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Effect of chemical modification on the mechanical properties of plasma-polymerized organosilicones

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ABSTRACT

Plasma-polymerized films of tetravinylsilane or its mixture with oxygen gas were deposited at low effective powers (0.1–10 W) using RF pulsed plasma. The Young's modulus and hardness of the plasma polymer films were characterized by conventional instrumented nanoindentation. Based on a chemical analysis of the deposited films, the chemical modification of the plasma polymer network was responsible for changing the mechanical properties. More cross-linked and stiffer plasma polymer networks resulted in increased mechanical properties of films deposited from pure tetravinylsilane. However, the oxygen atoms from the monomer mixture with oxygen gas resulted in the formation of stronger chemical species but decreased plasma polymer cross-linking that altered the mechanical properties.

1. Introduction

Mechanical properties of thin films are among the key parameters that influence their applicability in mechanical, electronic, optoelectronic, and optical devices. Plasma-enhanced chemical vapor deposition (PECVD) is a useful technology that enables the synthesis of thin films with a wide range of mechanical properties. Using hydrocarbons as precursors, the PECVD technique can be used to deposit polymer-like films with a low hardness (0.5 GPa) [1,2] or hard films (28 GPa) [3] by varying the deposition conditions. Fiber reinforced plastics (FRP) require a compatible material in the form of a thin film that is embedded between the reinforcing fiber and the polymer matrix. This interlayer may enable the shear stress between the fiber and the matrix to decrease when the polymer composite is under mechanical or thermal loading, and its mechanical properties along with interfacial adhesion are responsible for the shear strength of the composite interphase [4]. Experimental and model data suggest that the interlayer should be polymer-like and not a hard material [5]. An organic/inorganic interlayer, which is determined by the carbon to silicon (C/Si) ratio, must be used as a compatible material for glass fibers that will be used as reinforcements for FRP. The plasma-polymerized tetravinylsilane (pp-TVS) film with a controllable C/Si ratio [6] may be a suitable interlayer for glass fiber-reinforced polymer composites. The idea of using tetravinylsilane as a precursor molecule is based on the anticipated covalent bonding between the glass fiber surface and the pp-TVS film by Si—C and Si—O chemical species, and the vinyl groups at the film surface would be responsible for chemical bonding to the polyester resin used as the matrix in FRP. Our previous study indicated that the mechanical properties (i.e., Young's modulus and hardness) of the pp-TVS film can be controlled by the effective power of pulsed plasma [6].

Nanoindentation techniques are a standard tool for the characterization of the mechanical properties of thin films on the nanoscale. Conventional quasi-static nanoindentation uses simultaneous records of indenter displacement (penetration depth) and applied load. Such a load-displacement curve is analyzed based on knowledge of the tip area calibration function of the used probe, and the analysis enables the Young's modulus and hardness of the tested film to be determined [7].

In this study, polymer-like films were deposited at low effective powers from pure TVS monomers or their mixture with oxygen gas (O_2) by PECVD using pulsed plasma. The Young's modulus and hardness of the plasma polymer films were characterized using conventional instrumented nanoindentation. The addition of oxygen gas to the TVS monomer could improve the compatibility and adhesion of deposited films on silicon dioxide surfaces due to an increased number of siloxane (Si—O) species at the interface. However, an increase in oxidized chemical species (Si—O, C—O, C═O) in pp-TVS/O_2 films may significantly influence their mechanical properties. Therefore, this study aimed to investigate the mechanical properties of oxygen-free pp-TVS films versus oxygen-bound pp-TVS/O_2 films based on the oxygen fraction in the TVS/O_2 mixture.

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2. Experimental

A helical coupling plasma system was developed for thin film deposition on planar and fibrous substrates using PECVD. The plasma reactor consisted of a glass tube that was 400 mm long with an inner diameter of 40 mm. The plasma system allowed the deposition of films on planar substrates using a load lock chamber. Here, the substrate was positioned into the plasma reactor by a linear drive. The plasma energy was supplied by a radio-frequency power supply (2–50 W, 13.56 MHz) with the possibility of either a continuous wave or pulsed regime. The effective power (W_{eff}) of the pulsed plasma used in this study was controlled by changing the ratio of the time the plasma is switched on (t_{on}) to the period (T), defined as $T = t_{on} + t_{off}$. Therefore, $W_{eff} = t_{on}/T \times W_{total}$, where t_{off} is the time the plasma is switched off and $W_{total} = 50$ W. Tetravinylsilane (liquid, Si(–CH=CH$_2$)$_4$ (TVS, purity 97%, Sigma Aldrich)) was placed in the glass vessel of a thermostated bath, enabling temperature regulation in the −10 to +60 °C range, with an accuracy of 0.1 °C. The temperature for TVS was 18.0 °C to minimize the condensation of the monomer vapor in the gas distribution system. Argon gas (99.999%) was used to clean the plasma reactor and vacuum chambers. Oxygen gas (99.99%) was employed to pretreat substrates and was mixed with TVS vapors to deposit plasma polymer films with incorporated oxygen atoms. Monomer vapors, gases, and their mixtures were supplied to the plasma reactor by mass flow meters. Plasma polymer films were deposited on IR-transparent silicon wafers (100) (0.8 × 10 × 10 mm^3, ON Semiconductor). Details of the deposition system were published previously [8].

The plasma system was first evacuated to a basic pressure < 1 × 10^{-3} Pa. The silicon wafer was pretreated with oxygen plasma (5 sccm, 4 Pa, 25 W, continuous wave) for 10 min to remove contaminants and improve film adhesion. Then, the wafer was stored in a load lock, which was pumped separately, to avoid contamination, and the deposition chamber was cleaned for 10 min using argon discharge (10 sccm, 10 Pa, 25 W, continuous wave) to remove the remaining oxygen. In addition, the residual gases were checked by a process gas analyzer (HPR-30, Hiden Analytical). Using a linear driver, the pretreated wafer was placed into the plasma reactor after the deposition conditions had been set up and the plasma had reached a steady state that was characterized by constant deposition pressure. The effective power used was 0.1, 0.5, 2.5, 5.0, and 10 W at a constant $t_{on} = 1$ ms at various t_{off} (i.e., 499, 99, 19, 9, and 4 ms, respectively). A total flow rate (TVS + O_2) of 0.55 sccm was held constant, and the oxygen fraction in the TVS/O_2 mixture was set to 0.00 (pure TVS), 0.10, 0.21, 0.33, 0.46, and 0.71. The corresponding deposition pressure was 1.4 Pa. After film deposition, the plasma apparatus was flushed with argon gas (10 sccm, 10 Pa). After 30 min, the chamber was flooded with air to atmospheric pressure, and the prepared specimen was removed from the chamber into a desiccator to avoid contamination prior to the measurements.

The film thickness of all the films was approximately 1.0 µm, as determined using a phase-modulated spectroscopic ellipsometer UVISEL (HORIBA Scientific). The elemental composition of the thin films was studied by conventional and resonant Rutherford backscattering spectrometry (RBS) using a Van de Graaf generator with a linear electrostatic accelerator. The chemical structure of the plasma polymer was characterized using a NICOLET IMPACT 400 Fourier transform infrared (FTIR) spectrophotometer. The spectra were recorded in a range from 500 to 4000 cm^{-1} at a resolution of 0.96 cm^{-1}.

The nanoindentation measurements were carried out at room temperature using a TriboScope (Hysitron Inc.) attached to a Nanoscope III A (Veeco Instruments Inc.). A Berkovich diamond indenter with a radius of curvature of 150 nm was used, and accurate tip area calibration was carried out before the experiment using fused quartz. The loading, dwelling, and unloading times were maintained at 5 s for all indentations. The drift rate was ≤0.05 nm s^{-1} for all the nanoindentation measurements, which was achieved by loading at 2 µN for one minute. The nanoindentation loading causes both elastic and plastic deformation under the indenter, and unloading is dominated by recovery of the elastic deformation. The upper portion of the unloading curve can be used to calculate the mechanical properties (Young's modulus and hardness) at a given contact depth of the indenter according to the Oliver-Pharr method [9]. The unloading data were analyzed according to the following equation:

$$S = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}, \qquad (1)$$

where A is the projected contact area and S is the experimentally measured stiffness, which was determined as the slope ($S = dP/dh$, P is the applied force, h is the displacement) of the upper portion of the unloading curve. The reduced modulus, E_r, is defined by the equation

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i}, \qquad (2)$$

where E and ν are the Young's modulus and Poisson's ratio for the specimen, respectively, and E_i and ν_i are the same parameters for the Berkovich indenter (i.e., $E_i = 1141$ GPa and $\nu_i = 0.07$). The Poisson's ratio, ν, used in (2) was 0.5 for all films. The hardness is determined from the measured data using the following equation:

$$H = \frac{P_{max}}{A}, \qquad (3)$$

where P_{max} is the maximum applied force. Five indentations were made on each sample to a penetration depth of 10% of the film thickness, and the measurements were not significantly influenced by the substrate properties [10,11]. The Young's modulus and hardness were estimated by averaging the five evaluated values. Measurements were made at random locations in the central part of the sample, where the film thickness was measured by spectroscopic ellipsometry, and the indentation position changed with separation distances of at least 25 µm to avoid residual stresses in the vicinity of previous impressions.

3. Results and discussion

A typical example of the nanoindentation data for pp-TVS films deposited from the pure TVS monomer at 0.1 and 10 W is given in Fig. 1. The Young's modulus and hardness of the film may be determined from the load-displacement curves that were obtained from one complete cycle of loading, dwelling and unloading. Then, the unloading data were analyzed according to Eqs. (1)–(3) to determine the Young's modulus and hardness using the indenter parameters, where the experimentally measured stiffness, S, was determined from the slope of the upper portion of the unloading curve. The plasma polymer act approximately as an elastic material, and the plastic energy that corresponds to the area between the loading and unloading curves was relatively very low, as shown in Fig. 1. The deformation of the film material induced by the indenter in the loading portion of the measured

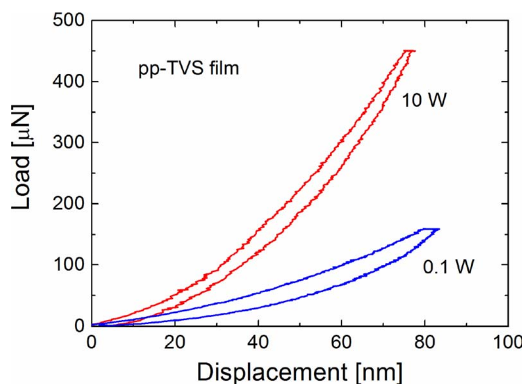

Fig. 1. Load (unload) as a function of the indenter displacement for pp-TVS films deposited from pure TVS monomer at different effective powers.

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