Characterization of Poly(Methylphenylsilane) Prepared by Plasma Polymerization

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SUMMARY: Poly(methylphenylsilane) plasma polymer layers of the thickness ranging from 10^{-2} to 10^{0} μm intended to engineer interphases in glass fibre reinforced polymer composites and light-emitting displays were prepared by r.f. glow discharge technique. The films synthesized from a mixture of dichloro(methyl)phenylsilane vapor and gaseous hydrogen were deposited on flat glass and silicon substrates and glass fibres as well. Deposition conditions were optimized to obtain required thickness, mechanical and electrical properties of interphases. Prepared layers were amorphous, relatively rigid and transparent at room temperature with excellent adhesion to substrates. The surface of plasma polymer is rough with isolated (silicon substrate) and conglomerate (glass substrate) grains. FTIR and XPS spectra revealed a great amount of atomic oxygen bound to silicon atoms and enabled to determine the atomic concentrations. The structure model is proposed assuming a carbosiloxane network with not-crosslinked methyl and phenyl groups.

Introduction

Polysilanes prepared by plasma polymerization in the form of thin layers are intended to create interphases with controlled properties in glass-fibre reinforced polymer composites and light-emitting electronic devices.

The plasma polymerization[1)] is a process where the activation of organic vapours and gases in a low-temperature plasma (glow discharge) leads to the formation of polymeric materials. In the chemical sense, plasma polymerization is different from conventional polymerization reactions. Monomer and gas molecules are fragmented and ionized in plasma producing excited species, free radicals and ions. Adsorbed activated fragments recombine forming the plasma polymer. This type of synthesis has an atomic character in contrast to conventional radical and condensation polymerizations. In many cases, plasma polymers show distinguished chemical composition, structure, and chemical and physical properties from those formed by conventional polymerizations using the same monomer.

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Polysilanes prepared by chemical syntheses are known for their unique electronic and optical properties, utilized in electronic and optoelectronic devices, originating from the delocalization of σ–σ^* conjugated electrons along the Si–Si backbone. Thin polysilane films are prepared by the spin coating technique from a dilute polymer solution in a volatile solvent.

The polysilane films prepared by plasma polymerization exhibit, in addition to interesting electronic and optical properties, *excellent mechanical properties* in contrast to those prepared by the spin coating technique. Moreover, plasma polymer films can be prepared even if the monomer does not have functional groups to participate in common polymerization reactions.

Conventional polysilanes were studied in detail for many years, however, only partial information about structure and properties of polysilanes prepared by the glow discharge polymerization technique was published[2,3]. Therefore, the aim of this paper is a basic but wide-range characterization of thin plasma polymer films prepared from a mixture of dichloro(methyl)phenylsilane (DCMPS) vapour and gaseous hydrogen. Chemical composition, structure, surface morphology and some mechanical, thermal, optical, and electronic properties of plasma-polymerized dichloro(methyl)phenylsilane (pp-DCMPS) were investigated. Some characteristics were compared with those of poly(methylphenylsilane) (PMPS) films prepared by spin coating of a conventionally polymerized material.

Experimental

Preparation of Plasma Polymer Films

Thin films were deposited on cleaned microscope cover glasses ($(12 \times 12 \times 0.2)$ mm^3), pieces of IR-transparent Si wafer, glass fibres (E-glass) and on pieces ((20×50) mm^2) of PP foil in a dual capacitive coupling system (13.56 MHz) for plasma polymerization (Fig. 1). However, only one part of the dual system was used for preparation of our samples. The electrode spacing was 2.5 cm, an area of the rectangle electrode was 103 cm^2 and substrates were placed on the grounded electrode. Prior to the deposition, the chamber was evacuated (two rotary oil vacuum pumps, one Roots rotary pump) to 0.1 – 0.5 Pa. First, argon gas was introduced into the chamber until the pressure reached 10 Pa and Ar-plasma was maintained for half an hour to eliminate water and contamination on the substrate and the wall of the chamber. Then, the reactor was evacuated

to 0.5 Pa and gaseous hydrogen was introduced into the chamber until the pressure 43 Pa with the glow discharge was reached. At last, the monomer (DCMPS, Aldrich Chemical Co.) vapour was introduced into the reactor by the needle valve until the total pressure reached 55 Pa. The polymer films were deposited at a power density of 1 W cm^{-2} and the substrate temperature was maintained at 80 °C. These deposition conditions were found to be optimal for the best adhesion of thin films to various substrates. Deposited films were subjected to the post deposition annealing at 160 °C for 1 h in the reactor with argon gas at a pressure of 100 Pa. pp-DCMPS films of the thickness ranging from 10^{-2} to 10^{0} μm were prepared under the above conditions and the mean deposition rate was about 0.3 nm s^{-1}.

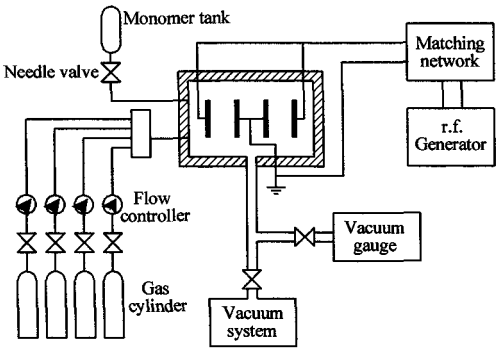


Fig. 1: Schematic illustration of the dual capacitive coupling system for plasma polymerization.

Preparation of Spin Coated Films

PMPS was prepared by Wurtz coupling polymerization[4]. Before the deposition, the polymer was three times purified by precipitation in methanol and toluene solution and centrifuged. Thin films of PMPS (100 nm – 2 μm) were prepared from a toluene solution by the spin coating technique on cleaned flat glasses ((10 × 10 × 0.7) mm^3, 1737 F, Corning Co.) and pieces of IR-transparent Si wafer. After the deposition the films were dried at a pressure of 10^{-3} Pa and a temperature of 57 °C for at least 4 h.

Preparation of Single-Layer LEDs

A usual sandwich structure was used (Fig. 2) to construct the single-layer light-emitting diodes (LEDs). The structure on a glass substrate consists of thin polymer film (pp-DCMPS or PMPS) together with an evaporated Au bottom contact as a hole

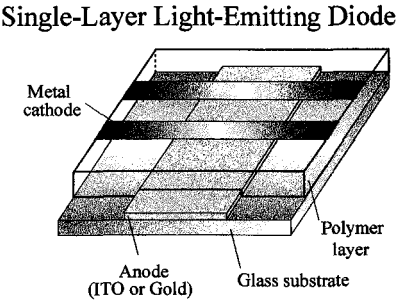


Fig. 2: Structure of a single-layer LED prepared from plasma polymer.

injector and an evaporated Al top contact as an electron injector for the case of pp-DCMPS film or an indium-tin-oxide (ITO) bottom contact for the case of PMPS film.

Characterization of Thin Films

Infrared measurements were carried out using a Nicolet Impact 400 Fourier transform infrared (FTIR) spectrophotometer in an H_2O-purged environment. Transmission spectra were obtained on films deposited on one-side polished crystalline silicon wafers. An absorption subtraction technique was applied to remove the spectral features of Si wafers. The Baseline Horizontal Attenuated Total Reflection (HATR) accessory with ZnSe or Ge crystal was used for measurements of infrared spectra of pp-DCMPS film on PP substrate and of the monomer.

The XPS (X-ray Photoelectron Spectroscopy) spectra were measured at room temperature on an ADES 400 VG Scientific photoelectron spectrometer employing Mg K_α (1253.6 eV) and Al K_α (1486.6 eV) radiations at 0° take-off angles with respect to the surface normal. The binding energy scale was calibrated by measuring the Au $4f_{7/2}$ core level (83.8 eV). All spectra were charge corrected with respect to the lowest binding energy component of the Au 4f line (evaporated dots of Au). Atomic concentrations were determined semi-quantitatively assuming a homogeneous model, accounting for photoelectron cross sections asymmetry parameters and the inelastic mean free paths. An exposure of polymer materials to X-ray irradiation results in their degradation. Specimens were exposed to X-radiation at the longest for 30 min. and therefore, an induced degradation amounted to less than 4%[5].

The surface morphology and the thickness of the polymer films were measured by a Profilometer Talystep (Taylor–Hobson) and observed by a scanning electron microscope (Jeol JXA-840A electron probe microanalyzer).

The X-ray diffraction measurements were performed using a Diffractometer D500 (Siemens) for an angle ranging from 5° to 80°. Total exposure time was 30 min.

An indication of the adhesive characteristics of the plasma polymer films can be obtained by the following simple test[6]. A cross-shaped scratch is made on the plasma polymer layer by a razor blade according to the procedure of the Adhesive Tape Test (American Society for Testing and

Materials). Then the sample is immersed in boiling water and periodically examined to see if the film starts to peel off from the substrate. If the boiling time exceeds 8 h, the adhesion is generally considered to be excellent.

Except this simple test, the scratch tester (developed by the Technical Academy of Brno) was employed to characterize the adhesion of films on substrates. The Rockwell ball is driven over the film surface to produce a scratch in this film. The load on the ball is linearly increased and the value of the load, at which adhesion failure is detected, is known as the critical load between the film and the substrate.

Determining the Young's modulus, E, is a key to evaluate the mechanical properties of plasma polymers and the ability of pp-DCMPS interphase to transfer load. This parameter can be obtained from a tensile test evaluating the elastic range of stress-strain relation. It is very difficult to isolate the plasma polymer film. However, a two-layer composite of the plasma polymer and a thin substrate can be used for this purpose[2]. A specimen was composed of thin PP foil, which modulus, E_{PP}, and thickness, t_{PP}, were known, and the plasma polymer film of known thickness, t_{film} , and modulus, E_{film}. The Young's modulus of plasma polymer film can be easily determined from the modulus, E_{comp}, of the composite film (if $E_{comp} > E_{PP}$) using the relation

$$E_{film} = E_{PP} + (E_{comp} - E_{PP})/V_{film}$$

where V_{film} is the volume fraction of the film in the composite

$$V_{film} = t_{film}/(t_{film} + t_{PP})$$

Optical properties of polymer films deposited on silicon substrates were characterized by the ellipsometric method. The measurements were performed in the λ-spectral range 240–830 nm and the angles of incidence were varied from 55° to 70° by the step of 5°. A UVISEL Jobin–Yvon phase modulated ellipsometer was employed in the reflection configuration.

Thermal Desorption Analysis (TDA) technique enables to investigate the chemical composition and the structure of thin polymer films and their thermal stability. The method is based on the mass spectroscopy of thermally released species from bulk of thin film during the thermal decomposition. The apparatus consists of the vacuum chamber (10^{-5} Pa) equipped with the mass spectrometer Leybold-quadrex 200 and the desorption chamber separated by a valve.

Results and discussion

Plasma polymer films of the thickness from 80 nm to 7 μm were prepared using the above deposition conditions. The mean deposition rate of 0.3 nm s^{-1} was determined from the thickness measurement and the corresponding deposition time.

The typical absorption IR spectrum of pp-DCMPS is compared with those of the spin coated PMPS and the monomer (DCMPS) in Fig. 3. Significant absorption bands are denoted by figures A–H and the assignments of the bands are listed in Table 1. The absorption due to the hydroxyl group is evident for the plasma polymer in three bands (A, C, G). All the spectra show absorption peaks corresponding to C–H vibrations in aromatic ring and CH_2, CH_3 as well (band B). Well evident peaks in the spectrum of the monomer and the spin coated PMPS are assigned to C–C vibrations in aromatic ring and Si–C_{arom} stretching (band D). The absorption band E corresponds to the deformation of Si–CH_3 bonds. The absorption peak of Si–C_{arom} is well distinguished in all the spectra but the peak of Si–O–Si bonds and probably of Si–CH_2–Si bonds[7] is even more higher (band F). The first peak in the band H corresponds to vibrations of Si–O group and reveals a contamination of the monomer by oxygen. Almost the same IR spectrum for the plasma polymer on PP substrate was obtained by the HATR technique.

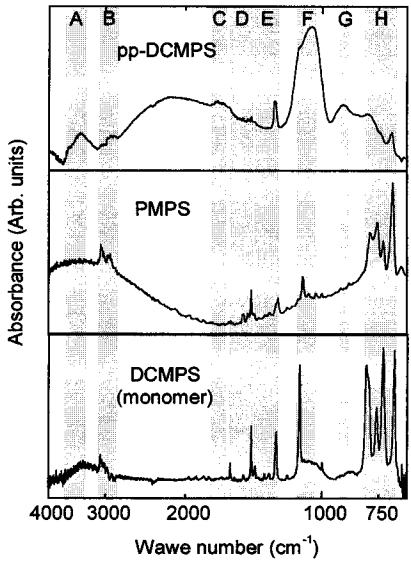


Fig. 3: FTIR spectra of the plasma polymer (pp-DCMPS) and the spin coated PMPS measured in transmission mode, and of the monomer (DCMPS) measured by HATR with Ge crystal.

Atomic concentrations in pp-DCMPS and PMPS films determined from XPS spectra are shown in Table 2. A use of Mg K_α radiation gives results more surface-sensitive. However, the measurements do not indicate a depth inhomogeneity. The mean element ratios are n(C)/n(Si) =

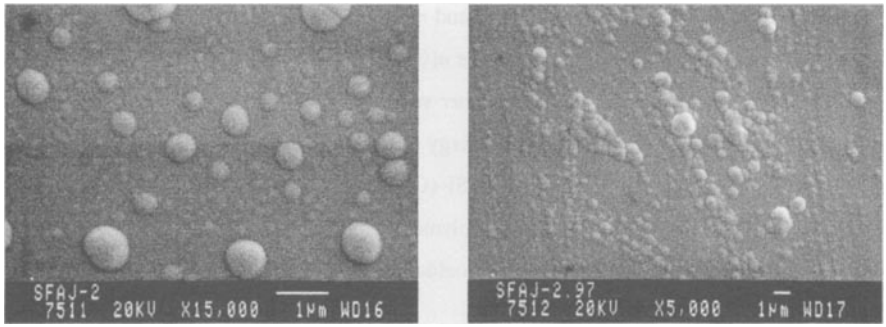
4.8 and $n(O)/n(Si)$ = 1.9 in pp-DCMPS films and $n(C)/n(Si)$ = 4.7 and $n(O)/n(Si)$ = 0.8 in spin coated PMPS films in contrast to the monomer $n(C)/n(Si)$ = 7. Binding energies of Si 2*p*, C 1*s*, and O 1*s* corresponding to the plasma polymer were 101.8–102.0 eV, 283.9–284.0 eV, and 531.8–531.9 eV, respectively. The binding energy of Si 2*p* was assigned to O–Si–O bonds and that of C 1*s* may be assigned to Si–CH_3 and/or Si–(C_6H_5) and/or Si–CH_2–Si bonds. It is assumed the great amount of oxygen in the plasma polymer originates from the oxygen-contaminated monomer (see IR spectrum) and subsequent postdeposition oxidation[5].

Table 1. Assignments of IR Absorption Bands.

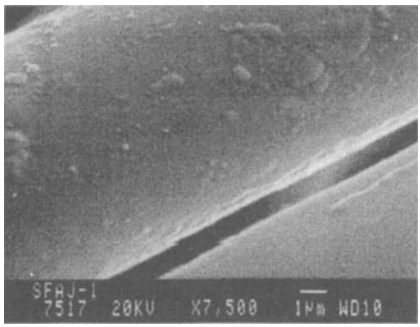
Band	Assignment	ν / cm^{-1}
A	O–H stretching	3400–3620
B	C–H stretching in ph C–H stretching in CH_2, CH_3	3049–3074 2856–2998
C	O–H stretching	1644–1704
D	C–C vibrations in ph Si–C_{arom} stretching in Si–ph	1487–1591 1427–1432
E	$\delta(CH_3)$ in Si–$\delta(CH_3)$	1261–1404
F	Si–C_{arom} stretching in Si–ph Si–O stretching in Si–O–Si CH_2 wagging in Si–CH_2–Si	1099–1126 1050–1056 1020–1070
G	O–H stretching	893–897
H	Si–O stretching C–C vibrations in ph	795–798 692–735

Table 2. Atomic concentrations determined from XPS Spectra

Polymer	Radiation	Atomic mole fraction / %			
		C	O	Si	C
pp-DCMPS	Mg K_α	60.4	25.7	12.9	0.9
pp-DCMPS	Al K_α	63.1	23.4	12.8	0.6
PMPS	Mg K_α	72.8	11.8	15.4	-



(a) (b)



(c)

Fig. 4: Scanning electron micrographs of pp-DCMPS films on (a) silicon wafer, (b) microscope cover glass, (c) glass fibers.

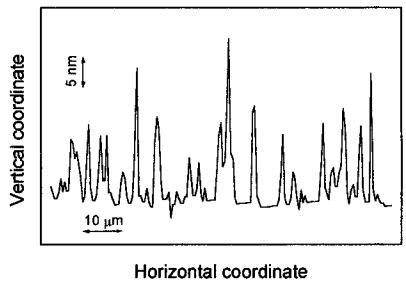


Fig. 5: Surface profile of the plasma polymer on silicon wafer.

Surface morphology of pp-DCMPS films on various substrates is depicted in Fig. 4. Scanning electron micrograph in Fig. 4a shows a rough surface of the film on a polished Si substrate. Grains of different size up to 1 μm are randomly dispersed across the surface and some grains can stick together. A height of the grains reaches up to 30 nm as it follows from measurements of surface profiles by the Talystep technique (Fig. 5). Areas of such a high roughness are alternated by areas with a low roughness (4 nm). Similar grain structure was observed at SEM micrographs obtained from the edge of a film on broken substrate that is an indication of a material toughness. The grain structure observed at plasma polymer surfaces[7-9] is apparently connected with the plasma polymerization mechanism. There are conglomerations of grains of different sizes on the whole surface of a film deposited on microscope cover glass (Fig. 4b). Scratches on the glass surface as nucleation centres are probably the cause of grains coordinated in straight lines. Similar conglomerations of grains can be seen on the surface of a glass fibre coated with pp-DCMPS

(Fig. 4c). The spin coating technique enables to prepare homogeneous PMPS films of a thickness ranging from 100 nm to 1 μm with a smooth surface. A low roughness of 1 nm was determined using the X-ray reflectivity.

pp-DCMPS is an amorphous material with a correlation length of 0.34 nm as follows from the X-ray diffraction measurements.

pp-DCMPS films exhibit excellent adhesion not only to glass substrates and silicon wafers, but even to metal substrates and organic materials (PE, PP, PC, Teflon). The simple adhesion test using the plasma polymer film with a cross-shaped scratch immersed in boiling water was carried out for the silicon substrate and no peeling of the coated layer was observed after 8 h indicating a remarkable adhesion. The deposition conditions were optimized to enhance the adhesion characterized by the scratch tester up to a normal loading of 18 N. It is assumed the adhesion of plasma polymer films to substrates results from siloxane bonds. An adhesion of the spin-coated PMPS to the same substrate is poor with a normal loading < 1 N outside the measuring range of the tester.

Composites consisting of the plasma polymer layer (t_{film} = 4.1 μm) and the PP foil (t_{PP} = 100 μm) were used to determine the Young's modulus of plasma polymer at room temperature, E_{film} = (6.0 ± 0.5) GPa. This value is higher than those of bulk conventional polymers (up to 3 GPa) and of the plasma polymer prepared from tetramethylsilane (TMS) (3 GPa[2]).

Results of ellipsometric measurements confirmed optical homogeneity of the pp-DCMPS films. The film refractive index can be expressed by the three parametric Cauchy formula used to fit ellipsometric data. The refractive index as a function of the wavelength for the plasma polymer and the spin-coated PMPS thin films is depicted in Fig. 6.

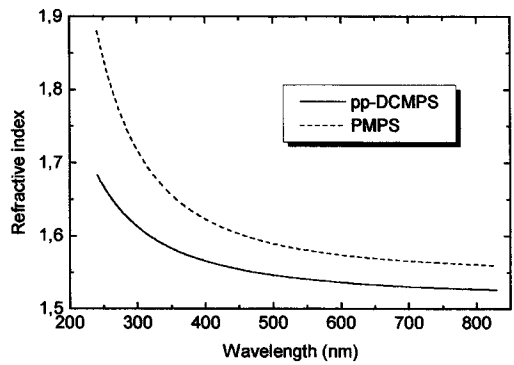


Fig. 6: The decay of the refractive index with the wavelength for the plasma polymer and the spin coated PMPS.

Heating a specimen the plasma-deposited film is partially decomposed and molecular fragments can be detected by the thermal desorption analysis (Fig. 7). Methyl and phenyl groups start to release the plasma polymer at 320 °C. The benzene group is formed from the phenyl one outside the film. The phenyl group releases pp-DCMPS up to a temperature of 550 °C and the methyl group up to 650° C. Hydrogen molecules are formed outside the film and hydrogen atoms originate partially from the plasma polymer film and partially from water molecules present in the apparatus and decomposed by the mass spectrometer ionizator. Spin-coated PMPS films cannot be examined by thermal desorption as the molecules of polymer leave the film on the whole or in the form of large polymer fragments. Relative molecular mass of such molecules or oligomers lies out of the range of the mass spectrometer (1–200 amu).

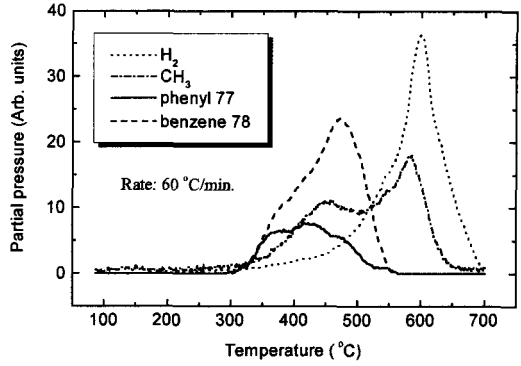


Fig. 7: Thermal desorption analysis of the plasma polymer.

The structural as well as the composition changes of these heat-treated plasma polymer films must be accompanied by some changes in their luminescence spectra. This effect is demonstrated in Fig. 8. The pp-DCMPS films were heated in vacuum to various temperatures and then the photoluminescence spectra were measured. A very distinct shift to smaller energies in both the excitation and the emission spectrum was found.

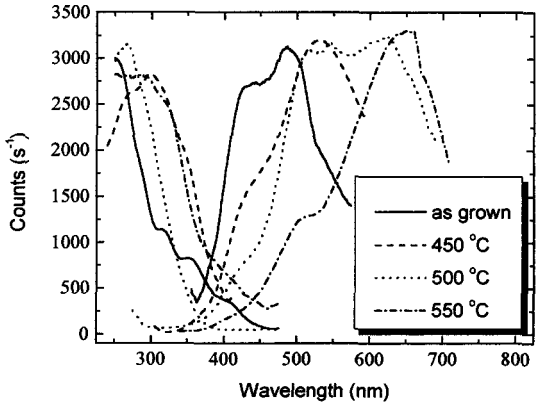


Fig. 8: Excitation (λ=480 nm) and emission (λ=300 nm) luminescence spectra of annealed specimens with pp-DCMPS films.

The electrical and electroluminescence (EL) properties of plasma polymer and spin-coated PMPS films in a form of the single-layer LED were investigated. The LEDs constructed from both the materials exhibit similar EL intensity characteristics and also the current-voltage characteristics are comparable. The blue-light intensity of LED increases with the applied voltage and the optimum bias is from 3 to 4 V. The charge carrier transport in PMPS is assumed to proceed predominantly along the σ-delocalized Si backbone while the transport in the plasma polymer is not understood.

The structure model of pp-DCMPS (Fig. 9) was suggested on the basis of results from FTIR and XPS measurements, adhesion and rigidity tests, and TDA. The model assumes the plasma polymer is highly branched and highly crosslinked forming a random carbosiloxane network with not-crosslinked methyl and phenyl groups.

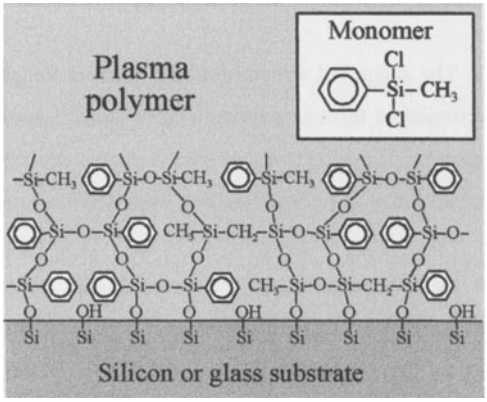


Fig. 9: **The structure model of pp-DCMPS film.**

Conclusion

Thin plasma polymer films were prepared by the r.f. glow discharge technique from a mixture of dichloro(methyl)phenylsilane (DCMPS) vapour and gaseous hydrogen. The pp-DCMPS layers deposited on glass and silicon substrates were characterized by many techniques suitable to investigate their mechanical, thermal, optical, and electrical properties.

1. The plasma polymer film was amorphous and relatively rigid material (E_{film} = 6 GPa) at room temperature in contrast to bulk conventional polymers and the plasma polymer prepared from TMS. This material was transparent in the visible region with the refractive-index value (1.52–1.55) similar to a glass. Layers exhibit an excellent adhesion to silicon and glass substrates probably due to siloxane bonds. Films had a rough surface with isolated grains (silicon wafer) of a diameter up to 1 μm and a height up to 30 nm or their conglomerations (glass substrate).

2. The IR spectra revealed a great quantity of oxygen atoms in deposited layers. The spectra show peaks assignable to methyl (1261–1275 cm^{-1}) and phenyl (1427–1432, 1123–1130 cm^{-1}) groups bound to the silicon atom, and Si–O–Si (1050–1056 cm^{-1}) (Si–O (795–798 cm^{-1})) and probably Si–CH_2–Si groups (1020–1070 cm^{-1}). These results are confirmed and quantified by those from XPS spectra. The element ratios are $n(C)/n(Si) = 4.8$ and $n(O)/n(Si) = 1.9$ for pp-DCMPS films. A high contents of oxygen originates from the contaminated monomer and the postdeposition oxidation.

3. The suggested structure model assumes the plasma polymer is highly branched and highly crosslinked forming a random carbosiloxane network with not-crosslinked methyl and phenyl groups. These methyl and phenyl groups are released from the plasma polymer film at heat treatment of a specimen starting from a temperature of 320 °C.

4. A decomposition of the material with increasing temperature results in a shift of the luminescence spectra to smaller energies, from blue (untreated material) to yellow light (550 °C) for the case of emission spectra. pp-DCMPS can be used to construct a single-layer LED with the blue light.

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