NANO-MECHANICAL PROPERTIES OF CARBON AND SILICON FILMS

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Keywords

Nano-mechanical properties, nanoindentation, thin films

Abstract

The mechanical properties of various types of amorphous thin films prepared by magnetron sputtering were measured using the nanoindentation technique. The indentation hardness and the elastic modulus were determined ranging from hundreds of nm to approximately 1 m maximal depth of penetration. Results obtained from the films are compared with the results of measurements on monocrystalline Si (111) substrate.

Experiments were conducted on the NanoTest^{TM} apparatus with a Berkovich indenter. It differs from others with an untraditional arrangement of measuring mode, which applies loading force in horizontal direction. The Oliver-Pharr method (as a part of user's software) for analyzing indentation load-depth data was used.

Introduction

Chemical resistance and high hardness of diamond-like carbon films predicate their tribological applications. Amorphous carbon (a-C) films [1] show resistance against abrasive and adhesive wear, and the low coefficient of friction. Special thin films can enlarge the operating lifetime of product. Research and development of new and superior procedures for such surface coating of material can bring significant increase of product qualities moreover its operating efficiency.

Amorphous silicon films (a-Si) [2] are to this goal of investigation prototypical structure that can offer insight into the mechanical properties of disordered materials. Its mechanical properties are readily be changed by parameters of deposition.

Investigation of mechanical properties tends to production of layers and coatings with exactly defined features.

The depth sensing indentation (DSI) offers advances in sensitivity, data obtaining and number of material characteristics that are can be determined. The benefits are significant in materials science particularly with reference to fundamental mechanisms of mechanical behaviour at micrometer and sub-micrometer volume. We used a commercial DSI instrument (the NanoTest^{TM} NT600) platform [3]. The apparatus has unique pendulum design with the ability to carry out measurements in a wide range of applied loadings to the material under examination.

Thin films obtained by magnetron sputtering

Studied amorphous (a-C, a-C:Si, a-Si) thin films were prepared by the pulsed DC magnetron sputtering using commercial Leybold Z 550M vacuum plant (see figure 1) on Si (111) substrates. The films were deposited from carbon target (silicon target respectively) in poor argon. A little Si sheet (in the case of the a-C:Si film) was adherent over erosion zone of the target.

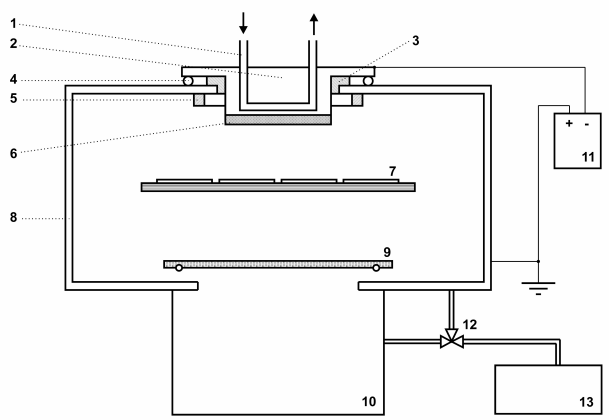

Fig. 1. Schematic drawing of a sputtering unit: 1 – cooling water, 2 – cathode, 3 – insulator, 4 – vacuum gasket, 5 – darkspace shield, 6 – target, 7 – substrates, 8 – vacuum chamber, 9 – high-vacuum valve, 10 – high-vacuum pump, 11 – sputtering power supply, 12 – two-way valve, 13 – backing vacuum pump.

Tab. 1. The deposition parameters of measured carbon and silicon amorphous films.

Sp.	Film type	Ar pressure [Pa]	Magnetron power [W]	Substrate bias [V]	Film thickness [μm]
A	a-C:Si	0,12	300	Ground	2,29
B	a-C	0,17	960	Floating	1,62
C	a-Si	0,17	300	Ground	5,40
D	a-Si	0,25	300	-80	6,58

Detailed description of the films preparation by magnetron sputtering was published elsewhere, e.g. [1]. There are main parameters of the deposition process with the thickness of investigated films in the Table 1. The thickness of layers was measured by the ALPHA STEP 500 apparatus.

Depth sensing indentation technique

The depth sensing indentation technique is also known as the instrumented indentation or the nanoindentation [4, 5]. It has been used in two recent decades to evaluate mechanical properties of materials having very fine microstructure such as thin films. In contrast to traditional hardness testers the instrumented indentation systems allow application of a specified force or displacement course. Moreover, the extremely small displacement resolutions often < 1 m are possible.

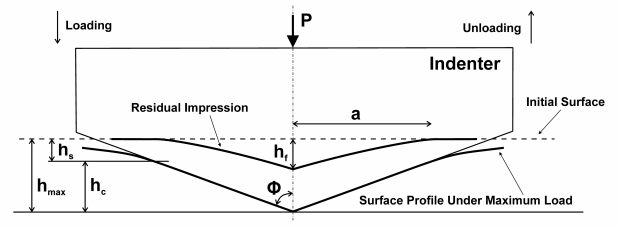

Fig. 2. Schematic illustration of the DSI technique showing specimen surface profile under maximum load and after total unload-

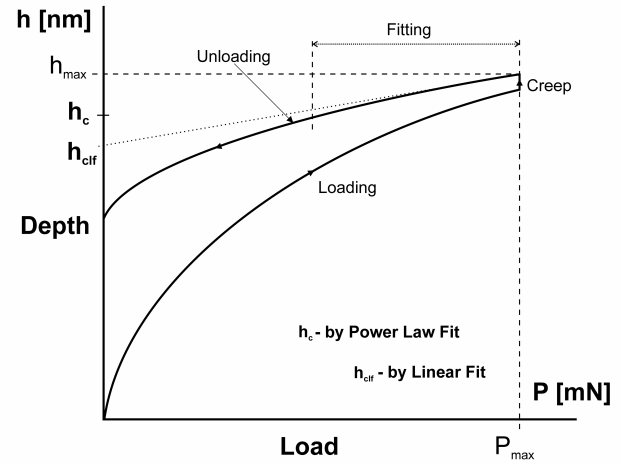

Fig. 3. Loading - unloading cycle with the contact depth determination.

Typical DSI test is illustrated in the figure 2. Load is applied to an indenter that is in contact with a measured specimen. After reaching a predefined maximum value the load is reduced and the penetration depth decreases due to elastic recovery of the deformed material. Load or displacement is controlled and both are measured simultaneously and continuously over the complete loading-unloading cycle (see figure 3). The course of load versus displacement allows both hardness and elastic modulus to be determined.

A residual impression left in the surface of the specimen. The projected contact area [6] of the residual impression is too small to measure by an optical method. Therefore an indirect measure of the area of contact is necessary.

Determination of the nano-mechanical properties from indentation load-displacement data

Different analytical approaches were developed to extract mechanical properties, generally the hardness *H* and the elastic modulus *E*.

The Oliver-Pharr method introduced in 1992 [6] and refined in 2004 [7] comes from former publications such as [8]. By this procedure mechanical properties can be determined from indentation load and displacement measurements without need to investigate the impression image. For this reason, the method has become a primary technique for determining the nano-mechanical properties of thin films and fine structures.

The method calculates the indentation hardness H_{IT} and the effective modulus E_r [7] of material from data obtained during one cycle of loading and unloading (see figure 3). The method is essentially an extension of the method proposed by Doerner and Nix [8], in which the contact depth is determined by linear fitting of unloading curve (h_{clf} in figure. 3). Experiments have shown that unloading curves are distinctly curved and *P-h* raw data are usually well approximated by the power law relation (1), where , h_f and *m* are constants.

$$P \quad (h \quad h_f)^m \tag{1}$$

From unloading curve must be obtained the maximum load P_{max}, the maximum displacement h_{max} and *S* the elastic unloading stiffness [7] defined after (2) as a slope of unloading curve at its initial point. Another important quantity is the final depth h_f (the permanent depth of penetration after the indenter is fully unloaded - see figure 2).

$$S \quad \left.\frac{\mathrm{d}P}{\mathrm{d}h}\right|_{h_{\max}} . \tag{2}$$

The contact depth h_c is the depth of indenter in contact with the sample under maximal load (3). The geometric constant for the Berkovich indenter = 0,75. This value comes from modelling [6] by paraboloid of revolution geometry

$$h_c \quad h_{\max} \quad \frac{P_{\max}}{S}. \tag{3}$$

The projected contact area A_p is determined by geometry of the indenter and the contact depth by area function (4). This function must be established experimentally prior to analysis

$$A_P \quad F(h_c). \tag{4}$$

The effective modulus E_r is related to the projected contact area and measured stiffness by (5).

$$E_r \quad \frac{\sqrt{\ }}{2}\frac{1}{\sqrt{A_p}} S \tag{5}$$

$$\frac{1}{E_r} \quad \frac{1}{E}^2 \quad \frac{1}{E_i}^2 \tag{6}$$

The equation (6) takes account effects of non-rigid indenters on the load-displacement behaviour. E_i and $_i$ are Young´s modulus and Poisson´s ratio for the indenter (diamond) which can be taken as 1 141 GPa and 0,07 respectively [3], *E* and are properties of the sample.

The indentation hardness is defined by equation (7)

$$H_{IT} \quad \frac{P_{\max}}{A_P}. \tag{7}$$

Experimental details

Measured carbon samples were stuck on duralumin holder by quick drying cyanoacrylate industrial glue "Permabond". The silicon films were affixed by wax on another duralumin holder. The melting temperature of the wax is approximately 60 °C.

The experiment was programmed in the control NanoTest software. Individual indents (places where the diamond indenter is penetrating into the film) were arranged to a matrix. The matrix consisted from indentation experiments. Each of indentation experiments consists of several indents in one column measured at identical loading – unloading course. Distance between indents was 30 m. The dimension of the matrix in horizontal direction is given by number of indentation experiments with different loading – unloading courses. There are possible up to 100 indentation experiments each containing up to 100 indents to be scheduled in the NanoTest control software [3].

The experiment was controlled by the electronic control unit and the computer. Before the auto-run we left the instrument and prepared samples at the constant temperature 26 °C during 6 hours.

Results and discussion

The results are summarized in three graphs (see fig. 4 - fig. 6). Values obtained from carbon and silicon films are grouped and completed with measurements on a nonocrystalline Si (111) - substrate. Mechanical characteristics of the substrate were determined over the same interval of peak indentation loads as in the case of the silicon films.

The maximum depths of penetration attained during the indentation at different loading – unloading courses are shown in figure 4. The deepest penetration of a-Si film (Specimen D) predicts its low indentation hardness (see fig. 5). The effective modulus E_r of films determined from indentation load - displacement data by the Oliver-Pharr method are summarized in figure 6.

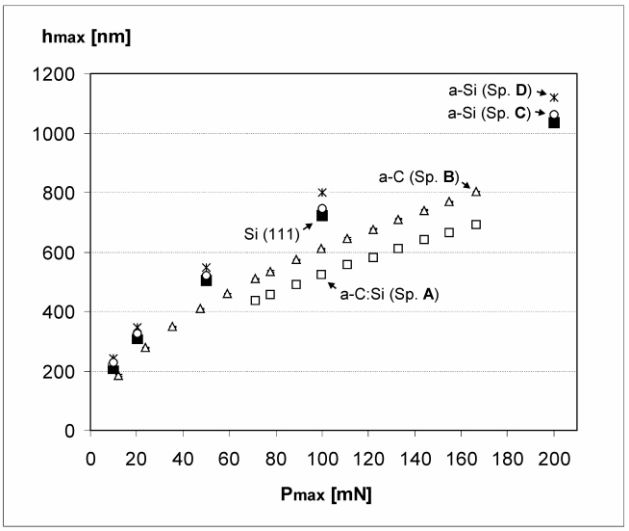

Fig. 4. The maximum depths of penetration attained at various indentation loads.

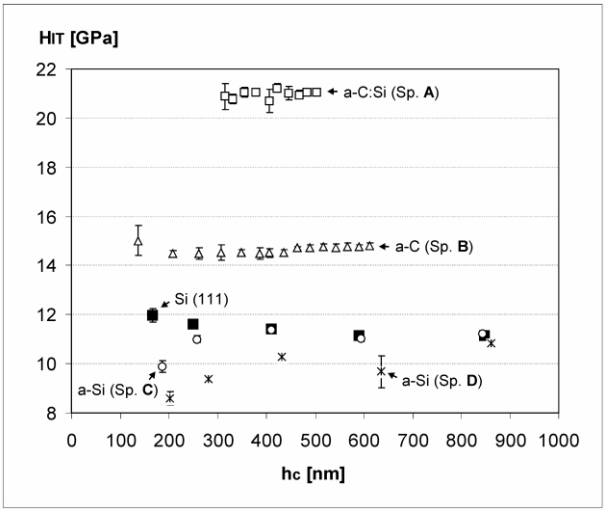

Fig. 5. The indentation hardness of different thin films and monocrystalline Si (111) measured in various contact depths (cal-

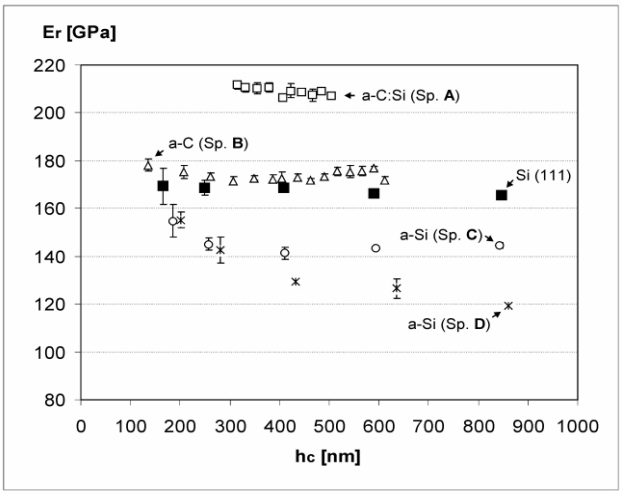

Fig. 6. The effective modulus of different thin films and monocrystalline Si (111) measured in various contact depths (calculated by the Oliver-Pharr method).

Conclusion

There are evaluated mechanical properties of thin films obtained by magnetron sputtering in the paper. Shortly described the Oliver-Pharr method is used for the extraction of elastic modulus and indentation hardness from the nanoindentation load–displacement data obtained using triangular Berkovich pyramid.

Presented results point out that it is possible to measure elastic-plastic properties of material by the NanoTest™ instrument with the Oliver-Pharr analysis at sub-micrometer scale.

The films were penetrated in the relatively wide interval of depths. The hardness and the modulus of all amorphous silicon films are always lower than for monocrystalline Si (111). In the case of deeper measurement of a-Si films values of hardness are getting near to values of substrate. The carbon films are harder than the silicon films and the influence of the substrate on hardness in the measured scales of depths was not observed.

Acknowledgements
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Measurement of Elastic Constants of Thin Films by the Law Method

MĚŘENÍ ELASTICKÝCH KONSTANT TENKÝCH VRSTEV METODOU LAW

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Keywords:
Young's modulus; Surface acoustic waves; Non-destructive testing thin films; Laser acoustic method; Silicon films; Silicon-carbid films

Abstract
One of possible applications of thin films is coating of contact loading components and tools for improving their surface properties. Mechanical features of films are crucial for their applicability in practice. They are partially characterized by elastic constants (Young modulus, Poisson ratio). Determination of these quantities through classical methods which are known from measurement of bulk materials is not possible. Therefore new ways of identifications of elastic constants has been developed. One of them is method LAW (laser acoustic waves) which elicits the constants from acoustic wave propagation. In this article principle of LAW is explained in simplified form. Conditions for applications and comparison with other methods are presented. The measurement of thin Si and SiC films deposited on silicon wafer by magnetron sputtering was carried out. Some problems and disadvantages of this method were discussed. Their feasible solution is outlined at the end of the article.

Abstrakt
Jednou z možných aplikací tenkých vrstev v praxi je povlakování kontaktně namáhaných součástí a nástrojů pro zlepšení jejich povrchových vlastností. O vhodnosti použití konkrétní tenké vrstvy rozhodují její mechanické vlastnosti, charakterizované z části také elastickými konstantami (Youngův modul a Poissonovo číslo). Zjiš ování těchto veličin klasickými metodami známými z měření kompaktních objemových vzorků však není možné. Pro stanovování elastických veličin v tenkých vrstvách proto vznikly nové metody. Jednou z perspektivních je tzv. metoda LAW (Laser Acoustic Waves), založena na kalkulaci elastických konstant ze šíření povrchového akustického vlnění. V článku je tato metoda blíže charakterizována. Je vysvětlen její princip, jsou uvedeny podmínky jejího užití a je porovnána s některými dalšími metodami. Byla provedena měření na tenkých vrstvách amorfního křemíku (aSi) a karbidu křemíku (SiC), nanesených magnetronovým naprašováním na substrát z křemíkového monokrystalu. Při praktickém užití se též ukázaly jisté problémy a nevýhody této metodiky měření. V závěru článku je nastíněno jejich možné řešení.

1. Úvod

Jako většina veličin charakterizujících daný materiál je i hodnota modulu pružnosti určena jeho vnitřní stavbou. Podle naměřených hodnot a díky znalosti velikostí elastických konstant kompaktního materiálu, lze usuzovat na vnitřní uspořádání materiálu tenké vrstvy. Např. v uhlíkových vrstvách se může Youngův modul pružnosti pohybovat v rozmezí hodnot 100 GPa až po 1000 GPa. Široký rozsah hodnot této veličiny je způsoben různými modifikacemi uhlíku, jež mohou být ve vrstvě zastoupeny v libovolném poměru. Ze znalosti složení, modulu pružnosti v tenké vrstvě a složek v kompaktním tvaru, které se v povlaku vyskytují, je možno ve vrstvě odhadnout jejich poměrné zastoupení.

Youngův modul a Poissonovo číslo charakterizují tuhost materiálu a patří k důležitým veličinám popisující mechanické vlastnosti tělesa. U látek, které obsahují kovalentní vazbu, tj. u většiny tvrdých povlaků, existuje přímá souvislost mezi hodnotou Youngova modulu