Mechanical properties of plasma polymer films controlled by RF power

Erik Palesch, Sona Kontarova, Vladimir Cech
Institute of Materials Chemistry, Brno University of Technology
Purkynova 118, CZ-61200 Brno, Czech Republic

Abstract

This study deals with plasma polymer films deposited on silicon substrates using tetravinylsilane monomer. The deposition technique was plasma-enhanced chemical vapour deposition. Nanoindentation was used as a method to investigate mechanical properties of samples prepared at different RF powers. The Young's modulus and hardness of thin films were estimated from load-displacement curves. The nanoscratch test was employed to determine the critical normal load needed for film delamination, as a parameter describing adhesion to the substrate. AFM images of scratches were carried out to correlate the data with nature and shape of scratches.

Keywords

Thin films, plasma polymer, mechanical properties, nanoindentation, nanoscratch test

1. Introduction

Thin polymer films prepared by plasma-enhanced chemical vapour deposition (PECVD) using organosilicon precursors are quite popular materials in many technological areas nowadays. Such films has found their use as corrosion protective layers [1], gas barrier coatings [2], low-k dielectrics [3], and as functional interlayers in glass fiber reinforced polymer composites [4]. In many of their applications, mechanical properties of the films are essential. They can be effectively controlled by choosing appropriate fabrication variables, such as power, monomer flow rate or pressure, during deposition process [4].

Nanoindentation proved itself to be one of the most important methods when characterizing mechanical properties of materials in form of thin films [5]. One cycle of nanoindentation measurement consists of loading segment, when indenter is sinking into the sample causing both elastic and plastic deformation, and unloading segment, when mostly recovery of elastic deformation occurs. In cyclic nanoindentation, the sample is reloaded immediately to higher depths/loads than in previous loading cycle. The reloading path should not overlap with the unloading path of the previous loading cycle, resulting in hysteresis loops. The cyclic nanoindentation is a rapid way to construct depth dependencies of mechanical parameters [6].

The nanoscratch test is extended feature of the nanoindentation device. Scratch is done by moving the indenter laterally while continuously penetrating into the sample. By recording the lateral force, normal force and normal displacement signal, one is able to investigate adhesive properties of the thin film.

In this study, we examined mechanical properties of single layer a-SiC:H films deposited from tetravinylsilane on silicon substrates by PE-CVD at different powers. Cyclic nanoindentation, nanoscratch test and atomic force microscopy (AFM) were methods used for determining the Young's modulus, E, hardness, H, and critical normal load for delamination, F_c.

2. Experimental

2.1 Sample preparation

Thin a-SiC:H films characterized in this work were prepared in plasma reactor working with capacitively-coupled plasma designed for deposition onto flat substrates. The monomer used was tetravinylsilane (TVS, Sigma-Aldrich, 97 %). The plasma polymer was deposited on double-sided polished silicon substrates with dimensions 10 × 10 × 0.6 mm (ON SEMICONDUCTOR CZECH REPUBLIC s.r.o). Before deposition, substrates were pre-activated with help of Ar plasma (5 W, 10 sccm, 5 Pa). The deposition of plasma-polymerized (pp) TVS films was performed at powers in range 10 - 70 W, system pressure was 3 Pa, and monomer flow rate was 3.8 sccm. The reaction chamber was flushed with argon gas for 1 hour after plasma polymerisation. Samples were held inside reactor till next day to prevent reactions with air and so to prevent thin film modification. The plasma reactor was equipped with *in situ* spectroscopic ellipsometer UVISEL (Jobin-Yvon), thus we were able to measure the thickness of films. Samples intended for indentation testing were deposited with a thickness of 1 μm to prevent substrate influence. Samples used for scratch testing had a thickness of about 100 nm.

2.2 Nanoindentation

Mechanical properties of samples were investigated using nanoindentation head TriboScope TS-70 (Hysitron, Minneapolis, USA) attached to Ntegra Prima scanning probe microscope (NT-MDT, Zelenograd, Russia). The head consists of the three-plate capacitive transducer capable of moving the indenter in both vertical and horizontal directions with high accuracy and sensitivity. The force and displacement resolution of this device are <1 nN and 0.0004 nm, respectively. Three-sided pyramidal Berkovich type indenter with curvature radius of 150 nm was used. Hardness and Young's modulus of thin films were evaluated from load-displacement curves of cyclic nanoindentation measurement using the widely known Oliver Pharr method [5].

2.3 Nanoscratch test

Nanoscratch tests were performed with the same equipment as the nanoindentation tests. We looked for the critical normal load for delamination as an indication of thin film failure. It is found in the normal force vs lateral force plot as the point where lateral force response abruptly changes for the first time. Material of thin film is removed from the substrate. This event could happen several times after initial delamination as the normal force is increasing during progressive load scratch test.

2.4 Atomic force microscopy (AFM)

For surface analysis of scratches, a scanning probe microscope Ntegra Prima (NT-MDT) was used in scanning-by-sample configuration. Semi-contact mode of atomic force microscopy measurements was employed to acquire topography maps of scratched areas. Also, amplitude images (feedback error signal) were recorded together with topography images to better observe outlines of scratches and smooth surface features. A cantilever NSG10 with a resonance frequency of 190 - 325 kHz was used for measurements. The curvature radius of tip apex is approx. 10 nm. We investigated scratch images for thin film failure points and they were used for comparison with the data obtained by nanoscratch test.

3. Results and Discussion

3.1 Nanoindentation measurements

Five samples were investigated to characterize their mechanical properties. The films were prepared at powers 10, 20, 25, 50 and 70 W. Deposited films with a thickness of approximately 1 μm were homogeneous, isotropic materials, according to ellipsometric spectroscopy, X-Ray photoelectron spectroscopy and Rutherford backscattering spectroscopy [7, 8]. The depth profiles of mechanical properties, the Young's modulus and hardness (Fig. 1), were constructed for all the samples using cyclic nanoindentation. Each cyclic nanoindentation consisted of 25 cycles. Measurements were performed four times for each sample, thus we were able to evaluate average value of the Young's modulus and hardness, together with the standard deviation.

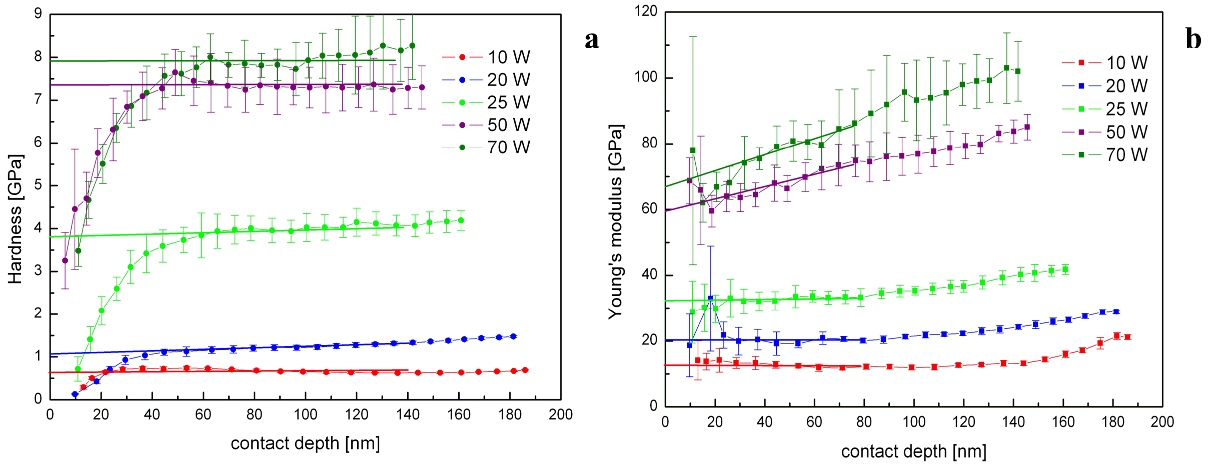

Fig. 1: Depth profiles of hardness (a) and Young's modulus (b) for samples prepared at different power

Hardness values are quite stable for all depths greater than 50 nm. For lower depths measured values of hardness are not reliable because unlike modulus, hardness is not defined when creating tip area calibration function. It is computed value dependent on the contact area of the probe, which in case of very low contact depths doesn't have perfect pyramidal shape for Berkovich indenter. Thus for hardness, the contact area calibration is not sufficient for low penetration depths.

There is an increasing trend in modulus profiles, when the contact depths are significantly greater than 100 nm. In case of stiffer films (50 W, 70 W) the profiles increase from the very beginning. The reason for this behaviour is the stiff silicon substrate (E = 170 GPa, H = 11 GPa), which affects the measurements. The 10% rule says that modulus values are not significantly influenced by the substrate in depths till 10% of film thickness. However, as observed in one of our previous studies [9], this rule is not valid for a-SiC:H films prepared at higher powers, like in this case of 50 or 70 W. We evaluated the Young's modulus and hardness by extrapolating linear part of each profile to zero contact depth (Fig. 1). As it is evident from the graphs, both the Young's modulus and hardness increased with enhanced power. The trend is the same for modulus as for hardness (Fig. 2). Enhancement of power for plasma deposition causes more intense fragmentation of monomer molecules (tetravinylsilane in this case) and it will increase the cross-linking of resulting polymer. The more cross-linked polymer, the stiffer it will be, what corresponds to higher values of Young's modulus and hardness.

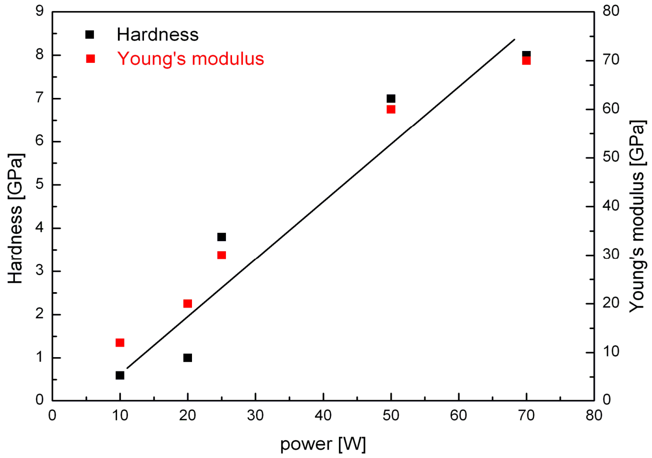

Fig. 2: Effect of power on hardness and Young's modulus

3.2 Nanoscratch test

For nanoscratch test, four samples were prepared at powers 10, 25, 50 and 70 W, all with thickness approx. 100 nm. Such a thickness enabled us to utilize a maximum load of 10 mN.

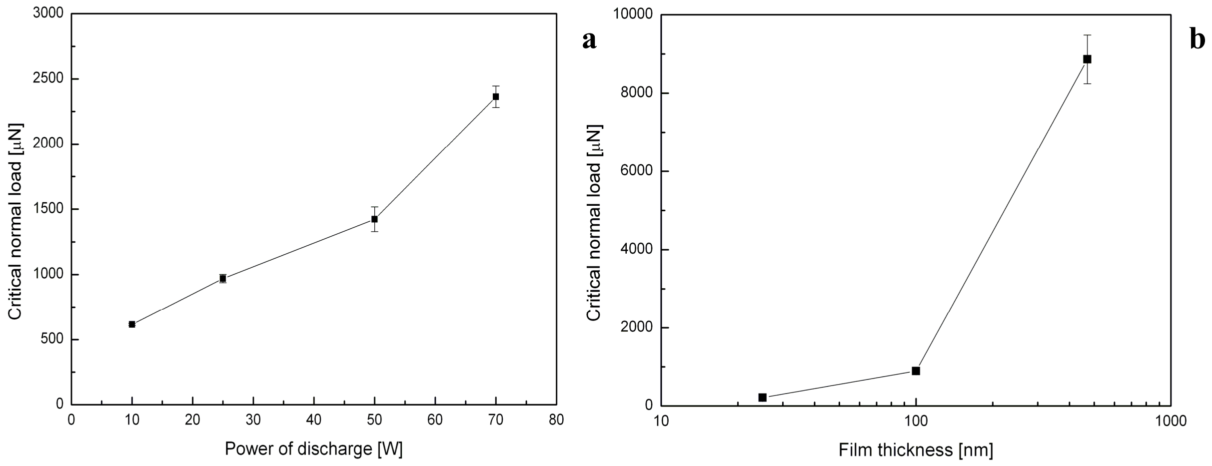

Fig. 3: (a) plot of critical normal load for delamination vs power of discharge, (b) effect of film thickness on critical normal load.

Every scratch was 10 µm long and it took 30 seconds to perform scratch. A peak normal load for each sample was chosen to initiate delamination approximately in the half of the scratch path. Results of samples prepared at different powers are graphically presented in Fig. 3a. We evaluated the critical normal load from lateral force vs normal force plots constructed from acquired data. Each sample was measured five times, so we obtained averaged values together with standard deviation (Fig. 3a). Like in the case of the Young's modulus and hardness, the critical normal load showed increasing trend when increasing the power. The trend of this dependence is quite linear in the range of powers we used for deposition. The critical normal load is the parameter characterizing adhesive properties of the film. The nanoscratch data were correlated with AFM images of scratch path. For this purpose, we used semicontact mode of atomic force microscope to obtain topography images of scratches, like that showed in Fig. 4, which is a representative scratch made in sample prepared at 70 W. Scratches in other samples had similar appearance. The point of film failure is obvious from AFM image and it correlates well with an abrupt change of the lateral force. The critical normal load for delamination was rising with enhanced power.

Besides this experiment, three samples with increasing thickness of 25, 100 and 470 nm were investigated for the critical normal load. All these samples were prepared at power of 10 W. Figure 3b shows that there is a

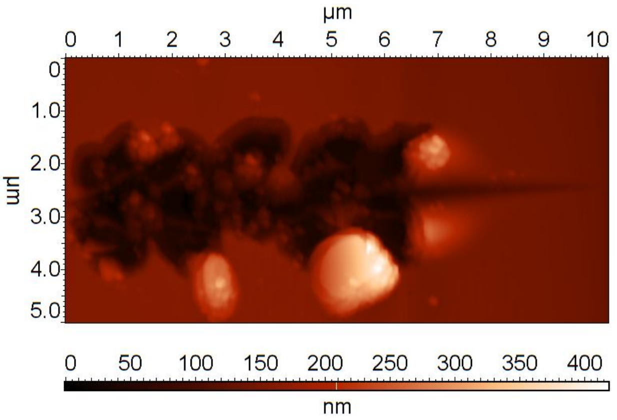

Fig. 4: AFM topography image of scratch in 70 W sample

significant increase of the critical load with enlarged thickness of the film. Such behaviour is expected as long as the residual stress in the film is not increased with the film thickness [10]. Increasing trend was also found out in the study of amorphous carbon coatings [11].

4. Conclusions

Pp-TVS films with the thicknesses from 25 nm to 1 μm were deposited by PECVD working in continual regime. The Young's modulus and hardness were determined using cyclic nanoindentation. For samples prepared at powers in range 10 – 70 W, we found out an influence of the power on measured mechanical properties, resulting in an increase of Young's modulus and hardness with enhanced power due to an increased polymer cross-linking. The same increasing trend was found for the critical normal load, parameter characterizing adhesion of the film to the substrate, evaluated from nanoscratch tests performed on samples with a thickness of 100 nm and prepared at above mentioned range of powers. The thickness dependence of critical normal load was examined, showing an increased F_c value for a thicker film.

Acknowledgements: This work was supported in part by the Czech Science Foundation, grants no. P106/11/0738, P205/12/J058 and 104/09/H080, the Czech Ministry of Education, grant no. ME09061 and the Technology Agency of the Czech Republic, grant no. TA01010796.

References

[1] C. Petit-Etienne, M. Tatoulian, I. Mabille, E. Sutter, F. Arefi-Khonosari, Plasma Process. Polym. 4 (2007) S562.
[2] A. Francescangeli, F. Palumbo, R. d'Agostino, C. Defranoux, Plasma Process. Polym. 6 (2009) 132.
[3] A.M. Coclite, A. Milella, F. Palumbo, F. Fracassi, R. d'Agostino, Plasma Process. Polym. 6 (2009) 512.
[4] V. Cech, in: S. Zhang (Ed.), Nanostructured Thin Films and Coatings, Volume 1, CRC Press, New York, 2010, pp. 481.
[5] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564.
[6] R. Trivedi, V. Cech, Surf. Coat. Technol. 205 (2010) S286.
[7] V. Cech, J. Studynka, B. Cechalova, J. Mistrik, J. Zemek, Surf. Coat. Technol. 202 (2008) 5572.
[8] V. Cech, J. Zemek, V. Perina, Plasma Process. Polym. 5 (2008) 745.
[9] R. Trivedi, L. Hoferek, V. Cech, Surf. Coat. Technol. 205 (2011) S470.
[10] P.J. Burnett, D.S. Rickerby, Thin Solid Films 157 (1988) 233.
[11] B.K. Gupta, B. Bhushan, Thin Solid Films 270 (1995) 391.