Volume 9, Number 10
1009-1963/2000/09(10)/0778-05
CHINESE PHYSICS
October, 2000
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POROUS AMORPHOUS FLUOROPOLYMER FILMS WITH ULTRALOW DIELECTRIC CONSTANT*

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(Received 23 March 2000; revised manuscript received 6 July 2000)

With the development of ultralarge scale integrated circuit, new interlayer dielectrics with low dielectric constant for multilevel interconnections are required, instead of conventional SiO_2 films. For the sake of seeking perfect dielectrics, amorphous fluoropolymer (AF) thin film with a thickness of about 0.9μm has been prepared by spin-coating method, following the principle of phase separation. By capacitance-voltage (C-V) measurements the dielectric constant of the thin film is equal to 1.57 at 1 MHz, which is attributed to numerous pores contained in the film matrix. X-ray photoelectron spectroscopy (XPS) spectra show that after annealing, about 71% CF_3 groups in the AF film have decomposed into CF_2, CF, etc. This leads to the increase of CF_2 groups by three times and CF groups by 8% in the AF film. In a word, compared with the film without being annealed, about 25% carbon, 7% fluorine and 12% oxygen atoms will be lost after annealing at 400°C for 30min.

Keywords: porous amorphous fluoropolymer film, low dielectric constant, spin-coating, X-ray photoelectron spectroscopy
PACC: 7755, 7360R, 8140

I. INTRODUCTION

Reductions in integrated circuit feature sizes and the continuing trend toward large chips have caused a parallel increase in resistance-capacitance (RC) delay associated with the on-chip interconnect. Indeed, interconnect related RC delay has become the dominant component of total circuit RC delay in complex designs of the 0.18 μm generation.[1] The steady decrease in the dimensions of interline spaces is leading to unacceptable increase in capacitance, cross talk and power dissipation. Bothra *et al.*[2] showed that only by introducing lower dielectric constant interlevel dielectrics, could significant performance enhancements be realized for submicron ULSI circuits by theory simulation. According to the Semiconductor Industry Association (SIA) roadmap, by the year 2001 a dielectric material with a dielectric constant (k) of 2.3 will be required for the feature size 0.15 μm, and after that a dielectric material with $k < 2$ will be needed.[3] Although many low k materials have been developed, including SiOF films, α-C:F films, organic polymer films, porous silica films and so on, it is difficult to find a low k material capable of meeting all the requirements for interlayer dielectric films. It is well known that if a material of solid-gas mixture can be fabricated, the dielectric constant of the two-phase material will be much lower than that of the solid. Accordingly, for the sake of acquiring ultralow dielectric constant films, many researchers have investigated extensively porous materials, such as porous silica (silica xerogel, silica aerogel and nanoporous silica),[4–6] polyimide nanofoams[7] and porous polymer.[3]

Teflon (PTFE) has for many years constituted the lowest dielectric constant polymer with good mechanical strength,[8] but a low glass transition temperature and poor adhesion to metal and silicon oxides have hindered its use in electronics applications.[9] However, amorphous fluoropolymers (AF) including the material Teflon AF 1600, a copolymer of tetrafluoroethylene and 2,2-bis (trifluoromethyl)-4,5-difluoro-1,3-dioxole, have many improvements in transparency, creep, adhesion to other materials, and its dielectric constant is lower than normal PTFE.[8] Therefore, the material is potentially useful as a dielectric layer in integrated circuit packaging. As for preparation techniques of AF films, numerous meth-

*Project supported by the National Natural Science Foundation of China (No. 69776026), and by the Foundation for University Key Teacher by the Ministry of Education, China.

ods have been reported, including thermolysis,[8] laser ablation,[10] direct liquid injection based chemical vapor deposition (CVD),[11] low temperature CVD following the principle of direct liquid injection in an ultraviolet light-assisted rapid isothermal processing system,[12] surface modification with vacuum ultraviolet irradiation[13] and spin-on.[12,14–16] Meanwhile, some reports on interaction of AF with metal have been published.[14–16] However, porous AF film with an ultralow dielectric constant seems to have not been reported. In this article we report the achievement of porous AF films with an ultralow dielectric constant by the spin-coating method for the first time so far as we know, and the investigation of the effect of heat treatment on film surface components.

II. EXPERIMENTAL

A solution containing 5% Teflon AF 1600, purchased from DuPont, was used as raw material. AF thin films were spun on the p-type Si(111) wafer with a resistivity of 10^{-3} $\Omega\cdot$cm by adopting a spin coating system (CONVAC, 1001, Germany) with a rotating speed of 0–9999 rpm, which was controlled by a computer. In our experiments, both the reduction in solvent volatilization space and the multistep control of rotating speed were introduced. Subsequently, the films were aged for a week in desiccator under the condition of normal pressure and room temperature. The thickness of thin films was in the range of 0.8–0.9 μm, confirmed by cross-sectional scanning electron micrograph (SEM) observation. For capacitance-voltage(C-V) measurements, a metal-insulator-semiconductor(MIS) structure was adopted, where the evaporation-deposited aluminum with an area of 1.539 mm^2 was used as the top electrode. To assure ohmic contacts between the back of the Si substrate and the stage of the prober, another thin layer of aluminum is deposited on the back of the Si substrate. In order to investigate thermal stability of AF film, the film was annealed at 400°C for 30 min in ambient atmosphere. The chemical bonding states of the thin films were analyzed by Fourier transform infrared (FTIR) spectrometer (American, Niconet 5DX). The cross-section view of the thin film was observed with field emission scanning electron microscope (FE-SEM) (Philips Company, XL 30 FEG). The chemical compositions on the film surface were analyzed with X-ray photoelectron spectrometer (XPS) (micro Lab 310-F, VG scientific, The surface analysis Company) using a Mg$K\alpha$ source.

III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR reflective spectrum of the AF film in the region of 400–1400 cm^{-1}. The spectrum above 1400 cm^{-1} is essentially featureless, and not presented here. With respect to FTIR spectrum, the fingerprint regions (700–1500 cm^{-1}) for our film are similar to that for spin-coated Teflon AF 1600 thin film in Fig.2 in Ref.[10], although there are slight differences between peak positions because of instrumental precision. The strong absorption at 990cm^{-1} is due to CF_3 vibration,[8] which indicates that AF film contains more end groups CF_3, as seen in Fig.2 of the chemical structure of AF. The appearance of adsorption peak at 730–750 cm^{-1} shows that the prepared film is amorphous.[8,17] The peaks at 1109, 1265 and 1303 cm^{-1} should be attributed to the fluorinated dioxole component.[8]

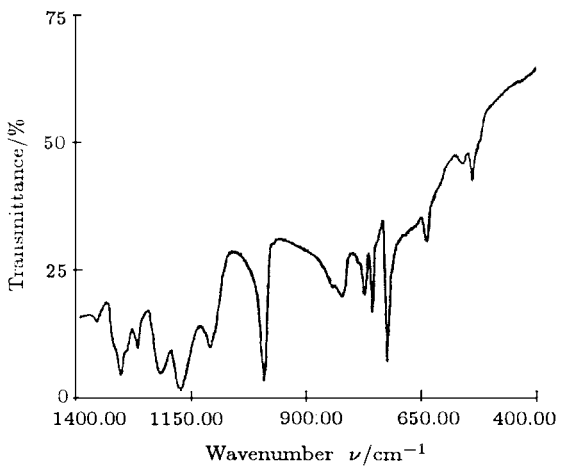


Fig.1. FTIR spectrum of the AF film in the range of 400–1400 cm^{-1}.

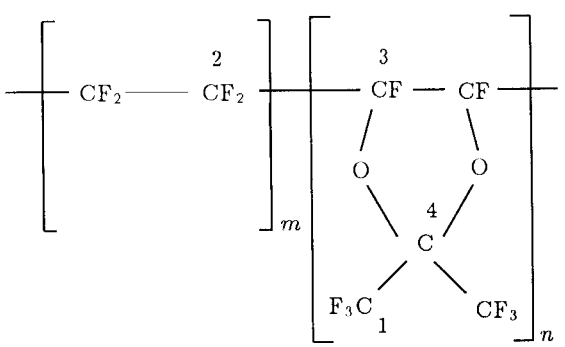


Fig.2. The chemical structure of AF m : n=1:2.

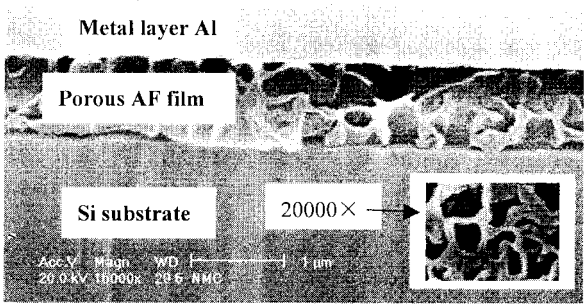


Fig.3. SEM of cross-sectional view for the film with metal-insulator-semiconductor structure.

The choice of the measurement frequency 1 MHz is a requirement in the SIA roadmap as a common standard.[18] The dielectric constant k of the film is calculated using the formula for a parallel plate capacitor

$$k = Cd/\varepsilon_0 A,$$

where C is the capacitance of MIS element, d is the thickness of the dielectric film, A is the area of the Al electrode, and $\varepsilon_0 (= 8.854 \times 10^{-12}$ F/m) is the permittivity of free space. In order to obtain accurate dielectric constant, we measure six points and average the results. That is, the dielectric constant for the AF film is equal to 1.57 at 1 MHz, and is much lower than 1.9 for poly (tetrafluoroethylene) (PTFE). The lower dielectric constant for AF film results mainly from its porous structure, shown in Fig.3. In addition, there are more fluorine atoms in AF film than PTFE, which causes a reduction in electronic polarization.[19] And film density also affects electronic polarization.[19] Owing to carbon-oxygen pentatomic ring structures in AF film, which have relatively big sterically hindered effect, the density of AF film is lower than that of PTFE. This induces lower dielectric constant of AF film. Here, it should be emphasized that the formation of porous AF film follows the principle of phase separation. In this principle one phase such as the polymer is induced to create the matrix, and the other (i.e., organic solvent) to create convex-surface shapes, which can be removed to leave free space by evaporation.

On account of thermal annealing required in the integrated circuit processing, it is valuable to investigate the thermal stability of thin films, especially the chemical changes occurring during annealing. With respect to the AF film before and after annealing, the high resolution X-ray photoelectron spectra of C1s, F1s and O1s were collected, and smoothed by Savitzky-Golay. Figure 4(a) is the C1s spectrum of the film before annealing, which is separated into four peaks by Gaussian fitting. It indicates that the AF film contains four different carbon environments, corresponding to —CF_3 (290.41 eV), —CF_2— (288.31 eV), O_2—$\underline{C}$—C—$(CF_3)_2$ (287.02 eV) and C—F (285.40 eV), respectively. The C1s spectrum of the film annealed at 400°C is shown in Fig.4(b). Obviously, compared with Fig.4(a), after annealing the peaks of CF_3 and O_2—$\underline{C}$—C—$(CF_3)_2$ decrease remarkably, and the areas of the two peaks all decrease by about 71%. However, the peaks of CF_2 and CF increase evidently, and the area of the former increases by three times, that of the latter increases by 8%. This shows that thermal decomposition of CF_3 groups produces a large number of CF_2 groups and a minority of CF groups. That is due to the requirement of higher energy for abstraction of F from CF_2 than CF_3, so it is relatively easy to generate CF_2 groups. The decrease

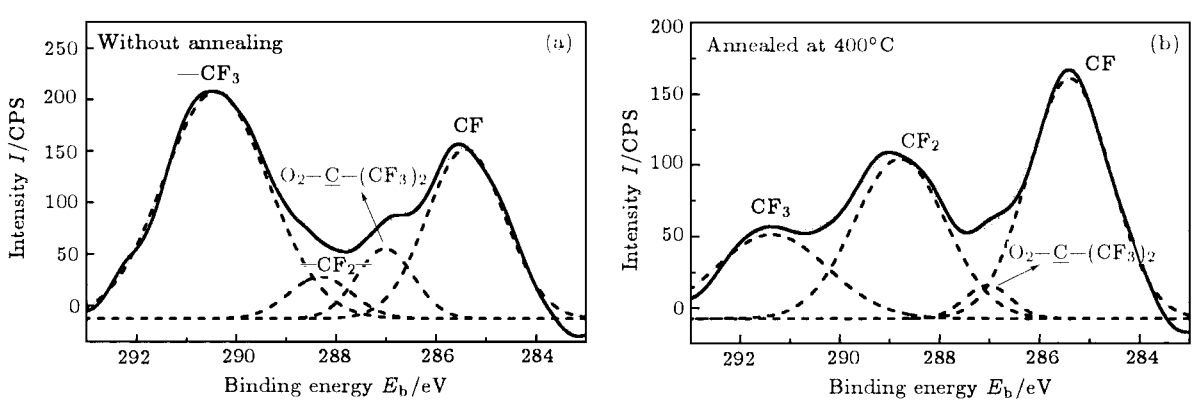


Fig.4. High resolution XPS spectra of C1s for the film (a) without annealing, (b) annealed at 400°C.

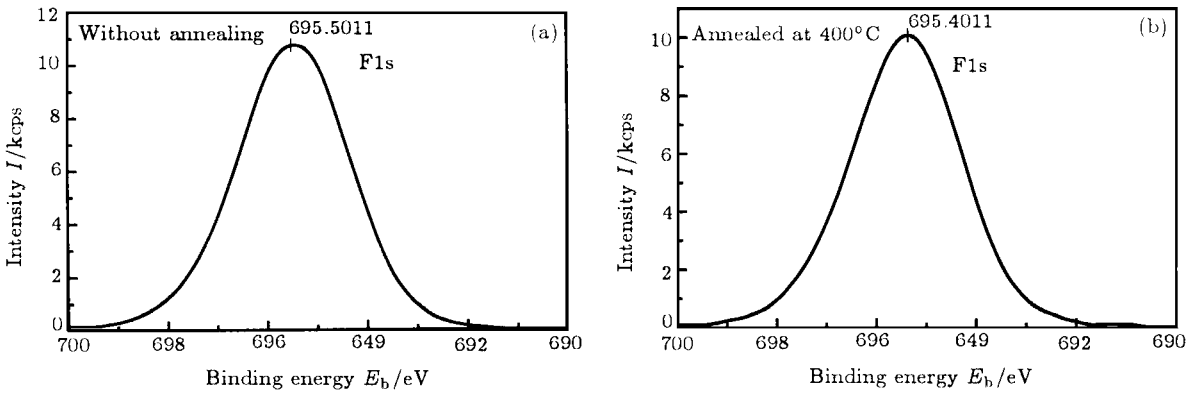


Fig.5. High resolution XPS spectra of F1s for the films (a) without annealing, (b) annealed at 400°C.

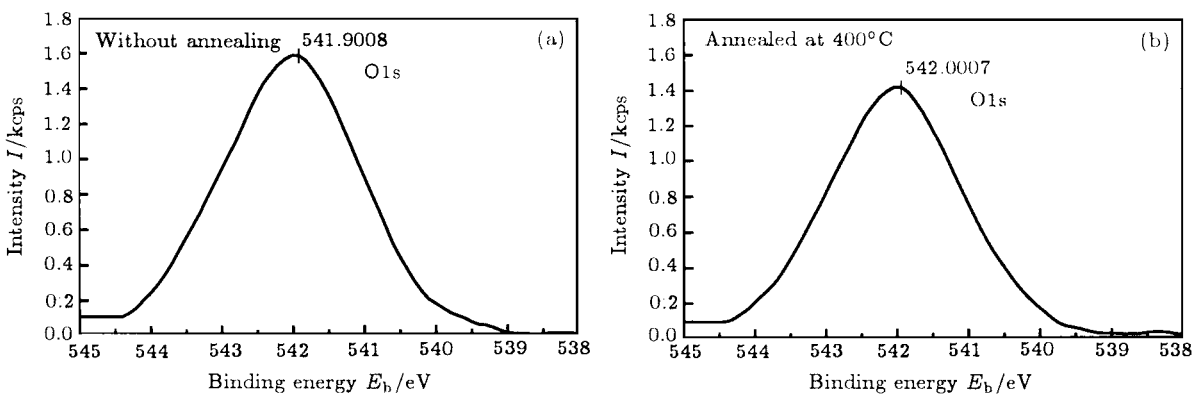


Fig.6. High resolution XPS spectra of O1s for the films (a) without annealing, (b) annealed at 400°C.

in the peak area of O_2—C—$(CF_3)_2$ results from a reduction in carbon atoms located in the original environment because of the decomposition of CF_3. Comparing the integral areas of C1s spectra in Figs. 4(a) and 4(b), we find that thermal annealing causes a decrease of 25% in carbon concentration.

Regarding the two spectra of F1s, shown in Fig.5, there is only one peak at about 695.4 eV for each. It indicates that fluorine atoms are located in the same chemical state as C—F binding configuration. By comparison of F1s peak areas for the film before and after annealing, it can be found that F atoms decrease by 7% after annealing. Figure 6 is the XPS spectra of O1s, only one peak can be found at about 542 eV. Similarly, it also indicates that there is a chemical environment for oxygen atoms, that is C—O—C. According to the peak area of O1s, it can be found that oxygen concentration decreases by 12% after annealing. In a word, the AF film will lose carbon, fluorine and oxygen atoms after annealing at 400°C. This agrees with the fact that thermal decomposition of Teflon AF generates hexafluoroacetone.[11]

IV. CONCLUSION

The AF thin films with an ultralow dielectric constant of 1.57 have been prepared by spin-coating method, the ultralow dielectric constant is attributed to the porous structure. After annealing at 400°C, about 71% CF_3 groups in the AF film decompose into CF_2 and CF groups, and CF_2 groups are dominating. On the whole, thermal annealing causes the loss of about 25% carbon, 7% fluorine and 12% oxygen atoms in the AF film. The porous AF film with such a low k may be a promising dielectric material in ULSI, according to Bohr's model,[20] when it is used as the interconnect dielectrics instead of conventional SiO_2(k=4.0), the RC delay will decrease by about 61%. Meanwhile, it also presents a lot of challenges, such as the control of pore size and porosity, integration compatibility.

ACKNOWLEDGMENT

The authors are grateful to Prof. F. Lu (Department of Physics, Fudan University) for his help in *C-V* measurements.

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