

Structural and electronic properties of low dielectric constant fluorinated amorphous carbon films

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Fluorinated amorphous carbon ($a\text{-CF}_x$) films were studied by high-resolution x-ray absorption, emission, and photoelectron spectroscopy. The composition and local bonding information were obtained and correlated with substrate temperature during deposition. The data suggest that the structure of the $a\text{-CF}_x$ is mostly of carbon rings connected by CF_2 groups. The cross linking increases with substrate temperature. © 1998 American Institute of Physics.

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Currently there are intense industry-wide efforts in searching for new low dielectric constant (low- κ) materials for use in future generations of ultralarge scale integrated circuits (ULSI). According to the 1997 National Roadmap for Semiconductors,¹ low- κ (<2.5) materials will replace silicon dioxide ($\kappa=4$) as the interlayer dielectrics in multi-level interconnect scheme starting around year 2000, reducing substantially the interconnect RC delay in ULSI circuits. There are a number of requirements for the new low- κ materials, such as low dielectric constant, thermal stability (400 °C or higher), being electrically insulating, high mechanical strength, and good adhesion to neighboring layers. These stringent requirements have reduced the candidates to porous silica and a few carbon-based materials. Among them fluorinated amorphous carbon ($a\text{-CF}_x$)^{2,3} and parylene^{4,5} polymer thin films showed significant promise. Since these materials are new in IC applications, a complete understanding of the properties of these films is essential before they can be reliably used in future ULSI circuits. In this letter we report high-resolution x-ray spectroscopy studies of $a\text{-CF}_x$ and parylene thin films. We will show that C 1s x-ray photoelectron spectra and C K -edge near edge x-ray absorption fine structure (NEXAFS) provide detailed information on the local bonding environment of carbon atoms. While unoccupied states were provided by the absorption spectra, we used soft x-ray emission spectra to probe the occupied states to get a more complete picture of the electronic structure of these films and correlated them with their electrical properties. Substrate temperature during deposition plays a significant role in the properties of the $a\text{-CF}_x$ films and its effect on the thermal stability of the $a\text{-CF}_x$ films was related to the spectroscopy information.

Fluorinated amorphous carbon films attracted attention in ULSI technology only recently.^{2,3} Dielectric constant as low as 2.1 and good thermal stability were reported. These films are usually prepared by plasma enhanced chemical vapor deposition (PECVD) technique. Parylene (poly- p -xylylene) and its derivatives have dielectric constants ranging from 2.25 to 3.1 and thermal stability of up to 450 °C.^{4,5} Parylene N (Pa-N) is the unsubstituted normal-type parylene

and has dielectric constant of about 2.8 and thermal stability of about 400 °C.

Thin films (100–400 nm) of $a\text{-CF}_x$ were prepared by PECVD using a parallel plate reactor with a rf power of 175 W. The feed gas was a mixture of octafluorocyclobutane (C_4F_8) and methane (CH_4), with a flow ratio of 6.7. The films were deposited on to Si wafers at substrate temperatures of room temperature, 180, 250, and 350 °C. The film prepared at 350 °C has dielectric constant of 2.35 and thermal stability of better than 400 °C. Room temperature grown film has a lower dielectric constant (<2.1) but also a much lower thermal stability (<300 °C). Pa-N film was vacuum deposited on to the Si wafer held at room temperature using dimer precursor. It showed a thermal stability of better than 380 °C and a dielectric constant of about 2.8.

The $a\text{-CF}_x$ films were characterized by x-ray photoelectron spectroscopy (XPS) (performed by Evans East, Plainsboro, NJ) using a monochromatic Al x-ray source. The C 1s spectra for $a\text{-CF}_x$ films grown at room temperature and 250 °C are shown in Fig. 1. The peaks in the spectra are well separated and can be identified to be due to carbon atoms in C–F, C–F₂, C–F₃, C–(C, H), and C–CF bonding environments. Fitting the spectra using Gaussian distribution, the relative abundance of the C bonding environment can be obtained. The results are listed in Table I with the composition given in atomic percent. The composition of these films was obtained by comparing the C 1s intensity with those of a Teflon (CF_2) standard. We notice that room temperature deposition produced a film with more fluorine than that of the high temperature film. These fluorine atoms mostly show up in CF_3 environment: the weight of CF_3 is increased while that of C–C and C–CF is reduced.

C 1s absorption and K emission experiments were performed at beam line 7.0 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The beam line comprises a 99-pole, 5 cm period undulator, and a spherical-grating monochromator.⁶ NEXAFS spectra were obtained by measuring the total electron yield from the sample. The resolution of the monochromator was set to 0.15 eV at the C K edge. The NEXAFS spectra were normalized to the incident photon current using a clean gold mesh to correct for inten-

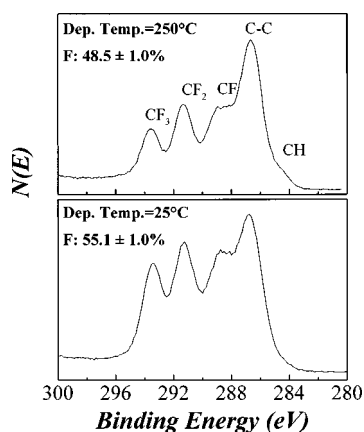


FIG. 1. XPS spectra of $a\text{-CF}_x$ films prepared at room temperature and 250 °C. Because of the charging effect, the two spectra are shifted with respect to each other, only the relative position of the peaks is relevant.

sity fluctuation of the photon beam. The x-ray emission spectroscopy XES spectra were recorded using a grazing-incidence x-ray fluorescence spectrometer.⁷ During the XES measurement, the overall resolution was about 0.5 eV.

Figure 2 shows the C K -edge absorption spectra of Pa-N and three $a\text{-CF}_x$ films grown at room temperature, 180, and 350 °C. These near edge absorption features directly measure the unoccupied orbitals of the carbon atoms. Remarkably detailed local bonding information of these new films can be obtained from comparing with existing literature on simple fluorocarbon molecules.⁸ Specifically, the peaks at 285 and 287 eV are due to the electronic transition from C $1s$ to π^* orbital and is a measure of the presence of unsaturated C-C bonds, e.g., C=C double bond.⁸ For example, this peak shows up prominently in the C K -edge spectra of graphite where carbon atoms has sp^2 hybridization and out-of-plane π bonds, but not in that of diamond with only sp^3 hybridization.^{9,10} In addition, the position of the π^* resonance depends on the other neighbors of the excited carbon atoms C*. For carbons with only H or C neighbors, e.g., C=C*H or C=C*C, the resonance is at around 285 eV. For C with one F neighbor the resonance shifted to around 287 eV and around 290 eV for carbon with two F neighbors.⁸ The absence of any peak at around 290 eV in Fig. 2 indicates that there is negligible amount of C=CF₂ groups in the $a\text{-CF}_x$ structure. Since XPS results (Table I) suggest that up to 20% of the carbon atoms has two F neighbors, they must predominantly bond in C-C*F₂-C environment, i.e., with

TABLE I. Results of C $1s$ XPS analysis for $a\text{-CF}_x$ films prepared at room temperature and 250 °C. The compositions are given in atomic percent. The errors are estimated to be around 0.5 at. %.

Peak	Position (eV)	Composition (27 °C sample)	Composition (250 °C sample)
C*-(C, H)	284.8	0.5	1.8
C*-CF	286.8	13.8	20.9
C*-CF'	288.4	4.6	6.2
C*-F	289.3	7.6	7.3
C*-F ₂	291.4	9.9	9.7
C*-F ₃	293.7	8.1	6.2
Total carbon		44.5	52.1
Total fluorine calculated		51.7	45.3

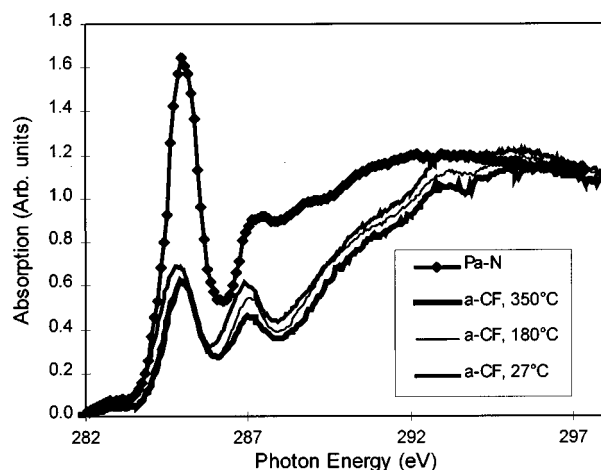


FIG. 2. C K -edge absorption spectra of Pa-N and $a\text{-CF}_x$ films prepared at substrate temperature of room temperature, 180, and 350 °C. These spectra were normalized at 297 eV.

saturated sp^3 bonds. This is an important observation and, as we will discuss later, it will have implications on the structure of the $a\text{-CF}_x$ films.

The π^* peak is very intense in the Pa-N film, reflecting the fact that this film is primarily phenyl rings connected by CH₂ groups.⁴ The structure of Pa-N is a chain of phenyl rings connected by CH₂. The six carbon atoms belonging to the phenyl ring out of the total eight carbon atoms has double bonds, i.e., 75% of the carbon atoms. The 285 eV π^* resonance of $a\text{-CF}_x$ films, which is associated with C with no F neighbors, is only about 40% that of the Pa-N. We can roughly estimate that about 30% of these carbon atoms have unsaturated bonds. From Table I, about 40% of the carbons in $a\text{-CF}_x$ have no F neighbors. This means that over 70% of these carbon atoms have unsaturated bonds in the $a\text{-CF}_x$ films. We should caution that because of the issues such as normalization, orientation of the π bonds, the surface sensitivity of the measurement techniques, and the complexity of the bonding environment in $a\text{-CF}_x$, the above estimate is highly qualitative. Still, from this qualitative argument we can conclude that the majority of the nonfluorinated carbon atoms have unsaturated, e.g., sp^2 , bonds.

The intensity of π^* resonance at 287 eV is higher in the films with lower substrate temperature during growth. Since this peak is associated with C=C*FX (X=C or H) environment, the reduction in intensity suggests that this kind of environment is not stable during high temperature depositions. From Table I, the total number of carbon atoms with one fluorine neighbor did not change much. This suggests that at higher temperatures the CF prefer to bond in single bond than in double bond. Consequently there is more cross linking in the film. Similarly, at higher temperatures the intensity of the π^* resonance at 285 eV did not change much, even though XPS results indicated that the total nonfluorinated carbon atoms increased substantially. Again this can be understood if we assume that those nonfluorinated carbons have saturated bonds, i.e., there is more cross link and less rings in the higher temperature grown films.

In Fig. 3 the C K -emission spectra of amorphous carbon, $a\text{-CF}_x$ and Pa-N were shown. Complementary to the x-ray absorption spectra, occupied electronic states were probed.

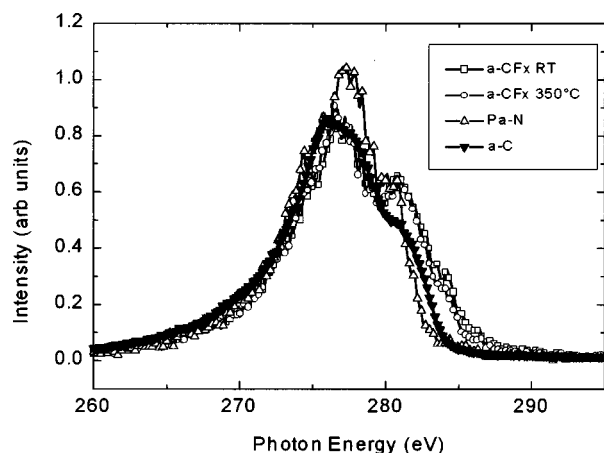


FIG. 3. C K-emission spectra of amorphous carbon, Pa-N, and fluorinated amorphous carbon prepared at room temperature and 350 °C.

From comparing with *a*-C, the intensity centered around 275 eV is mostly due to C–C bands. More importantly, in the region of 282–285 eV there is little intensity in the spectra of Pa–N and amorphous carbon. We conclude that the intensity in the spectra of *a*-CF_x is mostly due to F-induced states and due to the amorphous nature of the films. Since these states are at the top of the valence bands, this has important implications in the electrical properties of these *a*-CF_x films, it narrows the band gap. Because the x-ray absorption spectra of *a*-CF_x and Pa–N films have similar threshold, we can argue that the bandgap of *a*-CF_x is at about 2 eV smaller than that of the Pa–N. Again because the band edge is not well defined for amorphous films this conclusion is very qualitative. The effect of the core hole needs to be considered as well. Qualitatively this conclusion is supported by the fact that *a*-CF_x is not as good an insulator as Pa–N. While the Pa–N films is insulating with a volume resistivity of better than $1 \times 10^{17} \Omega \text{ cm}$,¹¹ a 2000 Å thick *a*-CF_x films showed a leakage current of 10^{-8} A/cm^2 at an electrical field of 0.5 MV/cm.¹²

From the XPS and NEXAFS results one can obtain a fairly good picture of the structure *a*-CF_x. In general, CF compounds are characterized by either chain or ring structures. Unsaturated bonds are typically associated with the ring structure. Since most of the nonfluorinated carbon atoms are found with unsaturated bonds, they are mostly associated with ring structures. We also found that CF₂ groups are mostly present with saturated bonds in the C–CF₂–C environment. This is typical of chain structures similar to, e.g., teflon which is composed of CF₂ chains. Note also that CF₂ groups are found only among about 20% of the carbon atoms, while nonfluorinated carbon atoms are found in about 40% of the carbons. The structure that emerges from this picture is nonfluorinated carbon and CF groups in mostly ring structures linked by CF₂ groups, and terminated by CF₃ groups.

The thermal stability of *a*-CF_x films has been found to be strongly dependent on the substrate temperature during deposition. For example, the room temperature deposited films lose about 50% of their weight after annealing at 400 °C, while the 350 °C deposited films remain essentially unchanged. This can be explained by the fact that, as is clear from XPS and NEXAFS results, there are less terminal CF₃

groups and more nonfluorinated carbon atoms with saturated bonds in the higher temperature films, indicating that the ring-chain structures are larger/longer in these films. Decomposition of C₄F₈ results in various radicals of C, CF, CF₂, CF₃, F, F₂. Growth of the films is a result of competition between the attachment of CF species and the etching of the F species. These are strong functions of substrate temperature, plasma power, reactor design, and presence of other gases such as the CH₄. Here we demonstrated the effect of substrate temperature. By properly adjusting the plasma power and the gas mixture ratio we have recently improved the thermal stability of the *a*-CF_x film even further.¹²

In conclusion, we performed spectroscopy studies on the fluorinated amorphous carbon films. The structure we derived is that of C–C, CH, and CF ring structures linked by CF₂ groups. CF₃ groups terminate the ring/chain structures. The amount of CF₃ groups can be reduced by depositing the films at higher temperatures, which also produce highly cross-linked structures with improved thermal stability. The band gap of the *a*-CF_x film is substantially smaller than that of the parylene film, resulting in a higher electrical leakage.

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