFM nanoindentation

The speed of indentation during loading and unloading was 20 nm/s, holding time was 15 s. The matrix of 49 sticks (7 × 7) was made on the area 20 × 20 μm on each sample. The tested area was first scanned by scanning probe microscopy technique. The areas without any surface artifacts were selected. The loading forces were 0.5; 0.75; and from 1 to 5 mN, with the step of 1 mN. The measurements with the smaller loadings (0.5 and 0.75 mN) had a wide variability of values and these measurements were not evaluated. The depth of indentation was up to 20% of the layer thickness (in Table 1. and in Fig. 3). The measured hardness of layers for energy density of 8 J/cm^2 was around 25.5 GPa, and for the energy density of 4 J/cm^2 it was 13.2 GPa.

The results of Young's modulus obtained by both RUS and AFM nanoindentation techniques are summarized in Table 1. Both of the methods give the same trend with respect to the laser energy density in spite of different measuring principles: dynamic versus quasistatic, average versus local quantity, in-plane versus out of-plane quantities. Due to the elasticity of the substrate and possible influence of the

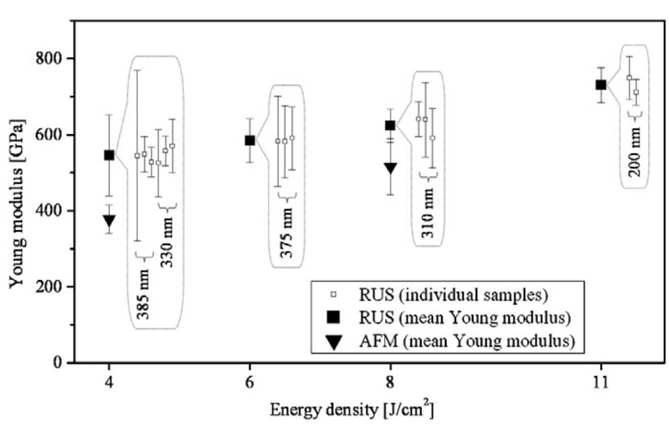

Fig. 3. The graph of Young modulus obtained from RUS and AFM tip measurements (for different energy densities of a laser beam).

relaxation processes during indentation, the lower statical values can be expected.

Nevertheless, both techniques exhibit the increasing trend in dependence on the laser energy (Fig. 3). The error estimations of both methods is also different. The pure statistic approach of results from the repeated sticks is used in the indentation case whereas the errors of the RUS results are determined from the calculated sensitivity for each experimental data-set (each sample measured before and after the deposition). In some cases (mainly, the sample 1 with the deposition of the energy 4 J/cm^2), the frequency shifts have another reason, not only the deposited film. It can be influenced by some additional damage, possibly the residual stresses.

Another difference of both methods is that method RUS is integral and non-sensitive to local material properties, whereas nanoindentation is a local method and it is depending on the local structure and topology. The method RUS is influenced by the inhomogeneity and cracks. The variability of Young's modulus is possible to interpret as the variation of the real layer and the homogenous model. It means, that it is possible to determine the layer homogeneity and the existence of cracks in the layer from these deviations.

4. Conclusion

We prepared thin homogenous DLC films on the SiC/Si substrates by PLD and PLD combined with magnetron sputtering. The thickness of the DLC layers was 200–385 nm and their roughness was under 1.4 nm. The XPS method determined the number of sp^3 bonds in the DLC layers in the range from 52 to 62% (in dependence on energy density of the laser beam from 4 J/cm^2 to 11 J/cm^2). The RUS method showed the values of Young's modulus within the range from 540 GPa (for 4 J/cm^2) to 730 GPa (for 11 J/cm^2). The variability of Young's modulus is possible to interpret as the variation between the real layer and the homogenous model. The comparable results, 378 GPa (for 4 J/cm^2) and 517 GPa (for 8 J/cm^2), were obtained from the AFM nanoindentation. The results of both methods are comparable, despite the fact that each method has an error caused by different measurement conditions. The method RUS is influenced by the inhomogeneity and the cracks. Nanoindentation is influenced by the indent depth and by the ratio of the indent depth/layer thickness. Another difference of these methods is that the RUS method is integral and non-sensitive to local material properties, whereas nanoindentation is the local method and it depends on the local structure and topology. The RUS and nanoindentation experimental methods confirmed successfully and independently that the material elastic stiffness of the DLC layers increases with the percentage of the sp^3 bonds and this higher percentage can be achieved by increasing the deposition laser energy density. The measurement of the ultrasonic waves is presented as the promising nondestructive approach to the evaluation of the elastic properties of the thin layers.

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