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Fracture toughness, hardness and elastic modulus of hydrogenated amorphous carbon films deposited by chemical vapor deposition

M.D. Michel [a,*], L.V. Muhlen [b], C.A. Achete [b], C.M. Lepienski [a]

[a] *Universidade Federal do Paraná, UFPR, Laboratório de Propriedades Nanomecânicas, Departamento de Física, Cx. Postal 19044, CEP 81531-990, Curitiba-PR, Brazil*

[b] *Engenharia Metalúrgica e de Materiais, Universidade Federal do Rio de Janeiro, Cx. Postal 68505, CEP 21945-970, Rio de Janeiro, RJ, Brazil*

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Abstract

Fracture toughness, hardness and elastic modulus of hydrogenated amorphous carbon thin films produced from butene gas deposited by chemical vapor deposition on silicon were measured by depth sensing indentation. Voltage bias varying from −60 to −400 V and pressures of 2 and 8 Pa were used for deposition. Cube corner indentation produces film chipping at loads lower than 400 mN. A new approach to measure toughness was proposed to determine the energy released during film chipping. Fracture toughness results from this new approach are in between of the ones obtained from methods proposed in the literature.

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1. Introduction

Amorphous carbon films, deposited by different methods have been intensively studied [1,2]. These films have been applied in optical, electronic, biomedical and tribological fields since the last two decades, due to their useful properties such as high optical transparency in the infra-red, high hardness, good electrical resistivity, chemical inertness, high wear resistance, and low friction coefficient. Some applications are like protective overcoat of magnetic storage hard disks and on emerging devices of microelectromechanical systems (MEMS) [1–5]. The mechanical properties of the films may be very different depending on the deposition method and, even for the same deposition method, they depend on the deposition parameters [1,2,5].

Chemical vapor deposition (CVD) processes are widely used to obtain hydrogenated amorphous carbon (a-C:H). Gas mixture composition in the chamber, pressure and voltage bias have a strong effect on the physical properties of the deposited film. Hardness and elastic modulus are strongly affected by these deposition parameters [1,6]. Films deposited from methane gas showed hardness of about 22 GPa [3,5], while hardness for films deposited from butene gas is not reported in literature. Hardness and elastic modulus of thin films can be obtained from depth sensing instrumented indentation (DSI) [7,8] using the Oliver and Pharr method [9].

Toughness of brittle materials is measured from the energy released during fracture. The conventional method to determine fracture toughness from indentation is based on the radial crack lengths [10]. This method cannot be straightly applied in thin films since the crack growth may be influenced by the substrate. Additional difficulties consist in measuring the radial crack length at shallow indentations, and in the fact that radial cracks are nucleated for loads higher than a threshold critical load. However, delamination and chipping can occur in thin brittle films during indentation [11]. Discontinuities on load versus displacement curves of instrumented indentation in thin brittle films using sharp indenters, can be correlated to cracking and chipping processes. Indentation energy can be calculated from the integral of the load as a function of depth. Since toughness is

* Corresponding author.
E-mail addresses: mdmichel@fisica.ufpr.br (M.D. Michel), lepiensm@fisica.ufpr.br (C.M. Lepienski).

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related to the energy involved in the fracture process, two methods were proposed to determine fracture toughness of thin films from energy released with chipping from depth sensing indentation data [12,13].

In this paper, the hardness, elastic modulus, and toughness of hydrogenated amorphous carbon thin films from 1-butene gas are presented. The existing methods to measure toughness are analyzed. A new method to measure the energy released during film chipping during indentations is proposed in order to determine fracture toughness.

2. Fracture toughness

Several concurrent processes occur during indentation with a sharp indenter in a brittle film deposited on a substrate. It is necessary to consider elastic–plastic deformation, the film–substrate delamination, and the cracks in the film and in the substrate. Cracks in the film can be radial, lateral and/or ring like cracks. Film toughness can be determined by chipping. In this case the energy released during cracking and the fracture area needs to be determined. During chipping the opening mode (mode I) is predominant compared to fracture modes II and III. Then the fracture toughness, K_{IC} is given by [14]

$$K_{IC} = \sqrt{\Gamma E'} \tag{1}$$

where Γ is the energy release rate and E' is the reduced modulus for plain stress, $E' = \frac{E}{(1-\nu^2)}$. E is the elastic modulus and ν is Poisson ratio.

It is observed that cracking is propagated almost instantaneously and then $dU/dc = U/t'$, where t' is the effective film thickness in the fracture. C_R and t' can be determined by microscopy. Then the energy release rate is given by [12]

$$\Gamma = \frac{U_{fr}}{A} \tag{2}$$

where U_{fr} is the strain energy released during the chipping fracture, $A = N2\pi C_R t'$, is the area of the fracture surface during chipping. N is the number of chipped regions (1, 2 or 3). C_R is the radius of the delamination crack and t' is the effective coating thickness of the film fractured region.

During indentation, the load versus displacement curve shows a discontinuity when chipping occurs. Two different methods were developed to determine the energy released during fracture [12,13]. Li at al. [12] extrapolated the loading curve in a tangential direction from the starting point of the discontinuity to the indentation depth corresponding to the end of the discontinuity. The energy dissipated, U_{fr}, is the difference between the areas from the measured and the extrapolated curves. Toonder et al. [13] use a more elaborated approach. According to the authors the elastic deformation energy, the plastic deformation energy and the delamination energy can be determined by several indentations at increasing loads. The areas under the load versus displacement curves are measured. The fracture energy, U_{fr} can be calculated through the difference from the total area under the curve and the energies of elastic–plastic deformation and delamination.

3. Experimental procedure

Hydrogenated amorphous carbon films were deposited by RF-glow discharge chemical vapor deposition (CVD). The gas was pure 1-butene at pressures of 2 and 8 Pa without plasma cleaning. Six different voltage bias were used: −60, −120, −200, −250, −370, and −400 V. The substrate used was Si (100) with 0.6 mm thickness and dimensions of 2 × 1 cm. The substrate was cleaned in an ultrasonic bath in isopropanol during 25 min. The films were deposited directly on a silicon wafer substrate without removing the natural oxide layer. Film thickness was measured by a stylus with a Dektak II Profilometer. Residual stresses in the films were determined from the curvature parameter δ, in a 10 mm scan, L, with the profilometer stylus. The residual stress σ was calculated from the Stoney equation [14].

$$\sigma = \frac{E_S}{(1-\nu)} \cdot \frac{t_S^2}{t_f} \cdot \frac{\delta}{L^2}, \tag{3}$$

where $E_S/(1-\nu)$ is the biaxial modulus of the substrate, t_s and t_f are the thicknesses of substrate and film, respectively. Table 1 shows the deposition parameters data, thickness and residual stress for each film.

Depth sensing indentations were made in a Nanoindenter XP (MTS System). A Berkovich indenter was used to determine hardness and elastic modulus according to the method of Oliver and Pharr [9]. Depth dependence of these quantities was observed in 9 indentations performed for each of the 8 different loads, being 400 mN the maximum load in the tests, made at room temperature.

Film cracking was observed after a single cycle indentation with a cube corner tip. Load versus displacement indentation curves were used to measure the energy evolution during the tests. Fractures induced by indentation were analyzed by scanning electron microscopy.

4. Results and discussion

4.1. Hardness and elastic modulus of the a-C:H films

Hardness as a function of penetration depths of samples deposited at 2 and 8 Pa are shown in the Fig. 1. Fig. 2 shows the results for elastic modulus for the same samples. Hardness and elastic modulus of silicon are plotted as a reference. The substrate effect can be observed in all cases at high penetration

Table 1
Voltage Bias (V_b), thickness (t), deposition rate (μ) and internal residual stress (σ) of a-C:H films deposited from 1-butene at pressures of 2 and 8 Pa

V_b (V)	t (μm)	μ (nm s^{-1})	σ (GPa)	t (μm)	μ (nm s^{-1})	σ (GPa)
	2 Pa			8 Pa		
−60	1.1	0.09	0.75	1.1	0.14	0.55
−120	0.8	0.11	2.86	1.0	0.25	1.29
−200	1.0	0.21	2.39	1.1	0.46	1.04
−250	0.7	0.20	2.42	1.0	0.55	0.9
−370	1.0	0.38	3.53	1.0	0.80	2.05
−400	1.0	0.43	3.18	1.5	0.63	2.65