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MICROHARDNESS STUDY OF TWO-LAYER NANOSTRUCTURES BY A NANOINDENTATION METHOD

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Abstract. The paper presents a model describing the Vickers microhardness of a two-layer film on a substrate as a function of a submergence depth of a nanoindenter. On the base of this model, the deformation characteristics of a two-layer silicon carbide nanofilm grown on silicon by an atom substitution method were derived. The Vickers microhardnesses of each layer of the film as well as of a layer of modified silicon, serving as substrate, were obtained. The thickness of each layer of the film was determined, and a good correspondence between the results obtained by an indentation method and data of spectral ellipsometry was exhibited.

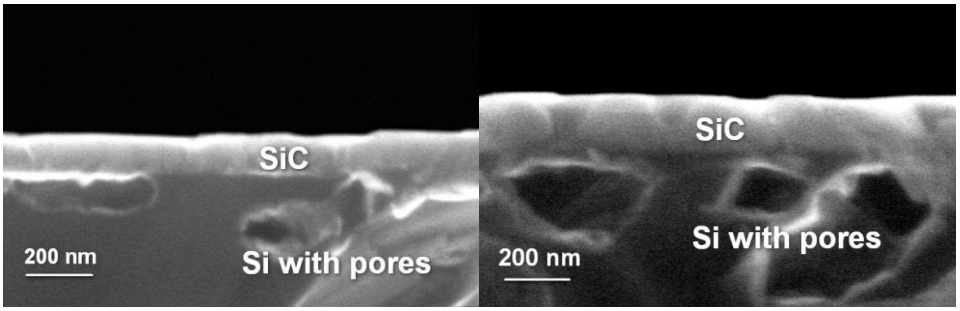
1. Introduction

The elaboration of adequate methods to study mechanical and structural characteristics of multilayer nanostructures has been one of the most important issues of material sciences at the present day stage [1]. Difficulties emerge in determining deformation properties of a film material even with a uniform one-layer 100 nm-film, which could be produced due to nano-scale structure [2]. Actually, however, uniform films about 100 nm thick do not exist, since at the film-substrate interface the various buffer or transient layers are formed, thickness of which generally is tens of nanometers [3]. Such layers essentially lower the energy of the film-substrate interface, which can be chemical or mechanical in nature. Since a thickness of transient layers becomes compatible with that of the film itself, nanofilms can't be considered as being uniform in thickness. In such a situation the film have to be looked upon as consisting of several uniform layers. A similar approach is used, for instance, in optical studies [3] which are very sensitive to the uniformity of layers. However, the multilayer approaches in studies of deformation characteristics of nanostructures, are not practical, which is caused by the fact that the effective models for description of elastic properties of multilayer nanostructures are presently lacking.

2. A microhardness model for two-layer nanostructures

We propose the strategy to extend the one-layer model used for a description of microhardness of the film-substrate system and developed for the case of a soft film on a soft substrate [4], to the multilayer system. The particular technique is applicable for studies of deformation properties of a two-layer semiconductor nanostructure on silicon (Si), which consists of a layer of silicon carbide (SiC) and, so called, buffer layer of solid solution of SiC and Si. Such a semiconductor-structure has been obtained by a chemical substitution method of Si-atoms by C-atoms [5] and is used as a template for further deposition of high energy-gap

semiconductors such as AlN, GaN [6], whose lattice parameters slightly differ from a lattice parameter of SiC. Therefore, the study of deformation properties of the latter is currently important but complicated by the fact that the method of chemical substitution does not give, in their true value, the deformation properties of silicon, containing a good fraction of pores and voids (Fig. 1). So, in this case, the microhardness of a substrate can be considered to be unknown along with the microhardness of layers, containing silicon carbide.



(a) (b)

Fig. 1. Microscopic image of the cuts for two SiC samples grown up on Si by an atom substitution method. An average thickness of the first sample (a) is 120 nm, the second (b) 180 nm. Si under the layer of SiC contains a great amount of pores.

The authors of paper [4] used the model of the Vickers effective microhardness of the film-substrate system, which, for simplicity, could be written in the form

$$H(h) = H_s + \left(H_f - H_s\right) \exp\left[-\left(\frac{\gamma h}{t}\right)^k\right] \tag{1}$$

Where $H(h)$ is the Vickers microhardness at penetration depth h of indenter; t, a thickness of the film; H_s, the microhardness of the substrate; H_f, the microhardness of the film; γ, a geometric factor; k, a dimensionless constant.

Notice that the parameter k is strongly dependent on various deformation characteristics both of the film and the substrate, specifically, on concentration of the defects and dislocations at the film-substrate interface [1]. The geometric factor is a dimensionless quantity and depends on the ratio of the Young modules and on the ratio of the yield points of materials of the film and substrate [1, 2, 4]. We propose to modify the model (1) for the case of a multilayer structure. In particular, in the case of a two-layer structure lying on a substrate, we propose to consider a lower layer together with a substrate as a substrate for an upper layer, i.e. as an intermediate or buffer substrate. In other words, it is supposed that the layers are independent of one another and have different parameters k, which are determined by concentration of defects and dislocations at the upper layer-lower layer and the lower layer-substrate interfaces. Within the limits of above assumptions, for a two-layer model we have

$$H(h) = H_b + (H_1 - H_b) \exp\left[-\left(\frac{\gamma h}{t_1}\right)^{k_1}\right], \tag{2}$$

$$H_b = H_s + (H_2 - H_s) \exp\left[-\left(\frac{\gamma h}{t_2}\right)^{k_2}\right], \tag{3}$$

Where H_b is the intermediate buffer microhardness; H_1, the microhardness of the upper layer of thickness t_1; H_2, the microhardness of a lower layer of thickness t_2. Substitution of Eq. (3) in Eq. (2) gives

$$H(h) = H_s + (H_1 - H_s) \exp\left[-\left(\frac{\gamma h}{t_1}\right)^{k_1}\right] + (H_2 - H_s) \exp\left[-\left(\frac{\gamma h}{t_2}\right)^{k_2}\right]\left(1 - \exp\left[-\left(\frac{\gamma h}{t_1}\right)^{k_1}\right]\right) \tag{4}$$

It follows from Eq. (4) that the contributions of the layers in the total microhardness are summed, similar to expression (1), but with different weight factors. The upper level enters with a weight $1 - \exp\left[-\left(\frac{\gamma h}{t_1}\right)^{k_1}\right]$, dependent of its thickness t_1. As could be expected, with $t_1 \to \infty$ this weight factor tends to zero. Similarly, one can build the model of microhardness for an n-layer system as well. For this purpose, beginning from the lowest layer, it is necessary to consider the lower layer together the substrate as an intermediate substrate for the next layer.

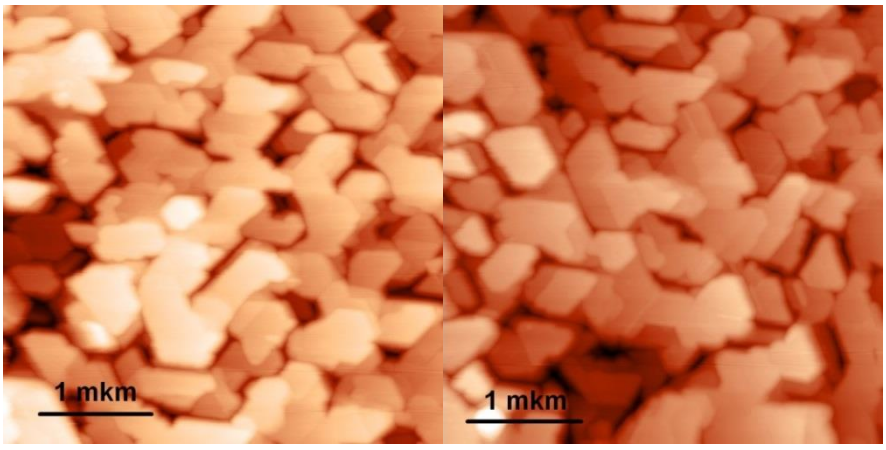
3. Experiment

An experimental testing of the given two-layer model was carried out with the silicon carbide samples grown on silicon by an atom substitution method [5]. Silicon carbide has been synthesized from silicon according to topochemical reaction.

$$2\mathrm{Si}(cr) + \mathrm{CO}(gas) = \mathrm{SiC}(cr) + \mathrm{SiO}(gas) \uparrow \qquad (5)$$

A key peculiarity of above reaction is the fact that it proceeds via an intermediate state [7], which is silicon saturated with dilatation dipoles [5]. Each dipole consists of a carbide atom, inserted into a silicon lattice, and of a silicon vacancy formed in Si due to a SiO-gas volatizing outward. Such point defects are formed only by vapors according to reaction (5), and then attracted together due to anisotropy of Si crystals [5, 8]. This attraction is so strong that balances the huge elasticity energy arising from the coherence conjugation of SiC crystals, which results in the growth of a defect-free and non-stress film of SiC on Si, in spite of the great difference in the lattice parameters of SiC and Si [8].

We studied two SiC/Si-samples. Sample 1 has been grown in a reactor at CO pressure of 2 Torr and temperature of 1270 ^{o} C, time of synthesis was 10 min. Sample 2 has been grown at CO pressure of 0.6 Torr and temperature of 1250 ^{o} C, time of synthesis was 20 min, in both cases we use the same silicon (111) of type KDB-10. Fig.1a, b displays the microphotographs of the cuts of the samples under study. There are clearly seen the voids in silicon under the SiC film, which are formed due to the fact that, first, a fraction of Si flies outward with SiO, and, secondly, the volume of a single cell of SiC (of a cubic polytype) half the volume of the cell of Si, i.e. the atoms are packed twice as dense. Fig. 2 a, b shows an image of the surface of the samples, obtained with the use of an atomic-force microscope.

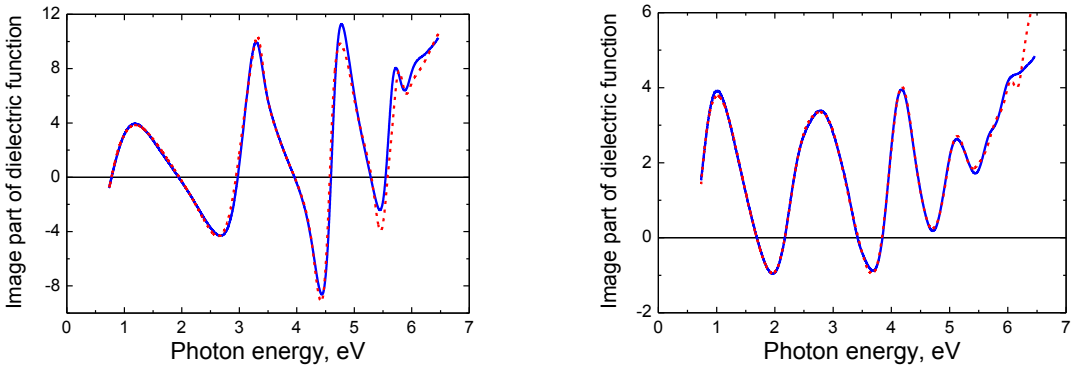


(a) (b)

Fig. 2. Images of the surface of samples 1(a) and 2 (b), obtained with the use of an atomic-force microscope.

The study of thickness and composition of the samples has been carried out by means of spectral ellipsometry [3]. Figure 3a, b shows the dependences of the imaginary part of

dielectric permittivity upon the photon energy measured with the use of a VASEJ.A. Woollam ellipsometer. A solid line marks the experimental data; dotted line is a theoretical curve derived in the limits of two-layer ellipsometrical model (Рис. 4).



(a) (b)

Fig. 3. Dependences of the imaginary part of the dielectric permittivity for samples 1 (a) and 2 (b) upon the photon energy. Solid line marks an experiment; dotted line, the two-layer ellipsometrical model.

On the base of the one-layer ellipsometrical model it is impossible to attain an agreement between the theoretical and experimental curves. In other words, the ellipsometrical analysis reveals that the particular SiC samples are the two- layer ones as are the majority of nanometer films. The layer of pure SiC (with a very small impurity of dilatation dipoles) is separated from the Si-layer with voids, by the layer of SiC-Si mixture, which, evidently, leads to a sharp lowering of energy of the SiC-Si interface.

For the sample 1 the thickness of the first two layers equals 80 and 40 nm, for the sample 2, 135 and 45 nm.

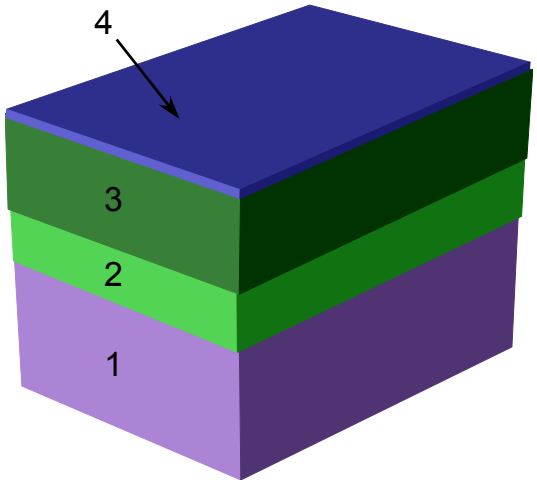


Fig. 4. Two-layer ellipsometrical model to interpret the data shown in Fig 3.
1, a substrate of Si with pores; 2, a lower layer which is a SiC-Si mixture; 3, an upper layer composing of SiC with a small fraction of dilatation dipoles.

The strength characteristics of the given samples have been studied by a nanindentation method with the help of a NanoTest 600 instrument (Micromatics). The measurements were carried out with the use of Berkovich indenter which has the form of a triangular pyramid rounded at the apex with a 100 nm radius. We have measured the loading as a function of penetration depth of the indenter in the loading-unloading conditions at the constant loading-

unloading of $0.05\ mN/s$. The maximum penetration depth was chosen to be larger than the total thickness of SiC. In the course of experiment the indenter was kept from a cavity in Si under the SiC film. The loading-unloading curves for samples 1 and 2 are shown in Fig. 5.

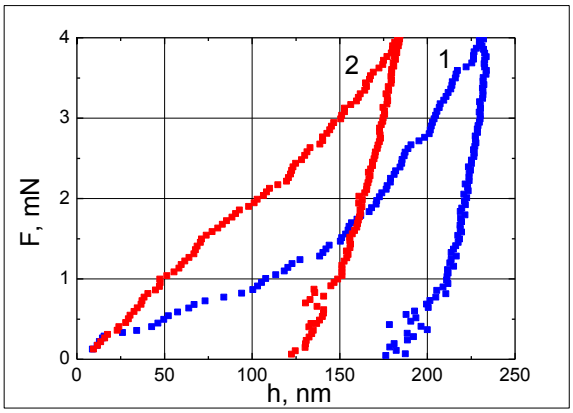
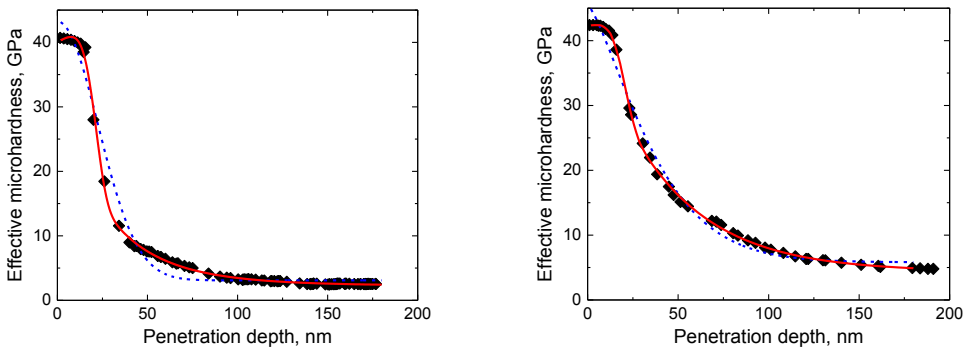


Fig. 5. Loading-unloading curves for SiC/Si samples 1 and 2, obtained by an atom substitution method; 1, sample 1; 2, sample 2.

A dependence of microhardness upon the indenter penetration depth is determined from the loading curve, i.e. from the left curve [2] (the unloading curve gives the Young modulus [2]). The results for both samples are presented in Fig.6 a, b. In the limits of the one-layer microhardness model (1) one can not attain a good agreement between the experimental (points) and theoretical results (dotted line). By contrast, in the limits of the two-layer model (4) (solid line) a roof-mean-square deviation of experiment from theory reduces more than ten times. From comparison of curve (4) with an experimental dependence obtained at the geometrical factor $\gamma = 3$, we have for sample 1: $H_1 = 40\ GPa$, $H_2 = 44\ GPa$, $H_s = 2.5\ GPa$, $t_1 = 78\ nm$, $k_1 = 1.0$, $t_2 = 57\ nm$, $k_2 = 4.6$; and for sample 2: $H_1 = 42\ GPa$, $H_2 = 48\ GPa$, $H_s = 4.4\ GPa$, $t_1 = 138\ nm$, $k_1 = 1.0$, $t_2 = 57\ nm$, $k_2 = 3.4$.



(a) (b)

Fig. 6. Vickers microhardness as a function of penetration depth of the indenter for samples 1 (a) and 2 (b), as obtained by an atom substitution method. A solid line marks the two-layer model (4), a dotted line, the one-layer model; points, experimental data. With taking into account of the second layer, a roof-mean-square error of approximation is decreased about 20 times approximately.

4. Discussion and conclusions

A comparison between the obtained results and ellipsometrical data leads to the following conclusions. The two-layer model (4) adequately describes the microhardness behavior of

multilayer nanostructures and permits the thickness of the layers to be approximately measured.

Obviously, it is best to use the different geometrical factors for each layer, since their elastic characteristics are different. Specifically, the factor $\gamma = 3$ exactly determines the thickness of the first layer but for the second layer the factor $\gamma = 2$ would be more accurate. However, a determination of the individual factor γ for each layer is beyond the scope of the proposed model and can be made with the help of numerical simulation or by comparison with the ellpsometrical data. In any case, for the given system the error in measuring of the total thickness was less than 10%.

Microhardness of the second layer in samples of SiC/Si, i.e. solid solution of SiC and Si, appeared to be somewhat higher than that of the first layer, i.e. SiC with dilatation dipoles, and also of volume SiC (~46 GPa, ~41 GPa, ~33 GPa, respectively). Microhardness of Si which acquired the pores and voids as a result of chemical reaction, has become much less than that of volume Si (~3.5 GPa and ~9 GPa, respectively).

The first and second layers in both samples of SiC/Si are coherently conjugate, there are no defects at the interface between them, and, as a result, the constant k_1 equals 1.0 for both samples. Between the second layer and the substrate there are a great deal of defects, that's why the quantity k_2 amounts to values of the order of 4.

Thus, the proposed two-layer model (4) makes possible to interpret adequately the experimental results about the microhardness of two-layer nanostructures and can be extended to the multilayer nanostructures.

Acknowledgment

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