

Surface properties of plasma polymerized tetravinylsilane

S. Lichovniková, L. Hoferek, R. Trivedi, V. Cech

Institute of Materials Chemistry, Brno University of Technology, Purkynova 118, CZ-612 00 Brno, Czech Republic

Abstract: Plasma-polymerized thin films of tetravinylsilane were deposited on silicon wafers using plasma-enhanced chemical vapor deposition. Deposited films were characterized by atomic force microscopy, ellipsometric spectroscopy, and contact angle measurements. The surface morphology of thin films and evaluated root mean square roughness changed with deposition conditions, especially with the effective power. The surface free energy was evaluated from contact angle measurements by Owens-Wendt and Wu approach. Surface properties can be modified by deposition conditions.

Keywords: PECVD, tetravinylsilane, thin films, AFM, wettability

1. Introduction

Plasma-polymerized organosilicones constitute a class of materials with a rich and varied scientific background [1,2]. This class of materials possesses a special characteristic, which distinguishes it from other plasma polymers – the ability to vary and control the degree of its organic/inorganic character by the appropriate choice of fabrication variables. This allows one to control many physicochemical properties over wide ranges resulting in an extraordinary potential for useful applications, which are only now beginning to be tapped. Reproducible deposition of plasma polymer films with desired physico-chemical properties is enabled by changing the deposition conditions, especially effective power, pressure, and monomer flow rate. Plasma polymer could be tailored according to the application of the film. The organosilicon plasma polymers are widely recognized for their potential not only in optical and electronic applications, but also in fiber reinforced or particulate polymer composites and nanocomposites with controlled interphase [3]. The interlayer (thin film) in fiber-reinforced composites has to contain functional groups for chemical bonding to both the materials (inorganic reinforcement and polymer matrix). In case of fiber reinforced composites, the good wettability and adhesion of reinforcement in resin matrix is necessary to enhance the load transfer from matrix to fibers. Plasma polymerized TVS films exhibited good adhesion to the glass substrate through siloxane bonding.

2. Experimental

Plasma polymer films of tetravinylsilane monomer (TVS, purity 97 %, Sigma-Aldrich) were deposited on polished silicon wafers (100, $0.8 \times 10 \times 10 \text{ mm}^3$, with impurity max. $6.9 - 8.9 \times 10^{17}$ at cm^{-3} , Terosil Co., Czech Republic) by plasma-enhanced chemical vapor deposition (PECVD). The substrates were pretreated with argon plasma (10 sccm, 5.0 Pa, 5 W, continual mode) for 10 min to improve the film adhesion. Plasma-polymerized tetravinylsilane (pp-TV) films were deposited at a mass

flow rate of 3.7 sccm and the effective power in a range of 10 – 70 W. The deposition rate was ranging from 140 to 173 nm/min as a function of the deposition conditions. Uniform plasma polymer films were deposited at a film thickness of about 1 μm . Deposition conditions (power, pressure, deposition time) are given in Table 1.

The internal setup of new deposition chamber, using plan-parallel electrodes, was derived from a typical capacitive coupling system, but our apparatus of new creative design was equipped with many non-standard components. A special construction of bottom rotary electrode (ϕ 114 mm) enabled us to stick in/out samples into/from the chamber under vacuum, and so without reactor contamination, using a magnetic drive (linear and rotary, BOC Edwards) and a special load lock mounted inside of differentially pumped side chamber. An upper electrode (ϕ 135 mm) of shower type can be positioned in a distance of 20 – 60 mm from the bottom one. A movable substrate shutter can be used to deposit film at steady-state plasma conditions. An RF-generator (Cesar 1310, 13.56 MHz, 1000 W, Dressler) was connected to the system using an automatic matching network (VM 1000A, Dressler). A turbomolecular pump (TMU 261 P, Pfeiffer Vacuum) with a dry scroll pump (TriScroll 300, Varian) as the first stage and an LN₂-cooled trap were selected to evacuate the system in order to eliminate oil vapor, minimize a rest of water in all vacuum chambers and thus acquire the basic pressure 9×10^{-6} Pa [4].

The surface morphology of samples was studied out in non-contact mode by an NTegra Prima Scanning Probe Microscope (NT-MDT). The single crystal silicon probe of typical 6nm tip curvature radius was used for this purpose. The scan area was $5 \times 5 \mu\text{m}^2$.

The ellipsometric spectra were recorded using an in situ phase modulated spectroscopic ellipsometer UVISEL (Jobin Yvon) in a spectral range of 250–830 nm (1.5–5 eV) with an increment of 3 nm and an angle of incidence of 70.3°. The dispersion dependence of the dielectric function was fitted using the five-parametric Tauc–Lorentz for-

mula, which has been derived for the parameterization of the opto-electronic response of amorphous dielectrics [5]. The deposition rate (nm/s) was evaluated as the film thickness, determined by ellipsometry, divided by the deposition time.

The sessile drop method (tangent method) employing an OCA 10 goniometer (DataPhysics) with Software SCA 20 was used to measure the equilibrium contact angles. Water and diiodomethane were used as probe liquids. Parameters of probe liquids were taken according to author Ström et al. (water) and Janczuk et al. (diiodomethane) [6]. The contact angle is obtained by measuring the angle between the tangents to the profile at the point of contact with the solid surface. The tangent method was selected because of sufficiently accurate measurements. The measurements were carried out at laboratory temperatures (23 – 25 °C), with 3.5-fold magnification of drop and circle fitting of snapped drop. The surface free energy was analyzed by Owens-Wendt geometrical mean method and Wu harmonic mean method [7].

Table 1: Deposition conditions for pp-TVS films.

P [W]	p_{dep} [Pa]	t_{dep} [s]
10	1.6	420
20	1.4	360
25	1.3	390
50	1.2	361
70	1.0	347

3. Results and discussion

The set of 5 samples of plasma polymerized TVS films were deposited on silicon wafers at different effective powers ranging from 10 – 70 W. A film thickness of about 1 μm and the deposition rate (nm/s) were measured and evaluated by ellipsometry. A dependence of the

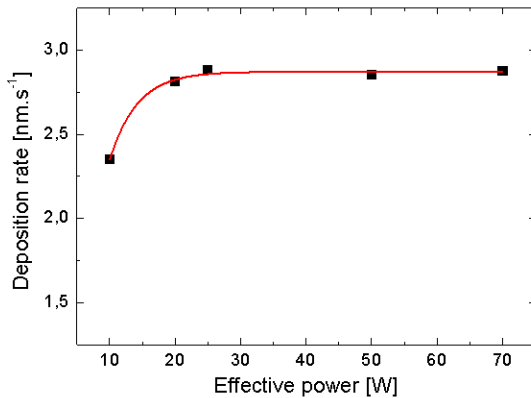
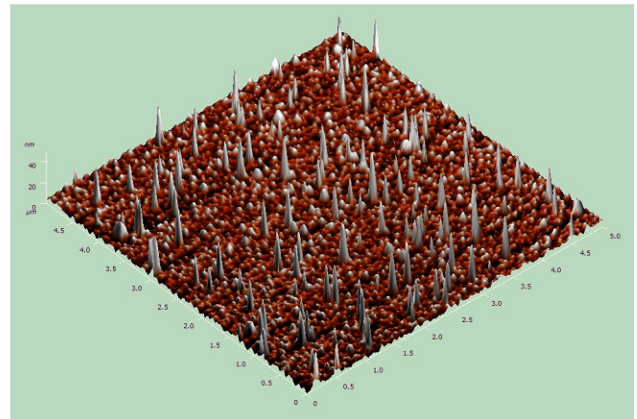


Fig. 1 Dependence of deposition rate on the effective power.

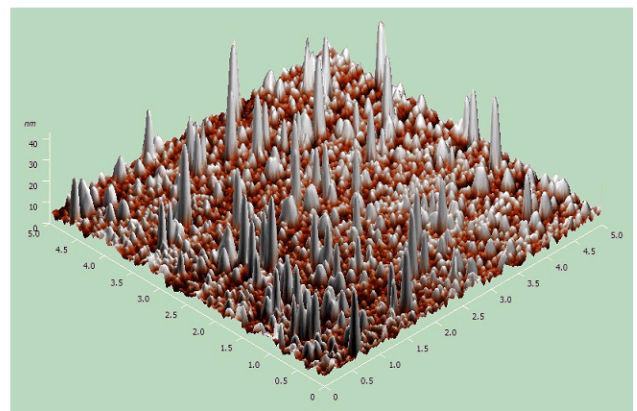
deposition rate on the effective power can be seen in Fig. 1. The deposition rate is almost constant at higher effective power (over 25 W) and saturation occurred. Also another monomers exhibited identical behavior [8]. The deposition rate was ranging from 140 to 173 nm/min as a function of the deposition conditions.

Surface morphology of deposited films was observed by atomic force microscopy (AFM). Differences in surface morphology of pp-TVS films prepared with identical thickness (about 1 μm) and different effective powers ranging from 10 to 70 W can be seen in Fig. 2(a)–(e). Small grains of dimension of tens of nanometers were found at the film surface (Fig. 2(a)) and their size increased with enhanced power to several hundreds of nanometers (Figs. 2(d) and 2(e)).

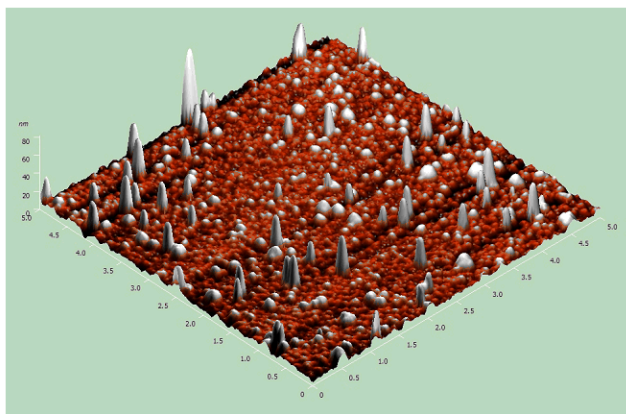
The root means square (RMS) roughness was evaluated using AFM images. A dependence of the RMS roughness on the effective power of pp-TVS layers deposited with thickness of about 1 μm can be seen in Fig. 3. Evaluated RMS roughness increased from 3.4 nm (10 W) to 22 nm (70 W) with enhanced power.



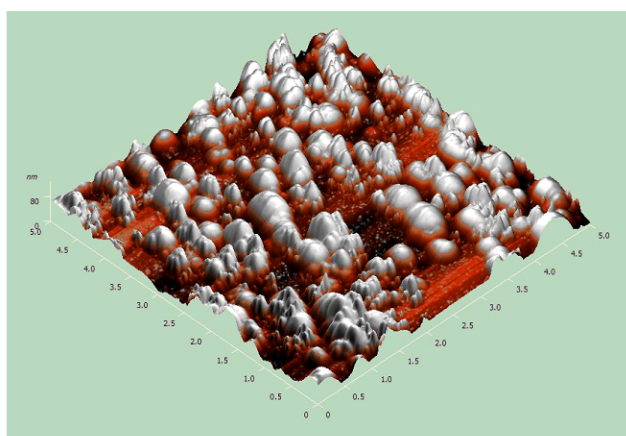
(a)



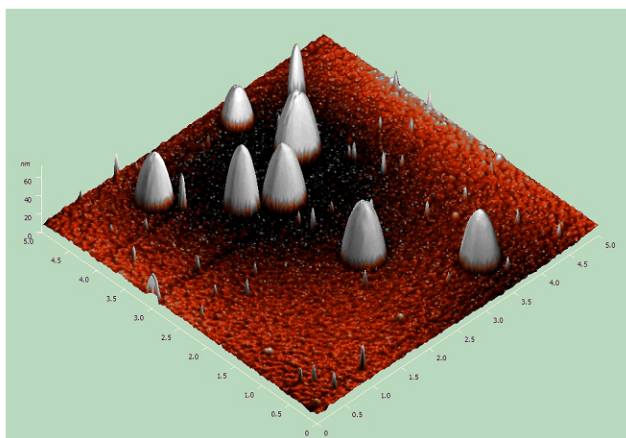
(b)



(c)



(d)



(e)

Fig. 2. Surface morphology of pp-TVS film deposited at (a) 10 W, (b) 20 W, (c) 25 W, (d) 50 W, and (e) 70 W.

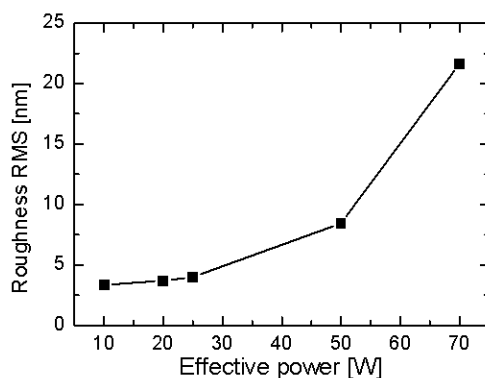


Fig. 3 Dependence of RMS roughness on the effective power for pp-TVS films.

Sessile drop measurements were employed to measure equilibrium contact angles and analyze the surface free energy of the pp-film. Measured contact angles (deg.) of probe liquids changed according to various magnitudes of the input RF power. A dependence of the contact angle of two probe liquids (water and diiodomethane) on the effective power can be seen in Fig. 4. The contact angle of water (bipolar probe liquid) slightly decreases with increasing effective power except of 70 W. Also, a decreasing trend of diiodomethane contact angles (apolar probe liquid) with the magnitude of the input RF power can be seen.

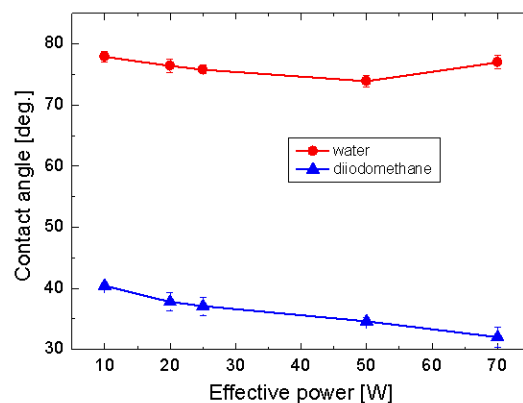


Fig. 4 Dependence of water and diiodomethane contact angles on the effective power.

The total surface free energy for set of samples, determined by Owens-Wendt geometric mean (O-W) and Wu harmonic mean (Wu) methods, depending on the effective power can be seen in Fig. 5. The total surface free energy is the sum of dispersion γ^d and polar γ^p components. Values obtained by Wu method are not exactly equal to the values obtained by O-W method due to a different γ^d and γ^p values of probe liquid diiodomethane.

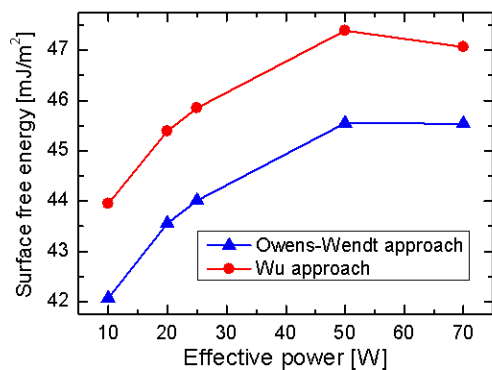


Fig. 5 Dependence of the surface free energy evaluated by Owens-Wendt and Wu approach on the magnitude of the input RF power.

The total surface free energy, according to both the methods, increased with increasing effective power. It means that pp-TVS thin films prepared at a lower effective power are less hydrophilic than films prepared at a higher effective power.

4. Conclusion

Thin films of tetravinylsilane were deposited on silicon wafers by plasma-enhanced chemical vapor deposition at different effective powers, ranging from 10 – 70 W, and uniform thickness of about 1 μm . The deposition rate could be controlled by power.

Surface morphology of pp-TVS films was analyzed by atomic force microscopy. Thin films deposited at a lower effective power have smaller roughness than thin films prepared at a higher effective power. The root means square (RMS) roughness increased from 3.4 nm (10 W) to 22 nm (70 W) with enhanced power.

Sessile drop measurements were employed to measure equilibrium contact angles and analyze the surface free energy of the pp-TVS films by Owens-Wendt geometric mean (O-W) and Wu harmonic mean (Wu) methods. The total surface free energy, according to both the methods, increased with increasing effective power. We are able to change surface morphology and wettability by modification of deposition conditions.

Acknowledgement: This work was supported in part by the Czech Ministry of Education, grants no. ME09061 and MSM0021630501, the Academy of Sciences of the Czech Republic, grant no. KAN101120701, and the Czech Science Foundation, grant no. 104/09/H080.

References

- [1] A.M. Wrobel, M.R. Wertheimer, in: R. d'Agostino (Ed.), *Plasma Deposition, Treatment, and Etching of Polymers*, Academic Press, New York, 1990, p. 163.
- [2] Y. Segui, in: R. d'Agostino, P. Favia, F. Fracassi (Eds.), *Proceedings of NATO ASI Plasma Processing of Polymers*, Acquafredda di Maratea, Kluwer Academic Publ., 1997, p. 305.
- [3] V. Cech, New progress in composite interphases: a use of plasma technologies, in: *Proceedings of FRC 2000, Newcastle upon Tyne 2000*, pp.246.
- [4] R. Prikryl, V. Cech, J. Studynka, *Czech. J. Phys.* **56** (2006) D1-6.
- [5] J. Tauc, R. Grigorovici, A. Vancu, *Phys. Stat. Solidi* **15** (1966) 627.
- [6] Operating manual Data Physics OCA. Filderstadt, DataPhysics Instrument 1998.
- [7] S. Wu, *Polymer Interface and Adhesion*. New York, Marcel Dekker, 1982.
- [8] H. Yasuda *Plasma polymerization*. Academic Press, New York, 1985, p. 432 .