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Poly(tetraflouro-p-xylylene), a low dielectric constant chemical vapor polymerized polymer

Jay J. Senkevich and Seshu B. Desu[a)]
Virginia Tech, Department of Materials Science and Engineering, 213 Holden Hall, Blacksburg, Virginia 24061-0237

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A low dielectric constant polymer, poly(tetrafluoro-p-xylylene) (VT-4) was synthesized by a chemical vapor polymerization process using 4,5,7,8,12,13,15,16-octafluoro-[2.2]-paracyclophane as a precursor. The VT-4 polymer has a dielectric constant of 2.42 and a dielectric loss of 0.008 at 1 MHz, perpendicular to the plane of the film. Thermal stability of VT-4 satisfied the SEMATECH criteria, exhibiting an onset of degradation at 460 °C, and 1% weight loss at 480 °C in an argon environment. The x-ray diffraction data suggest a disordered semicrystalline polymer as-deposited (at ~12 °C). The crystalline phase became more ordered due to a decrease in the *d* spacing from 4.850 to 4.594 Å and an increase in the percent crystallinity from 39% as-deposited to 66% after successive postdeposition anneals to 300 °C. Optical measurements showed a highly anisotropic thin film with n_e @630 nm=1.601 and n_0 @630 nm=1.471, progressively becoming more negatively birefringent after postdeposition anneals, reaching a plateau at ~250 °C, due to the polymer chain becoming more conformationally ordered. © *1998 American Institute of Physics.* [S0003-6951(98)02402-4]

Decreasing the dielectric constant ($\epsilon_r<3$) while still keeping a high thermal stability (>425 °C) are the two most important properties of the intermetallic dielectric as outlined by SEMATECH to solve the problem of RC delay for ultralarge scale integration (ULSI) technology.[1] To satisfy the material as well as the processing needs, chemical vapor deposited polymers (e.g., parylenes) have been intensely investigated.[2–8] Among the parylenes, $\alpha,\alpha,\alpha',\alpha'$ poly(tetrafluoro-p-xylylene) (AF-4) has the best properties.[9–13] However, currently the precursors for AF-4 are expensive and are not readily available. Therefore, a need exists to find new low dielectric constant materials whose precursors are inexpensive and readily available which produce a material satisfying the SEMATECH criteria for an intermetallic dielectric. Out of this need poly(tetrafluoro-p-xylylene) (VT-4) has been synthesized from the 4,5,7,8,12,13,15,16-octafluoro-[2.2]-paracyclophane (DVT-4) precursor.

The VT-4 thin film polymers were synthesized using a custom built modified CVD reactor with separate sublimation, pyrolysis, and near-room temperature deposition chambers. DVT-4 was sublimed at 114–115 °C and the pyrolysis chamber was heated to 650 °C converting the cyclophane precursor into the monomer diradical reactive intermediate, which was transported and subsequently deposited at ~12 °C. The substrates used for depositing the VT-4 films were (111) silicon for optical and XRD characterization, and platinum substrates for electrical characterization. Thermal analysis was accomplished using polycrystalline sintered NaCl substrates, which were subsequently placed in a water bath where the film was floated and dried. This method works well with the parylene polymers due to their low permeability to water.

Thermal degradation studies of VT-4 were accomplished using a Perkin-Elmer thermogravimetric analyzer (TGA) in an inert argon environment at 10 °C/min. The glass transition temperature (T_g) of the VT-4 polymer was obtained by using a Perkin-Elmer DSC-7 differential scanning calorimeter. The samples were heated to above T_m and then rapidly cooled to prevent crystallization and hence increase the amorphous phase fraction. The samples were then reheated at 5 °C/min to determine the T_g. X-ray diffraction data were obtained using a Scintag XDS-2000 x-ray diffractometer at a scan rate of 2° 2θ/min. The thickness and optical characterization was carried out by using a variable angle spectroscopic ellipsometer (VASE) from the J. A. Woollam Company. The wavelength of light used was 400–1000 nm and three angles normal to the sample were 60°, 65°, and 70°.

Since VT-4 is a new material, it was analyzed qualitatively by Fourier transform infrared (FTIR) spectroscopy to ensure the desired polymer was synthesized. The two peaks present in the FTIR spectra at 2949 and 2875 cm^{-1} are due to C–H stretching from the aliphatic -CH_2- groups. The presence of fluorine atoms on the aromatic ring pulls electrons away from the benzene ring weakening the C–C bond. The rather large peak at 1487 cm^{-1} is attributed to this aromatic C–C stretch and is shifted from 1507 cm^{-1} for poly(p-xylylene) (PPXN).[14] The small somewhat obscured peak at 1460 cm^{-1} is attributed to bending of the methylene group -CH2- and is shifted slightly to higher wave numbers as compared to PPXN due to the presence of fluorine atoms on the benzene ring.[14] The major peaks at lower wave numbers 1301 and 1174 cm^{-1} are attributed to the aromatic C–F stretch. Compared to AF-4, which has aliphatic C–F bonds (1262 and 1146 cm^{-1}), VT-4's C–F bond frequencies are shifted to higher wave numbers accounting for their higher strength.[13] Finally, the aliphatic C–C stretch at 938 cm^{-1} is close to what is seen in AF-4 when strong electron withdrawing groups are present.[13]

The thermal stability of VT-4 is shown in Fig. 1. The

[a)] Electronic mail: sdesu@vt.edu

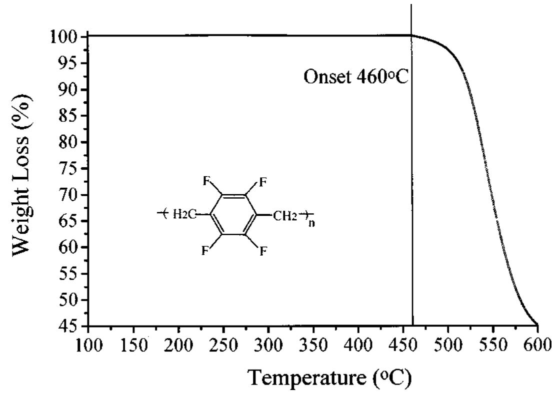

FIG. 1. Thermal stability of VT-4 in Ar measured at a rate of 10 °C/min.

onset of degradation occurs at 460 °C and 1% weight loss occurs at 480 °C. Thereafter rapid degradation occurred. This result is encouraging for the future development of VT-4 since thermal stability is a prime concern as a result of the currently used back-end-of-line processing temperature. However, thermal stability as tested by TGA is less demanding than isothermal anneals, which more resemble a real processing environment.

As a result of the high symmetry of VT-4, it would be expected to crystallize much like PPXN; however, VT-4 does not exhibit any irreversible crystal transformations and its glass transition temperature is above room temperature. PPXN exhibits a α–β irreversible transition at 220 °C. PPXN has a T_g of 13 °C,[15] and the measured T_g of VT-4 was 63.9 °C at the inflection point with a range of 59.7–66.3 °C and $\Delta C_p = 5\times10$ J/mol °C. Below T_g depositions of poly(chloro-p-xylylene) (PPXC) at low precursor sublimation rates, most often produce an amorphous polymer due to low chain mobility, but VT-4 possesses high symmetry therefore crystallization below its T_g is more probable, much like PPXN. Figure 2 shows the XRD spectra of VT-4 as-deposited and after successive anneals at 100, 200 and 300 °C. The major peak at 18.28° is most probably attributed to the (400) reflection of the hexagonal unit cell with an $a = b$ axis of 22.40 Å. It is assumed the other lattice constants are the same as that of B-PPXN, namely $c = 6.55$ Å. A 5% increase in $a = b$ lattice constant is for VT-4, compared with B-PPXN, is reasonable since F atoms occupy more space than H atoms.

After successive postdeposition anneals, the d spacing of the (400) peak became smaller: 4.850, 4.802, 4.691, and 4.594 Å. The decrease in d spacing may be attributed to a disordered crystallite being formed as-deposited, which becomes more ordered after higher temperature postdeposition anneals. The disorder in the crystalline phase may represent the overall disorder in the thin film since a similar effect is seen in the birefringence data (Fig. 3). Birefringence is defined as

$$\Delta = n_{\text{out-of-plane}} - n_{\text{in-plane}}. \quad (1)$$

The birefringence is sensitive to both the crystalline and amorphous phases. The out-of-plane index of refraction is low when the plane of the benzene ring is parallel to the substrate and is high when it is perpendicular to the substrate. As can be seen from Fig. 3, the thin film becomes more ordered after postdeposition anneals probably due to more ordered crystallization. The thin film is becoming more negatively birefringent which means the benzene ring is parallel to the substrate and as a result the in-plane capacitance is high for VT-4 relative to its out-of-plane capacitance. The birefringence plateaus at ~250 °C, which could mean no further crystallization is taking place.

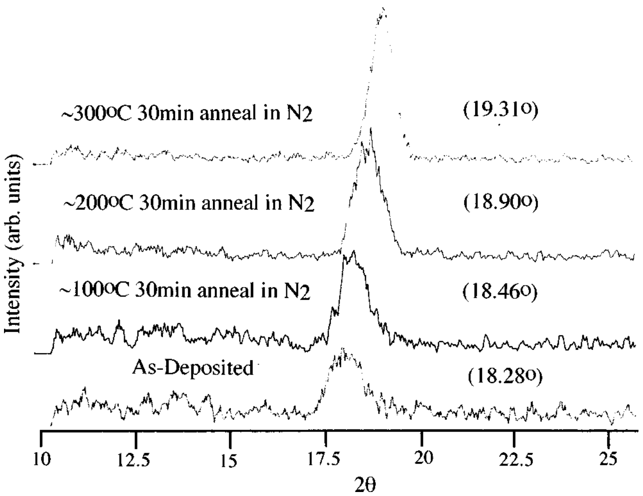

FIG. 2. X-ray diffraction spectra of VT-4.

A more ordered crystallite would contribute to a sharper peak, hence a smaller full width half maximum (FWHM). However, both stress in the thin film and a change in crystallite size may also contribute to a change in FWHM.[17] A change in stress state of the thin film should only be seen between the as-deposited sample and the annealed samples. The annealed samples should have the same stress state since they were all heated significantly above the T_g for long enough for stress relaxation to occur. The resulting annealed thin films should be in tension with similar values of tensile stresses.[18] This is due to the low coefficient of thermal expansion of Si relative to that of the parylene polymers. The FWHM for the as-deposited 100, 200, and 300 °C annealed samples was experimentally found as: 0.912, 0.833, 0.793, and 0.674. No significant increase or decrease in the FWHM can be seen between the as-deposited and 100 °C sample. Therefore, it can be concluded stress contributes minimally to the FWHM values. More likely, crystallite size and crystalline disorder contribute to the FWHM values. The crystallinity of the as-deposited, 100, 200, and 300 °C annealed samples was found from the XRD data as: 39%, 54%, 59%, and 66% (±5%). These percent crystallinity values should

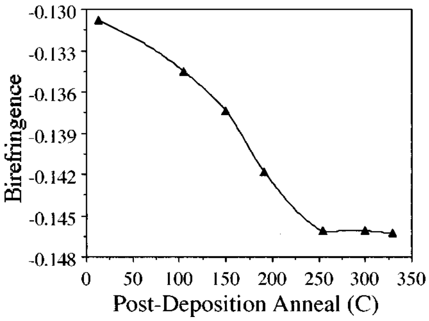

FIG. 3. Birefringence of VT-4 as a function of postdeposition anneals.

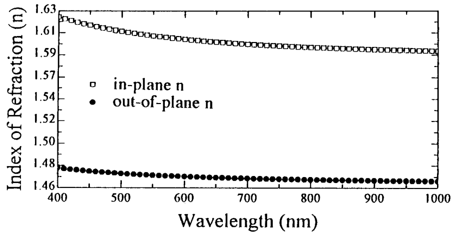

FIG. 4. Dispersion in the extraordinary and ordinary indexes of refraction for the VT-4 as deposited at ∼12 °C.

TABLE I. Electrical properties of VT-4.

Dielectric constant	@ 10 kHz	2.50
	@100 kHz	2.46
	@ 1 MHz	2.42
Dielectric loss	@ 10 kHz	<0.001
	@100 kHz	0.006
	@ 1 MHz	0.008
Leakage current	@ >2.7 MV/cm	$<3.0\times10^{-13}$ A/cm^2

only be used for general trends. As can be seen, an increase in percent crystallinity corresponds to a decrease in the FWHM, indicative of crystallite growth contributing to an increase in crystallinity.

The dispersion in the indexes of refraction from 400 to 1000 nm for as-deposited VT-4 is shown in Fig. 4. The dispersion is nearly the same as PPXN and PPXC as reported before.[3] Much like PPXN, VT-4 exhibits optical anisotropy but unlike PPXC, VT-4 has a high index of in-plane refraction. The dielectric constant of VT-4 is shown as a function of frequency in Table I. It shows some dispersion from a maximum of 2.50 at 10 kHz to a minimum of 2.42 at 1 MHz. PPXC and PPXD also show dispersion in their dielectric constants; therefore, this result is not surprising. However, the dielectric loss increases as the frequency of analysis increases. It is expected that the dielectric loss due to an AC loss mechanism should decrease if the frequency is further increased. The low dielectric constant of VT-4 is encouraging since few low dielectric constant materials are able to be deposited by thermal CVD methods. The rest of the electrical properties of VT-4 are listed in Table I. For the 367 nm thin film deposited on platinum, an applied voltage of 100 V did not cause dielectric breakdown. More encouraging, a 100 V applied voltage did not produce any measurable leakage current. Therefore, the films are highly resistive like the other parylene polymers.[14]

The need for low k (<3), high thermally stable (>425 °C) thin film materials to reduce RC delay in ultralarge scale integration devices has prompted the search for polymeric materials which have the suitable properties to fit this need. Poly(tetrafluoro-p-xylylene) is a promising candidate material which was prepared by the method of chemical vapor polymerization.

The results here show VT-4 possesses a dielectric constant of 2.42 and a dielectric loss of 0.008 at 1 MHz perpendicular to the plane of the film. A very low leakage current was measured ($<10^{-13}$ A) even at 100 V. The polymer shows an onset of degradation at 460 °C and a 1% weight loss at 480 °C in an Ar environment. Thereafter rapid weight loss occurred. VT-4 also shows anisotropic optical properties like the other polymers in the parylene family such as PPXN and PPXC. Correlations were made between birefringence data, based on the orientation of the benzene rings relative to the substrate, and XRD data, based on full width at half maximum, d spacing, and percent crystallinity data. VT-4 is semicrystalline as deposited and after postdeposition anneals it showed evidence of a more ordered crystalline phase from a decrease in d spacing. The birefringence decreased concurrently with an increase in the crystalline phase of the polymer until reaching a plateau at ∼250 °C. Finally, the glass transition temperature was measured at 63.9 °C at the inflection point, which is reasonable since PPXN possesses a T_g of 13 °C and VT-4 has a much higher energy of rotation due to its higher mer unit molecular weight.

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