Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 61 (2007) 4647–4650
materials letters
www.elsevier.com/locate/matlet

Effects of mass density on the microhardness and modulus of tetrahedral amorphous carbon films

Manlin Tan *, Jiaqi Zhu, Aiping Liu, Zechun Jia, Jiecai Han

Center for Composite Materials, Harbin Institute of Technology, No.2, Yikuang Street, Nangang District, Harbin 150001, China

Received 11 January 2006; accepted 27 February 2007
Available online 7 March 2007

Abstract

Tetrahedral amorphous carbon (ta-C) films were deposited by filtered cathodic vacuum arc technique with substrate negative bias setting in the range of 0–200 V. The film density, hardness and Young's modulus were respectively obtained from the X-ray reflectivity and nanoindentation measurements. A maximum value of density was identified in the middle range of incident ion energy. Correlations between the density and elastic behavior of the films were then discussed theoretically based on the constraint-counting model of Philips and Thorpe. The measured Young's modulus and hardness almost vary linearly with the increasing density which agrees quite well with the theoretic predictions.

Keywords: Deposition; Mechanical properties; Tetrahedral amorphous carbon; Thin films

1. Introduction

Recently, tetrahedral amorphous carbon (ta-C) films have been widely studied due to their optimistic mechanical hardness, chemical inertness and optical transparency [1,2]. Various characterization methods have been employed to study the structure modifications of ta-C films at different deposition or processing conditions such as ion energy, deposition temperature and post-annealing [3–5]. It has been proved that the unique mechanical behavior of ta-C film is largely determined by its high percentage of sp^3 hybridization [1]. This makes it as an ideal protective material in the field of coating technologies [6].

Compared with the sp^3 carbon content, density is also a very important parameter for ta-C films which includes both the micro- and macro-structure information about the films [7–10]. Roberson [11,12] had ever employed density to describe the process of sub-plantation. He proposed that the sub-plantation process creates a metastable increase in film density, which tends to cause the local bonding to change into sp^3 hybridization. This means that the variation of density has a great effect on the arrangement of local bonding which determines the final mechanical properties of the films.

In the present work, a detailed theoretic discussion on the potential relation between density and mechanical properties of ta-C films is tentatively carried out. For comparison, the film hardness and Young's modulus are plotted as a function of the film density obtained from X-ray reflectivity (XRR) measurements. The values agree quite well with the model proposed in this paper.

2. Experimental details

Ta-C films with different densities were prepared by FCVA deposition with substrate negative bias setting from 0 to 200 V. A detailed description of the deposition conditions is given elsewhere [13]. The film density was indirectly obtained from the XRR measurements which were conducted on a high resolution Philip X-Pert GIXA reflectometer. The source was a copper target X-ray tube monochromatized to the Cu K_α ($\lambda = 1.5418$ Å). Sample alignment was performed by lateral movement and rocking the specimen across the primary beam (ω-scan) until the maximum intensity of ω-scans equals half the intensity of the primary beam. A scintillation detector was used to measure the specular and off-specular curves for each sample, with incident angle θ_i ranged from 0 to 2.5° at a step of 0.0025°.

---

* Corresponding author. Tel.: +86 451 86402954; fax: +86 451 86417970.
E-mail address: tanmanlin@yahoo.com.cn (M.L. Tan).

0167-577X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2007.02.073

The hardness and Young's modulus were measured by an XP type Nano-indenter produced by MTS Co. at room temperature with 30% relative humidity. The load and displacement resolutions are 75 nN and 0.1 nm respectively. In the measurement, each of the samples was tested for 10 times at different local fields using a diamond indenter head. A final result was then obtained by averaging the sum of the values measured for the samples.

3. Results and discussion

3.1. Density

The refractive index n of most material in the X-ray wavelength range is slightly less than 1, and can be written as $n = 1 - \delta - i\beta$, where [10]

$$\delta = \frac{r_e \lambda^2}{2\pi} N_A \rho \frac{Z + \Delta f'}{A} \quad \text{and} \quad \beta = \frac{\lambda}{4\pi}\mu. \tag{1}$$

Here r_e is the classical electron radius, N_A is Avogadro's number, ρ is the mass density, λ is the X-ray wavelength, Z is the atomic number, A is the atomic mass, $\Delta f'$ is the real part of the anomalous scattering factor, and μ is the linear absorption coefficient. Thus applying Snell's law at the air/film interface gives the mass density [10]

$$\rho = \frac{\pi M_c \theta_c^2}{6\lambda^2 N_A r_e}, \tag{2}$$

where M_c is the molar mass and θ_c is the critical angle of total reflection shown in the inset of Fig. 1. From the above equations, mass density of ta-C films can be indirectly calculated. Fig. 1 shows the density variations of ta-C films with the substrate negative bias. Without bias applied, the film has a low value of 2.71 g/cm^3 due to much less C$^+$ ions implanted into the subsurface in the initial stage of deposition. As the negative bias voltage increased, the density passes a maximum value at the bias voltage of −80 V and then decreases gradually. This is consistent with the changes of sp^3 content in the films as identified from structural characterization using Raman spectroscopy in another work [14]. The dependence of film density on the ion energy was well interpreted by Roberson's subplantation model [11]

$$\frac{\Delta\rho}{\rho} = \frac{f\phi}{1 - f\phi + 0.016(E_i/E_0)^{5/3}}, \tag{3}$$

where the definition of each parameter can be found in Ref. [1].

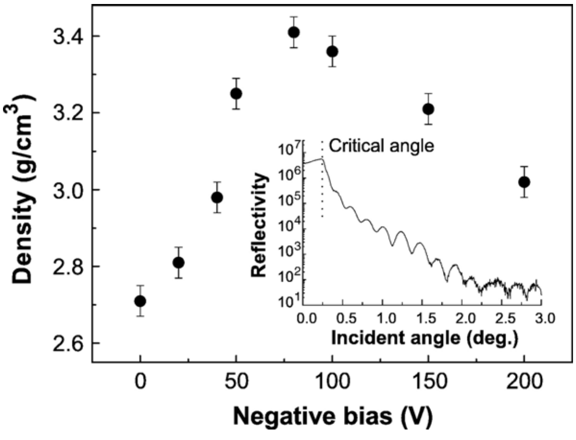

Fig. 1. Variations of mass density with substrate negative bias for the ta-C films. A typical XRR curve is also plotted in the inset.

3.2. Mechanical properties

The most tractable mechanical properties of ta-C films, elasticity and Young's modulus depend on the rigidity of the individual bonds and average coordination of the network, and can be quantified by the constraint-counting model of Philips and Thorpe [15,16]. The model assumes small vibrations such as bond-stretching and bond-bending of the network can be described by a potential

$$V = \frac{1}{2}\sum_{<ij>} \alpha_{ij}(\Delta r_{ij})^2 + \frac{1}{2}\sum_{<ijk>} \beta_{ijk}(\Delta\theta_{ijk})^2, \tag{4}$$

where Δr_{ij} is the change in nearest neighbor bond length between atoms $<ij>$, and $\Delta\theta_{ijk}$ is the change in the bond angle between two adjacent bonds $<ij>$ and $<jk>$. The α_{ij} and β_{ijk} are the force constants whose precision will not be considered [15]. For a network with N atoms, there are many ways for deformation at zero energy cost. The number of the zero-frequency vibration modes is given by the difference between the numbers of freedom degrees ($3N$) and linearly independent constraints N_{con}. N_{con} varies with coordination r. One constraint corresponds to a bond-stretching shared between two atoms and $2r-3$ constraints correspond to angle variations for an r-coordinated atom. Thus the total number of constraints

$$N_{\text{con}}(r) = \frac{5}{2}r - 3 \tag{5}$$

is obtained at each site, except that monovalent atoms like hydrogen are defined as

$$N_{\text{con}}(1) = \frac{1}{2}. \tag{6}$$

Then the fraction of zero-frequency modes is

$$f = 3\sum_r n_r - \sum_r n_r[r/2 + (2r - 3)], \tag{7}$$

which setting $f = 0$ yields

$$r_p = <r> = \sum_r r n_r \Big/ \sum_r n_r = 2.4. \tag{8}$$

Here n_r and $<r>$ are the concentration of r-fold atoms and the mean coordination respectively. r_p is the phase transition point between soft ($<r> < r_p$) and rigid ($<r> > r_p$) networks [15].

He and Thorpe [16] found the Young's modulus E to vary as

$$E = E_0\left(\frac{-f}{-f_0}\right)^{1.5} = E_0\left(\frac{<r> - 2.4}{r_0 - 2.4}\right)^{1.5} \tag{9}$$

for $r > 2.4$, and reach E_0 at $r_0 = 4$ in the case of ta-C films. The model was slightly modified to include the effects of graphite clusters by Roberson [17]. This is because all the constraints of a three-fold graphite layer are in the planar direction and no rigidity exists vertically. A simple approximation was proposed including the clustering effect which was to displace the critical coordination r_c to a larger value than 2.4. Then Eq. (9) should be written as

$$E = E_0\left(\frac{<r> - r_c}{r_0 - r_c}\right)^{1.5} \tag{10}$$

In the atomic scale, density is determined by the atoms arrangement and is related with the mean coordination in the case of our mono-atomic network. Now, suppose there are only sp^2 and sp^3 sites in the ta-C films, and let r_{sp^2} and r_{sp^3} stand for their corresponding coordination respectively. In the micro-field, each sp^2 site is thought to be contained

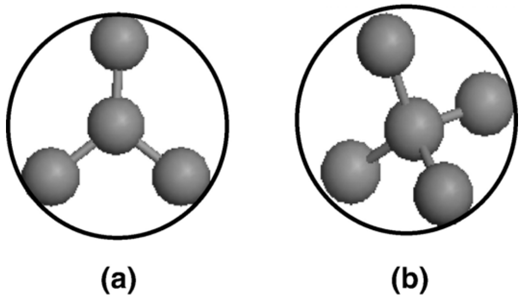

Fig. 2. Supposed micro-unit of sp^2 and sp^3 sites (a) sp^2 site in a cylinder with bottom circle radius $R_{sp^2}=3R_a$ and cylinder height $h \approx c$ (b) sp^3 site in a sphere unit with sphere radius $R_{sp^3}=3R_a$.

in a cylinder unit with bottom circle radius $R_{sp^2}=3R_a$ and cylinder height $h \approx c$, where R_a is the atomic radius of carbon and c is the space between layers of graphite (see Fig. 2(a)). The density of sp^2 site is proportional to the volume occupation percentage of carbon atoms in the cylinder, which is described as

$$\rho_{sp^2} \propto \frac{\frac{4}{3}\pi R_a^3 (r_{sp^2}+1)}{\pi (3R_a)^2 c}. \tag{11}$$

As it is known that $c=0.335$ nm, $R_a=0.091$ nm, then $c \approx 4R_a$ can be replaced in the above expression as

$$\rho_{sp^2} \propto \frac{\frac{4}{3}\pi R_a^3 (r_{sp^2}+1)}{\pi (3R_a)^2 \cdot 4R_a} = \frac{r_{sp^2}+1}{27}. \tag{12}$$

While for a sp^3 site, it is thought to be placed into a sphere unit with sphere radius $R_{sp^3}=3R_a$ (see Fig. 2(b)). Then the density of an sp^3 site can be also described using occupation ratio as,

$$\rho_{sp^3} \propto \frac{\frac{4}{3}\pi R_a^3 (r_{sp^3}+1)}{\frac{4}{3}\pi (3R_a)^3} = \frac{r_{sp^3}+1}{27}. \tag{13}$$

For the network of ta-C, the total density is

$$\rho = \frac{X_{sp^2} \cdot \rho_{sp^2} + X_{sp^3} \cdot \rho_{sp^3}}{X_{sp^2} + X_{sp^3}} \propto \frac{<r>+1}{27}, \tag{14}$$

where X_{sp^2} and X_{sp^3} are the concentrations of sp^2 and sp^3 sites.

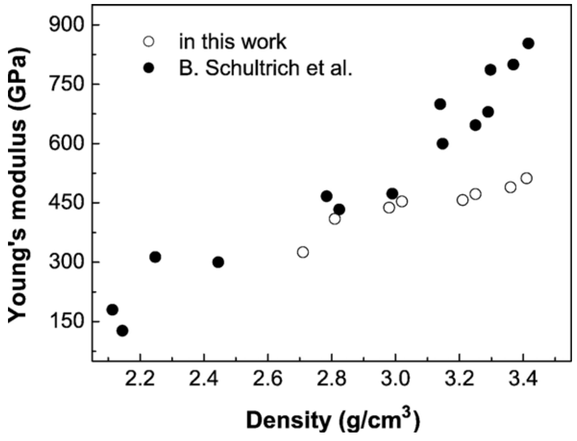

Fig. 3. Variations of Young's modulus for ta-C films as a function of mass density (blank circles). The values obtained from Ref. [17] are also plotted for comparison (black circles).

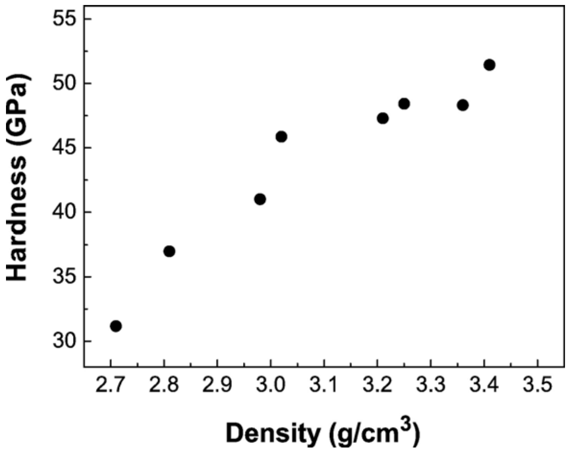

Fig. 4. Variations of hardness with mass density for ta-C films.

Thus from Eqs. (10) and (14), a similar correlation between the density and Young's modulus can be established. Although the exponent in the function requires further theoretical and experimental determination, the proportional relation between the two can be easily speculated at least. Fig. 3 shows the measured Young's modulus as a function of mass density of ta-C films. As it has been expected, the Young's modulus rises gradually with increasing density. Such a steady increase in modulus with increasing density was also reported by Schultrich et al. [18], as shown in Fig. 3. In their work, diamond and hydrogenated amorphous carbon were also included and both have the same dependence between density and Young's modulus as ta-C films.

The hardness is a measure of the yield stress of a material. The values measured by nano-indenter depend on the loading time, temperature and deformation of the solid [16]. Hardness H, yield stress Y and Young's modulus E can be empirically united by [17]

$$\frac{H}{Y} = 0.07 + 0.06 \ln\left(\frac{E}{Y}\right) \tag{15}$$

In brittle materials like DLC, yield occurs by bond cleavage [1]. According to the Orowan approximation [17], the yield stress can be calculated, and

$$\frac{E}{Y} = \pi. \tag{16}$$

From formulae (15) and (16), it gives

$$\frac{H}{E} = 0.16. \tag{17}$$

Thus the density and hardness can be also proportionally related. As it has been expected, the experimental results are also consistent with the predictions very well qualitatively which are shown in Fig. 4. The hardness of ta-C primarily rises up as density increases in spite of a little of data floatation.

4. Conclusions

Ta-C films were deposited by FCVA at different substrate negative biases. The density of ta-C film has a low value of 2.71 g/cm^3 at 0 V bias voltage and passes a maximum value at the bias voltage of −80 V. A simple model was established between the density and elastic behavior of ta-C films based on the constraint-counting model of Philips and Thorpe. The model predicts the experimental data quite well from the plot of modulus and hardness vs. mass density for the films.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Grant no. 50602012).

References

[1] J. Robertson, Mater. Sci. Eng., R 37 (2002) 129.

[2] Q. Wei, J. Narayan, Int. Mater. Rev. 45 (2000) 135.

[3] P.J. Fallon, V.S. Veerasamy, C.A. Davis, et al., Phys. Rev., B 48 (1993) 4777.

[4] M. Chhowalla, A.C. Ferrari, J. Roberson, A.J. Amaratunga, Appl. Phys. Lett. 76 (2000) 1419.

[5] R. McCann, S.S. Roy, P. Papakonstantinou, et al., Thin Solid Films 482 (2005) 34.

[6] Y. Lifshitz, Diamond Relat. Mater. 8 (1999) 1659.

[7] C.A. Lucas, T.D. Nguyen, J.B. Kortright, Appl. Phys. Lett. 59 (1991) 2100.

[8] Y. Huai, M. Chaker, J.N. Broughton, E. Gat, H. Pépin, Appl. Phys. Lett. 65 (1994) 830.

[9] Q. Zhang, S.F. Yoon, J. Rusli, H. Ahn, J. Yang, Appl. Phys. 86 (1999) 289.

[10] A.C. Ferrari, A. Libassi, B.K. Tanner, et al., Phys. Rev., B 62 (2000) 16.

[11] J. Roberson, Diamond Relat. Mater. 2 (1993) 984.

[12] J. Roberson, Diamond Relat. Mater. 3 (1994) 361.

[13] M.L. Tan, J.Q. Zhu, J.C. Han, et al., Trans. Nonferr. Met. Soc. China 14 (2004) 238.

[14] J.Q. Zhu, J.C. Han, S.H. Meng, et al., Vacuum 72 (2004) 285.

[15] J.C. Philips, J. Non-Cryst. Solids 34 (1979) 153.

[16] H. He, M.F. Thorpe, Phys. Rev. Lett. 54 (1985) 2107.

[17] J. Roberson, Phys. Rev., B 68 (1992) 220.

[18] B. Schultrich, H.-J. Scheibe, D. Drescher, H. Ziegele, Surf. Coat. Technol. 98 (1998) 1097.