

α -C:F:H films prepared by PECVD^①

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Abstract: Fluorinated amorphous hydrogenated α -C:F:H carbon thin films were deposited using radio frequency plasma enhanced chemical vapor deposition(RF-PECVD) reactor with CF_4 and CH_4 as source gases and were annealed in a N_2 atmosphere. The properties of these films were evaluated by FTIR spectrometry, UV-VIS spectrophotometry and single-wavelength spectroscopic ellipsometry. A correspondence relativity connection between the deposition rate and technology was found. The chemical bonding structures and the content of CH_x and CF_x in the films are transformed and the optical band gap decreases monotonically with increasing temperature after annealing. The dielectric constant is increased with decreasing content of F in the films and the optical band gap is decreased with decreasing the content of H in the film.

Key words: α -C:F:H thin films; PECVD; dielectric constant; optical band gap

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1 INTRODUCTION

Recent advances in ultra large scale integration devices(ULSI) have led to a need for new interconnections materials with low resistivity and interlayer materials with low dielectric constant to reduce the interconnection delay, interfere, noise and wastage caused by parasitic capacitance. Replacing Al in traditional Al/ SiO_2 system with Cu, it has reached a unanimous agreement. Materials under research to replace SiO_2 mainly contain PTFE, SiOF , F-PI and α -C:F:H. PTFE($\kappa \approx 2.0$) and SiOF ($\kappa \approx 3.0 \sim 3.5$) have low dielectric constant; however, as for PTFE, organic polymers, their low adhesive force, poor thermal stability, and difficulty of manufacture have hindered their use in microelectronics. Furthermore, SiOF and F-PI easily absorbed water and decomposed while exposed to air because of their poor wet resistance. On the other hand, α -C:H:F films have high electrical resistivity, good thermal stability due to their highly cross-linked structures, and good industrial process ability^[1-5]. Thus it is one of the most promising low dielectric constant interlayer dielectrics. Contradictions between α -C:H:F films' dielectric constant and thermal stability, and α -C:H:F films' low deposition rate are the main hindrance to their utility in the ULSI at present.

2 EXPERIMENTAL

The process tool employed is a commercially available parallel plate RF-PECVD reactor as shown in Fig. 1. The diameter of the parallel plate is 25 cm. The upper electrode is a showerhead design, which supplies both power and process gases to the reaction chamber. Power is supplied from a 13.56 MHz generator and it can be adjusted from 0 to 500 W. The substrate platform is electrically grounded and has embedded resistive heaters to control substrate temperature. Process temperature can be regulated from room temperature to 400 °C. Process gases are delivered to the reaction chamber using D08-3BLZM mass flow controllers. The flow controllers ensure accurate and repeatable gas flow to a mixing chamber. The base pressure of the vacuum chamber was pumped with a ZXZ-8 mechanical pump and an HTFB turbomolecular pump, and the ultimate base pressure can be achieved 1.0×10^{-4} Pa. Working pressure of the chamber was maintained by mechanical pump and ZL-30 roots pump.

The source gases were CF_4 and CH_4 , and the flow rate is fixed at 30 cm^3/s and 10 cm^3/s , respectively. Argon was used for plasma stabilization and plasma emission reference, and its flow rate is 2 cm^3/s . The substrates were N-type (100) silicon wafers and quartz wafers. Before loading into the chamber,

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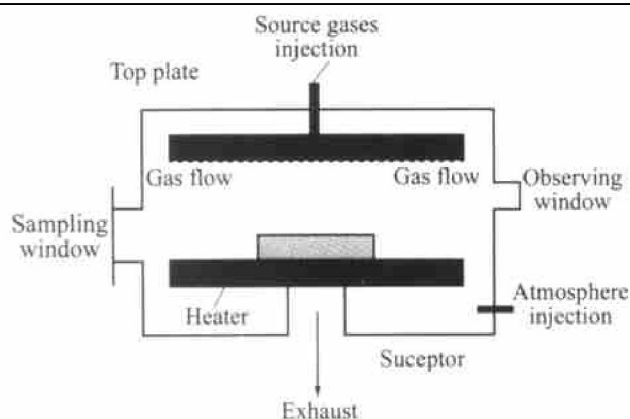


Fig. 1 Sketch of PECVD chamber

the substrates were cleaned in an ultrasonic bath of acetone to remove residual organic contaminants, washed in deionised water and dried by blowing nitrogen. Prior to deposition, the chamber was evacuated to 10^{-3} Pa, and then argon was introduced for sputter cleaning in order to eliminate any impurity on the substrates (treatment parameters: 100 W, 10 min). The samples were annealed in argon at 300 °C and 400 °C, respectively.

The thickness and dielectric constant of the deposited films were measured by an ELL-FB ellipsometer, and the deposition rate was calculated according to deposition time. The chemical bonding structure of the films was examined by a NEXUS-470 FTIR spectra. The structural of carbon investigation was carried out by a Dilor LabRam-INFINITY Raman spectra on the annealed samples. Relations between the optical band gap and powers were analyzed from optical absorption coefficient that was measured by a TU-1800 UV-VIS spectra.

3 RESULTS AND DISCUSSION

3.1 Influence of power and temperature on deposition rate

The deposition rate of the films was mainly affected by RF-power and deposition temperature, besides, flow rate R and base pressure have a little effect on it. Fig. 2 shows the films' deposition rate at varied temperatures or RF-power. The deposition rate increased with increasing RF-power at lower powers, while larger than 200 W it increased slowly, even showed a tendency of decline^[6]. This is because the increase of RF-power leads to an augment of electronics density and a rising of the temperature, and it is beneficial to reactive gases' decomposing, thus more plasma radicals produced and thus films' growth accelerated. Furthermore, negative voltage of the plasma's scabbard in the chamber was elevated by increasing powers, and it made the gap between the intensities of the ions flow moving towards the wall of

the chamber and electronics flow was enlarged. That means it's beneficial for the film-depositing radicals moving towards the substrates, therefore the deposition rate increased. But after the power augmented to a certain higher value (200 W), when increasing power, the ions' etching to the film enhanced more acute than the power and temperature did, thus leading to the decrease of the deposition rate. There was an extremum on the curve of $R-T$. The deposition rate rose a little at first and then minished sharply with increasing the temperature, and it is similar to Ref. [7]. The energy of the exterior ion of the α C:H:F thin films would increase with increasing temperature, consequently, the ion which links infirmly with other atom would be divorced from films and recurred in the vacuum chamber. Any more, atom and atoms group which link infirmly with the substrate would break away the substrate too. These devoted to descend the deposition rate of thin films and boosted up the capability of the α C:H:F thin films.

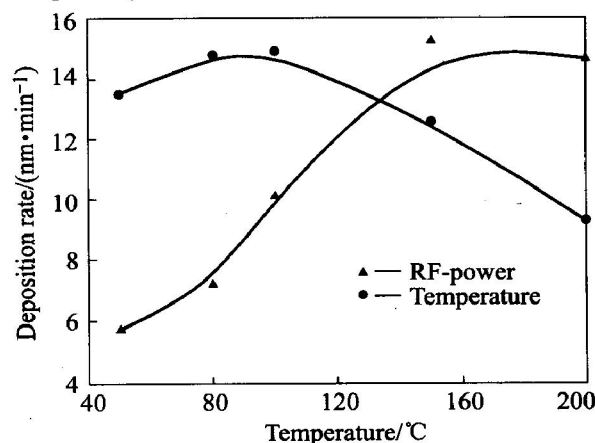


Fig. 2 Deposition rate as a function of temperature and RF-power

3.2 FTIR analysis of films

The FTIR spectra of as-deposited and annealed samples at different T_A are presented in Fig. 3. The chemical bonding structures were strongly influenced by annealing temperature. After annealing, three strong absorption peaks in the range of "radicals frequency" of the α C:H:F films, which were assigned to the $\text{sp}^3\text{-CH}_3$ (2870 cm^{-1}) symmetry stretching vibrations, the $\text{sp}^3\text{-CH}_2$ (2920 cm^{-1}) asymmetry stretching vibrations, and the $\text{F}_2\text{C}=\text{C}$ (1710 cm^{-1}) stretching vibrations disappeared while $\text{C}=\text{C}$ (1634 cm^{-1}) absorption peak strengthened^[8,9]. In the range of "dactylogram", intensities of some peaks also changed but not so obvious as those in the range of "radicals frequency". The leading absorption peaks in this range were assigned to CF_x ($x = 1, 2, 3$) vibrations, that were CF ($1030, 1070\text{ cm}^{-1}$), CF_2 ($1050, 1160, 1220\text{ cm}^{-1}$) and CF_3 ($980, 1340\text{ cm}^{-1}$). It's difficult to point out which peak should

be assigned to a frondose vibration because these absorption peaks usually resulted from coupling vibrations between F atoms and other bonds in CF_x radicals. Therefore we usually get the bonds' contents through gauss analysis. The FTIR spectra results also suggest that the content of H atoms decreases obviously after annealing, meanwhile, the relative contents of CF, CF_2 and CF_3 also change.

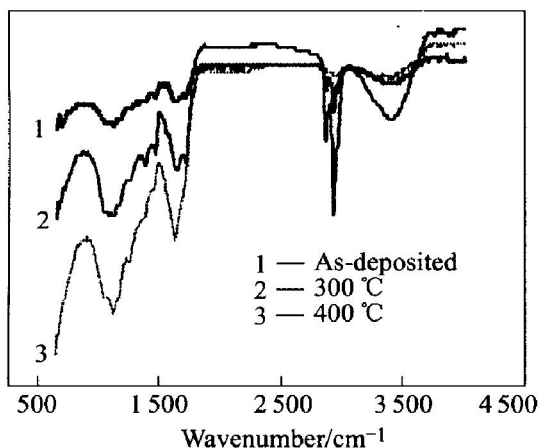


Fig. 3 FTIR spectra of films as-deposited and annealed at different temperatures

3.3 Raman analysis of films

Typical Raman spectra of the $\alpha\text{-C:H:F}$ films as-deposited and 400 °C annealed are shown in Fig. 4. It is well known the G band (G for 'graphitic', 1575 cm^{-1}), originates from the symmetric E_{2g} vibrational mode in graphite-like materials, while the D band ('disorder'-band, 1355 cm^{-1}) arises from the limitations in the graphite domain size induced by grain boundaries or imperfections. The curve of the film as-deposited was flat with almost no dispersion peaks while the one annealed at 400 °C had a distinct peak at around 1550 cm^{-1} (G peak). It indicates that the film annealed at 400 °C is amorphous carbon which is constituted by sp^3 and sp^2 mixed structures, and has minicrystals in it^[5,10].

3.4 UV-VIS analysis of films

To investigate the influences of RF-power on the optical properties of the films, these deposited films on quartz wafers substrates were analyzed by UV-VIS spectra. The $\alpha\text{-C:H:F}$ films had preferable transmission ratios in the visible light range while in the ultraviolet range they had a strong absorption. The curves became more abrupt after annealing. The optical band gaps were calculated from Tauc equation: $(\alpha E)^{1/2} = \beta(E - E_g)^{1/2}$ ^[11]. Fig. 5 shows the optical band gaps as a function of the annealing temperature. The optical band gaps decreased with increasing annealing temperature, which indicates that the optical properties of the films are ameliorated after annealing. Banding FTIR spectra together, it can be demonstrated that

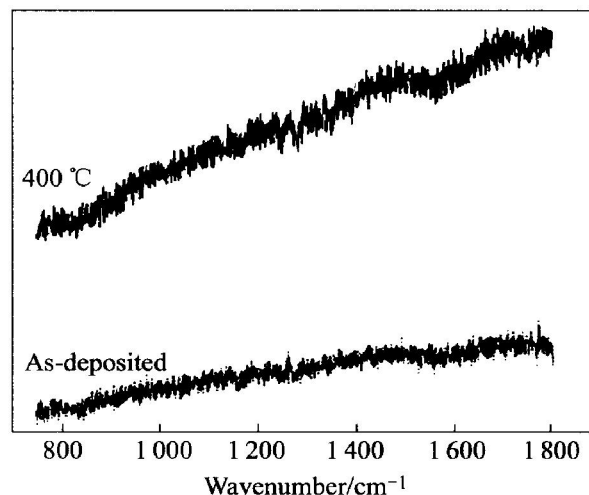


Fig. 4 Raman spectra of thin films as-deposited and annealed at 400 °C

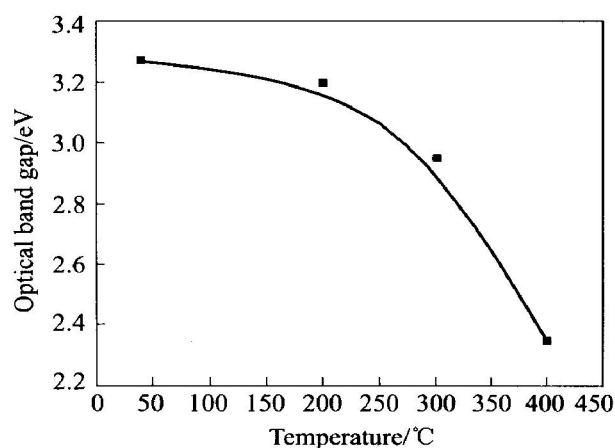


Fig. 5 Optical band gap as a function of annealing temperature

the decreasing of the optical band gaps mainly attribute to the notable decrease of the content of H atoms in the annealed films, and it is similar to Jeong^[8].

3.5 Dielectric constant

Fig. 6 shows the dielectric constant as a function of RF-power. It is clear that the dielectric constant increased with increasing RF-power. The dielectric constant of the $\alpha\text{-C:H:F}$ films mainly rested with the electronics polarization in the films, while the electronics polarization in the $\alpha\text{-C:H:F}$ films mostly relied on C-F radicals^[6]. Therefore, it can be explained as follows: augmentation of powers enhanced the ion bombardment to the surface of the films and weak bond F combined with H got away from the surface in the form of HF, thus the content of F decreased leading to the rise of the dielectric constant. Meanwhile, weakly combined bonds in the films reduced at high powers and the correlation enhanced, therefore the films deposited at high powers had better thermal stability. And how to minish the dielectric constant and

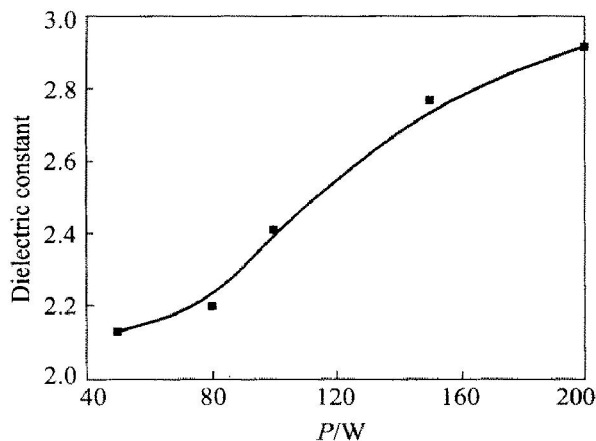


Fig. 6 Dielectric constant as a function of RF-power

improve its thermal stability at the time has always been the problem that the researchers concerned mostly^[12,13].

4 CONCLUSIONS

1) α C:H:F films are deposited by PECVD using CH and CF as source gases. At proper power and lower temperatures, a optimum deposition rate is achieved.

2) The chemical bond of the films has distinct changes after annealed at high temperature. Microcrystal appears in the films and almost all the H transgressed from the films and content of CF_x of the films change a lot.

3) Dielectric constant rests with content of F in the films, and dielectric constant minishs while content of F augments. The optical band gap relies on the content of H in the films. Furthermore, it also bears on the content of CF_x in the films.

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