

Analysis of Annealed Thin Polymer Films Prepared from Dichloro(methyl)phenylsilane by Plasma Polymerization

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ABSTRACT: Thin plasma polymer films were deposited from a mixture of dichloro(methyl)phenylsilane (DCMPS) vapor and gaseous hydrogen in an rf (13.56 MHz) capacitive coupling deposition system on pieces of silicon wafers. Some of samples were annealed in a vacuum to temperatures ranging from 450 to 700°C. The chemical composition, structure, and surface morphology of the annealed samples and those stored in air at room temperature were studied by FTIR, XPS, SEM, and optical microscopy. The thermal stability and decomposition of the plasma polymer with increasing temperature were characterized using thermogravimetry together with mass spectrometry. The plasma polymer was stable to a temperature of 300°C. Above that temperature, the material started to decompose together with additional crosslinking due to the incorporation of extra oxygen atoms forming new siloxane bonds. The plasma polymer was tough at room temperature but much more brittle after annealing. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2106–2112, 2001

Key words: plasma polymerization; thin films; thermogravimetric analysis (TGA); FTIR; ESCA/XPS

INTRODUCTION

Plasma-enhanced chemical vapor deposition (PE CVD) enables us to synthesize polymer materials of very interesting electronic, optical, mechanical, and thermal properties. A wide class of plasma polymers are prepared from organosilanes.^{1,2} An activation and fragmentation of monomer molecules using low-temperature plasma (glow discharge, microwave discharge) result in the formation of thin

polymer films with properties depending on deposition conditions (power density, flow rate, pressure, substrate and its temperature, and geometry of the deposition chamber) during the competitive processes of deposition and ablation. This type of synthesis is called plasma polymerization.³ A gas (Ar, H₂, O₂, N₂, air) is mixed with the monomer vapor to modify the plasma polymer properties.

Polyphenylsilanes prepared by conventional polymerization are interesting materials for their photoelectronic properties.^{4,5} This fact results in attempts to deposit thin polymer layers by PE CVD (rf glow discharge) using phenylsilanes as monomers.^{6,7}

In our previous article,⁷ we reported on the deposition and basic characterization of thin poly-

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mer films prepared from a mixture of dichloro(methyl)phenylsilane (DCMPS) vapor and gaseous hydrogen using the rf glow discharge (13.56 MHz). The deposited polymer was a fully amorphous and transparent material exhibiting the electroluminescence phenomenon which was used to construct a single-layer light-emitting diode (LED) with blue light. The surface of the layers was nonuniformly covered by isolated grains of up to 1 μm in diameter and up to 30 nm in height or their conglomerations. The adhesion of plasma polymer films to various substrates was very good due to etching of the substrate surfaces by hydrogen ions, and it was excellent for glass and silicon substrates due to a strong siloxane bond. Films with a cross-shaped scratch were immersed in boiling water for 8 h without the coated layer peeling off from the glass and silicon substrates, probably due to the high density of the siloxane bonds. The hydrolytically stable bond between the glass and the plasma polymer can be used for glass-fiber-reinforced polymer composites as the commercial coatings (silane coupling agents) are hydrolytically unstable.⁸ Therefore, glass fibers coated by the plasma polymer were tested as well. The aim of the article was to characterize annealed plasma polymer films of DCMPS and to obtain complete information about this material and its thermal stability with respect to the possibilities of film application.

EXPERIMENTAL

Plasma Polymer Preparation

Plasma-polymerized films were prepared from a mixture of DCMPS vapor and gaseous hydrogen in an rf (13.56 MHz) capacitive coupling deposition system. Pieces ($10 \times 10 \text{ mm}^2$) of IR-transparent Si wafers (Terosil Co., Roznov, CR) and KBr crystals ($10 \times 30 \text{ mm}^2$) were used as substrates. The wafers were one-side polished and used as prepared for the deposition of films on the polished surface. First, the deposition chamber was evacuated and cleaned by argon plasma and then gaseous hydrogen and DCMPS (Sigma Aldrich, Prague, CR) vapor were introduced into the chamber at partial pressures of 43 and 12 Pa, respectively. The substrate temperature was 80°C during the whole deposition process and the power density used was approximately 1 W cm^{-2} . After deposition, the glow discharge was switched off and the introduction of the gas and the mono-

mer was stopped. The chamber was filled with argon gas to a pressure of 100 Pa and samples with layers were annealed at 160°C for 1 h to reduce the free radicals. In the end, samples were removed from the deposition system after slow cooling (5 h) and stored in a dark and dry place. Several days later, some of them were annealed in a vacuum, using a heating rate of $20^\circ\text{C min}^{-1}$, to temperatures ranging from 450 to 700°C and then they were slowly cooled. Further details about the deposition system and the deposition process were given in ref. 7.

Plasma Polymer Characterization

The thickness of polymer films was measured by a Profilometer Talystep (Taylor–Hobson) using a defined scratch in the layer as deep as the substrate. The first observation of the films was done by an optical polarizing microscope (Leitz) with a digital microphotocamera and details of the surface morphology were observed by a scanning electron microscope (JEOL JXA-840A electron-probe microanalyzer).

Infrared measurements were carried out using a Nicolet Impact 400 Fourier transform infrared (FTIR) spectrophotometer in a H_2O -purged environment. An ambient-temperature deuterated triglycine sulfate (DTGS) detector was used in the wavelength range from 400 to 4000 cm^{-1} . The Happ–Genzel apodization function was used in the whole region. The spectral resolution was 2 cm^{-1} . Approximately 300 scans were coded to achieve the signal-to-noise ratio shown. Coherent reflections in Si substrates were eliminated by decreasing the instrumental resolution to 8 cm^{-1} . An absorption subtraction technique was applied to remove the spectral features of the Si wafers. The refractive index difference at the film–substrate interface gives rise to broad, shallow interference fringes in the transmission spectra.

The composition of the elements in the surface region (top 6–8 nm) of the deposited layers was studied by X-ray-induced photoelectron spectroscopy (XPS) on an ADES 400 VG Scientific photoelectron spectrometer using $\text{MgK}\alpha$ (1253.6 eV) or $\text{AlK}\alpha$ (1486.6 eV) photon beams at the normal emission angle. Atomic concentrations were determined semiquantitatively, assuming that the model concerns a solid that is homogeneous in composition.⁹ Peak areas were corrected for an inelastic background,¹⁰ photoelectron cross sections, asymmetry parameters,¹¹ inelastic mean free paths,¹² and the measured transmission

function of the electron energy analyzer.¹³ The measurement of the concentration depth profiles was performed by sequentially applying Ar ion-beam sputtering (4000 eV ion-beam energy, 1×10^{-5} A cm⁻² ion-beam density, impact angle of 60° with respect to the surface normal) and XPS analysis.

Thermogravimetry (TG) was used to characterize the decomposition and the thermal stability of the plasma polymer. The mass change characteristics of the material were acquired from a TGA 6 Perkin–Elmer thermogravimetric analyzer using a nitrogen atmosphere (20 mL min⁻¹). Plasma-polymerized DCMPS (pp-DCMPS) was deposited on a flat surface of the KBr crystal, which was dissolved in water after the preparation of the layers, and the thin films obtained were dried at room temperature. Fragments of the film were utilized for TG measurement. Mass change characteristics were combined with those measured on a Leybold-quadrex 200 mass spectrometer to identify thermally released species from the bulk of thin films during thermal decomposition.

RESULTS

The thickness of characterized pp-DCMPS films was in the range of 1.2–1.6 μm for layers on a silicon substrate. Using optical microscopy, we did not observe any details on the surface of the prepared films (RT, stored at room temperature). However, fine flaws were revealed on the surface of the film annealed to 550°C [Fig. 1(a)]. A broken film with distinct cracks and uncovered substrate (white places) corresponds to the sample annealed to 650°C [Fig. 1(b)].

Scanning electron microscopy (SEM) enabled us to find grains of up to 1 μm in diameter and up to 30 nm in height, determined by the Profilometer, on the surface of pp-DCMPS films (RT), as was reported in ref. 7. To show a cross section of the layer (RT), the silicon substrate with the film was broken and scanning electron micrographs from the edge of the film are given in Figure 2. The film seems to have a grain structure on the cross section [see detail in Fig. 2(b)] similar to isolated grains on the flat surface (bottom part of the picture). The appearance of the fracture evidenced material toughness. There were no grains observed on the surface of annealed films (450–700°C).

Absorption IR spectra corresponding to the plasma polymer film stored at room temperature

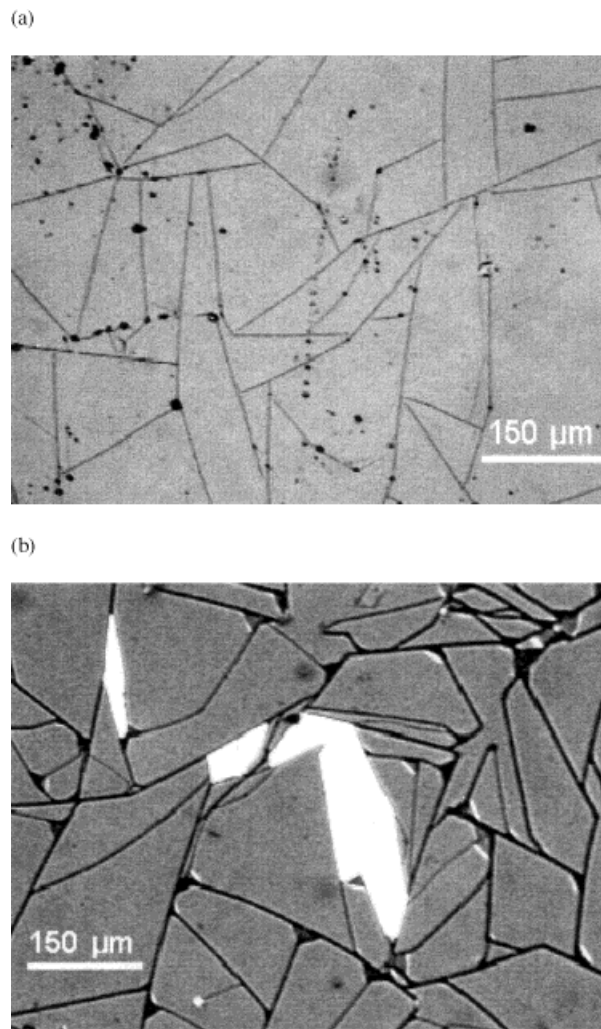


Figure 1 Broken annealed plasma polymer films observed by optical microscopy: (a) film annealed to a temperature of 550°C; (b) film annealed to a temperature of 650°C. White places correspond to uncovered substrate.

(RT) and those annealed up to temperatures of 450, 500, 550, 600, 650, and 700°C are depicted in Figure 3. In general, the shape of all the spectra is very similar, but a certain development with the annealing temperature is well apparent. The assignment of IR absorption bands was done according to ref. 14 and with respect to the results of many other articles on plasma-polymerized organosilanes and organosiloxanes.^{6,15} A broad absorption band at 3100–3700 cm⁻¹, assigned to the characteristic O–H stretching vibrations, was found in the spectrum of the RT sample and films annealed above 550°C. The band in the region of 1560–1750 cm⁻¹ corresponds to the O–H bending vibrations and a broad band at 2300–3500

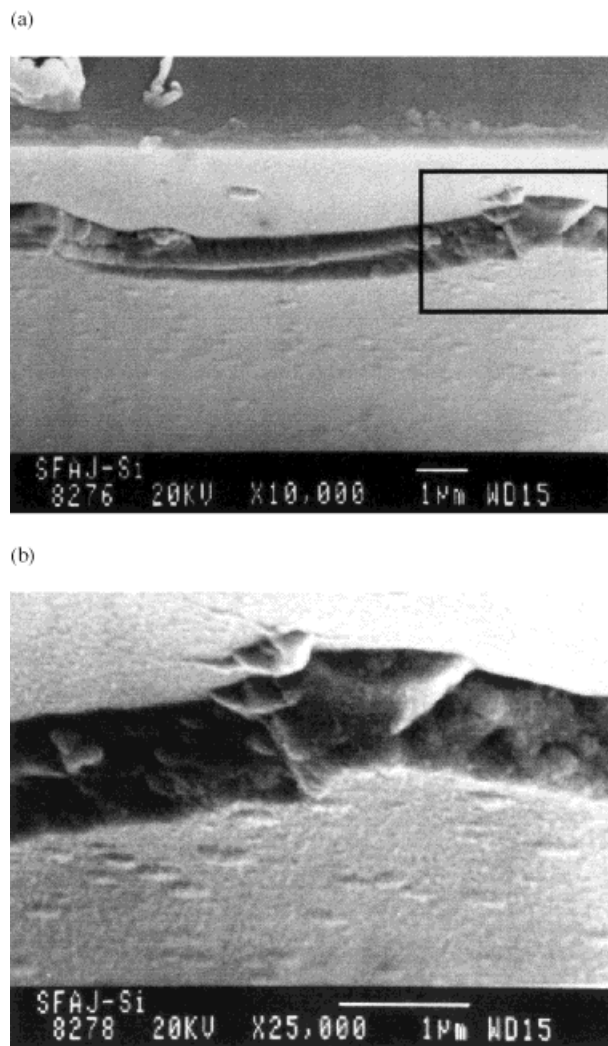


Figure 2 Scanning electron micrographs of the plasma polymer film on a silicon wafer: (a) edge of the film; (b) detail of the edge.

cm^{-1} (sample annealed up to 700°C) corresponds most probably to the formation of hydrogen bridges. The strong absorption band of Si—O—Si asymmetric stretching vibrations at $960\text{--}1100\text{ cm}^{-1}$ is characteristic of siloxanes. This band overlaps the Si—phenyl vibrations situated at $1118\text{--}1126\text{ cm}^{-1}$. The relatively strong band in the spectra of RT to 600°C at $1240\text{--}1290\text{ cm}^{-1}$ corresponds to the CH_3 symmetric bending vibrations in the Si— CH_3 group. The band evidently vanishes at elevated temperatures. The Si—O stretching frequencies in the Si—OH groups are located in the region of $850\text{--}950\text{ cm}^{-1}$. This band may coincide with out-of-plane O—H bending vibrations due to the internal rotation and association of this vibration. These bands are overlapped

by the broad Si—O—Si asymmetric stretching band for films annealed to $600\text{--}700^\circ\text{C}$. One can observe the Si— CH_3 rocking and probably some Si—C stretching vibrations in the region of $740\text{--}870\text{ cm}^{-1}$. The aging of plasma polymer films was registered in the IR spectra: For 3 days after the deposition, small changes in the bands of Si—O—Si (Si—O) stretching vibrations appeared.

The surfaces of pp-DCMPS films were analyzed employing XPS. The observed layer was about $6\text{--}8\text{ nm}$ thick. The XPS spectra were recorded for several samples (RT, 450 , 600 , 700°C) and they consist of C $1s$, Si $2p$, and O $1s$ spectra¹⁶ of simple shapes. Details on binding energies corresponding to the surface of the RT sample were given in ref. 7. Owing to the great amount of oxygen atoms found in the deposited films by IR and XPS spectra, we were interested in the depth profile of atomic concentrations. Therefore, pp-DCMPS film of the RT sample was gradually sputtered by Ar ions to determine the concentration depth profile. Atomic concentrations were determined from the XPS spectra (Experimental section) and depth profiles across the whole film with a thickness (L) of $1.4\text{ }\mu\text{m}$ are shown in Figure 4. The depth profiles of atomic concentrations corresponding to carbon, silicon, and oxygen atoms are completed by profiles of the element ratios. The interfaces of the film are designated in that figure. The ratio of carbon to silicon concentrations in a monomer molecule is expressed as $n(\text{C})/n(\text{Si}) = 7.0$. The concentration of oxygen atoms decreases slowly with the depth while the concentrations of carbon and silicon atoms are almost

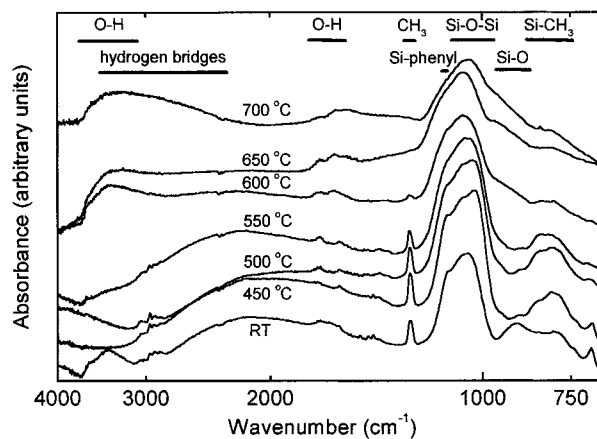


Figure 3 FTIR spectra of the plasma polymer stored at room temperature (RT) and those annealed at elevated temperatures. The assignment of absorption bands is included.

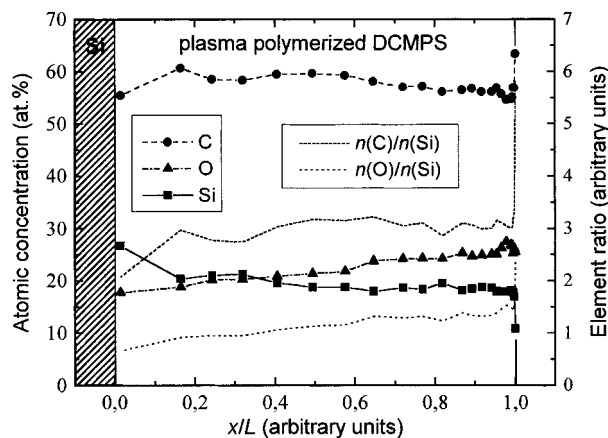


Figure 4 Depth profiles of atomic concentrations across the plasma polymer film together with element ratios. Interfaces of the film are marked out. Thickness of the deposited film was 1.4 μm .

constant in the bulk, except for interfaces. The atomic concentrations of several annealed samples are plotted as a function of the annealing temperature in Figure 5. As evident from the figure, the concentration of carbon atoms decreases whereas that of oxygen atoms increases with the temperature and $n(\text{Si})$ is approximately constant except for the value at a temperature of 700°C.

A typical thermogravimetric characteristic curve of the plasma polymer with a starting mass of 2.23 mg is shown in Figure 6 together with the mass spectrometry (MS) results, which identify released species during thermal decomposition of the material. A heating rate of 20°C min^{-1} was applied. The benzene groups and hydrogen mole-

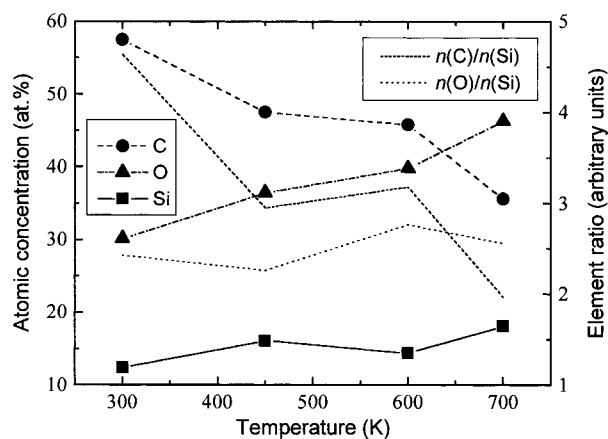


Figure 5 Atomic concentrations and element ratios as a function of annealing temperature.

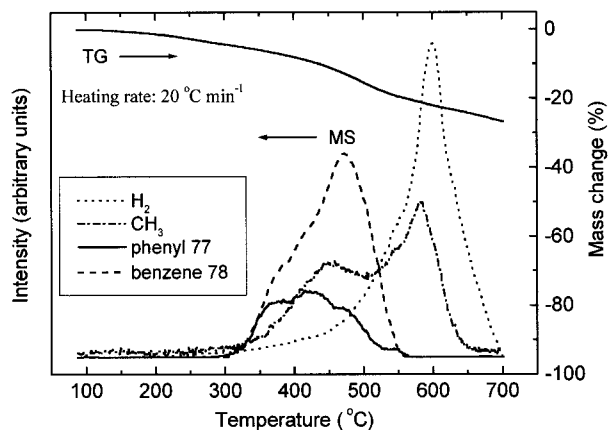


Figure 6 TG characteristics compared with the MS ones to identify released species during thermal decomposition of the plasma polymer.

cules are formed outside the film. The mass change increases with the temperature but its value is only 4% at 300°C, 27% at 700°C, and 38% at 1000°C. The highest slope of the dependence seems to correspond with the methyl groups released.

DISCUSSION

The examined plasma polymer stored at room temperature may be a tough material with respect to the fracture character depicted in Figure 2. The IR spectra (Fig. 3) revealed a great number of siloxane bonds in the film, which may be connected with a postdeposition oxidation¹⁷ as plasma polymers are known to be susceptible to oxidation after fabrication. There may be a great number of free radicals in the freshly prepared material and the free radicals initiate oxidation by reacting with in-diffusing atmospheric O_2 . Therefore, we may expect an increase of oxygen atoms at the surface of a plasma polymer film. However, the depth profile of oxygen concentrations in Figure 4 showed a great number of oxygen atoms across the whole film, meaning that the deposition chamber was contaminated with the rest of the water molecules embedded on the chamber wall, which resulted in the incorporation of oxygen atoms into the plasma polymer during deposition.

An abrupt change in the concentrations of carbon and silicon atoms at the surface (Fig. 4) can be explained as follows: There is no reason to expect great changes in the number of silicon

atoms across the film. This assumption means that the numbers of carbon and oxygen atoms at the surface are higher than are those in the bulk of the film, as it corresponds to element ratios (Fig. 4). The surface element ratios are $n(\text{C})/n(\text{Si}) = 5.8$ and $n(\text{O})/n(\text{Si}) = 2.3$, while after the first sputtering, they are $n(\text{C})/n(\text{Si}) = 3.4$ and $n(\text{O})/n(\text{Si}) = 1.5$. Therefore, there may be a layer of a thickness of 3–4 nm at the surface with different chemical composition and structure. The value $n(\text{C})/n(\text{Si}) = 5.8$ is close to a monomer ratio of 7.0 and it can be underestimated as the XPS observed layers are 6–8 nm thick. With respect to the deposition process (Experimental section), we know that monomer vapor is still in the chamber for a short time after the glow discharge is switched off. Hence, monomer molecules are not fragmented and can react with a deposited polymer, which contains many free radicals, and/or can be physisorbed on the surface, which may explain the high number of carbon atoms at the surface. The surface layer of films stored in the open air can react with atmospheric humidity–postdeposition oxidation (rest of chlorine atoms react with water molecules), which may explain the high number of oxygen atoms at the surface.

The results of thermal analysis (Fig. 6) showed that weakly bonded methyl and phenyl groups released the plasma polymer if elevated temperatures are used and this fact was confirmed by the IR spectra (Fig. 3). A reduction of carbon atoms at the surface of the annealed films is also evident from the XPS analysis (Fig. 5). The atomic concentration of silicon atoms for the sample annealed up to 700°C seems to be overestimated as the XPS analysis was influenced by the Si substrate [see white places in Fig. 1(b)] and, in fact, the ratio of $n(\text{O})/n(\text{Si})$ increases with the temperature. Thus, the reduction of carbon atoms seems to be compensated by oxygen atoms. As reported by Assink et al.,¹⁸ the heat treatment of plasma-polymerized hexamethyldisiloxane (pp-HMDSO) films in air forms additional silicon–oxygen bonds. According to their NMR study,¹⁸ the number of oxygen atoms increased with the temperature and most of the monofunctional silicones were replaced by tri- and tetrafunctional ones. By analogy with the pp-HMDSO, additional crosslinking of the plasma polymer material can be expected for the annealed pp-DCMPS. Silicon atoms with free bonds can react with the oxygen ones, increasing the crosslinking of the polymer as weakly bonded methyl and phenyl groups are released from the heated material. The Si—C

bonds are, therefore, replaced by the Si—O ones at elevated temperatures. Such a highly crosslinked material should be brittle and this mechanical property is indicated by the broken film in Figure 1.

The last question is as follows: How can the extra oxygen be incorporated into the bulk of the annealed film if heat treatment was carried out in a vacuum? Experimental and model studies realized by Klaptchenko¹⁹ with water sorption of the pp-DCMPS films suggested that the plasma polymer has a highly dispersive and microporous structure. The interaction of the material with water was very strong and the structure exhibited swelling and time relaxation as reported in ref. 19. The volume fraction of pores was about 6% in normal laboratory conditions and the value increased with the relative humidity.¹⁹ Sorbed water in our specimen was confirmed by the IR spectrum (Fig. 3) for a sample stored at room temperature. Water molecules in a porous bulk of pp-DCMPS film can, therefore, be the source of extra oxygen atoms incorporated into a highly crosslinked network of the annealed material. Atomic force microscopy (AFM) was employed to identify the pores but with no definite results.

CONCLUSIONS

Plasma-polymerized material in the form of thin films (1.2–1.6 μm) was synthesized from a mixture of DCMPS vapor and gaseous hydrogen by the rf glow discharge technique (plasma-enhanced chemical vapor deposition). The films were deposited on polished silicon wafers. After the deposition, several samples were annealed to temperatures ranging from 450 to 700°C. Analyses of the annealed samples and those stored at room temperature were done, applying optical and electron microscopy, a Profilometer, infrared and XPS, and TG with a mass spectrometer.

The films stored at room temperature had a branch and crosslinked carbosiloxane network with side methyl and phenyl groups. The material seemed to be tough and probably microporous with sorbed water. There was a thin (3–4 nm) surface layer of a composition and chemical structure similar to those of oxidized monomer (DCMPS) and different from the bulk of the film. The surface element ratios determined from the XPS spectra are $n(\text{C})/n(\text{Si}) = 5.8$ and $n(\text{O})/n(\text{Si}) = 2.3$ and the bulk ones are $n(\text{C})/n(\text{Si}) = 3.4$ and $n(\text{O})/n(\text{Si}) = 1.5$ with respect to the monomer with a

ratio of $n(\text{C})/n(\text{Si}) = 7.0$. The number of oxygen atoms slowly decreased with the film depth. The rest of the water molecules in the deposition chamber was probably the reason for the great amount of siloxane bonds in the bulk of the plasma polymer.

The plasma polymer films were thermally stable to a temperature of 300°C. Weakly bonded methyl and phenyl groups were released from the material when it was heated in the temperature range 300–700°C. This phenomenon was observed by thermal analysis, IR, and XPS spectroscopies. The increase in oxygen atoms with increasing temperature was explained as additional crosslinking of the polymer material with new siloxane bonds, where most of the monofunctional silicones were replaced by multifunctional ones. The plasma polymer starts to be much more brittle with increasing temperature.

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REFERENCES

1. Wrobel, A. M.; Wertheimer, M. R. In *Plasma Deposition, Treatment, and Etching of Polymers*; D'Agostino, R., Ed.; Academic: New York, 1990; Chapter 3.
2. Segui, Y. In *Plasma Processing of Polymers*; D'Agostino, R.; Favia, P.; Fracassi, F., Eds.; Kluwer: Dordrecht, 1997; p 305.
3. Inagaki, N. *Plasma Surface Modification and Plasma Polymerization*; Technomic: Lancaster, PA, 1996.
4. Eckhardt, A.; Herden, W.; Nespurek, S.; Schnabel, W. *Philos Mag B* 1995, 71, 239.
5. Nespurek, S. *Macromol Symp* 1996, 104, 285.
6. Nagai, H.; Nakata, Y.; Suzuki, M.; Okutani, T. *J Mater Sci* 1998, 33, 1897.
7. Cech, V.; Horvath, P.; Jancar, J.; Schauer, F.; Nespurek, S. *Chem Pap* 1999, 53, 165.
8. Plueddemann, E. P. *Silane Coupling Agents*; Plenum: New York, 1991.
9. Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Co.: Eden Prairie, MN, 1992.
10. Shirley, D. A. *Phys Rev B* 1972, 5, 4709.
11. Band, I. M.; Kharitonov, Y. I.; Trzhaskovskaya, M. B. *At Data Nucl Data Tab* 1979, 23, 443.
12. Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf Interface Anal* 1991, 17, 911.
13. Jiricek, P. *Czech J Phys* 1994, 44, 261.
14. Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic: Boston, 1991.
15. Inagaki, N.; Kondo, S.; Murakami, T. *J Appl Polym Sci* 1984, 29, 3595.
16. Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers*; Wiley: Chichester, 1992.
17. Gengenbach, T. R.; Griesser, H. J. *J Polym Sci Part A Polym Chem* 1998, 36, 985.
18. Assink, R. A.; Hays, A. K.; Bild, R. W.; Hawkins, B. L. *J Vac Sci Technol A* 1985, 3, 2629.
19. Klaptchenko, V. I., unpublished results.