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Kow Ming Chang, Shih Wei Wang, Chin Jen Wu, Ta Hsun Yeh, Chii Horng Li, and Ji Yi Yang
Department of Electronic Engineering and Institute of Electronics, National Chiao Tung University, National Nano Device Laboratory, Hsinchu, Taiwan

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In this letter, fluorinated silicon oxide (F_xSiO_y) films were deposited in the electron cyclotron resonance (ECR) chemical vapor deposition system with SiH_4, O_2, and CF_4 as the reaction gases. The CF_4, in contrast to SiF_4 or $FSi(OC_2H_5)_3$ used in other reports, is an indirect fluorinating source. The fluorinating mechanism is similar to that of the etching of oxide by fluorocarbon plasma, therefore, the thermal stability of the incorporated fluorine must strongly depend on the deposition temperature. It is found that the thermal stability and moisture resistance are greatly improved by increasing the deposition temperature. However, the higher deposition temperature also results in a higher compressed stress and dielectric constant. Besides, to get the moisture resistance, the deposition temperature must be above 300 °C. On the other hand, ECR-SiO_2 (without fluorination), even deposited at room temperature, is shown to have a good water resistance. Therefore, by choosing deposition temperature for F_xSiO_y to have enough thermal tolerance and capping with ECR-SiO_2, the moisture resistor is suggested for the inter metal dielectric applications.
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There has been an increased interest in low dielectric constant (~3.0) fluorinated silicon oxide (F_xSiO_y), with various inexpensive precursors and its easy integrated property for intermetal dielectric (IMD) applications.[1] Concurrently, how to maintain other desired properties for IMD applications (such as low mechanical stress, high thermal stability, and low moisture absorption)[2] becomes another important subject of research. In our study, F_xSiO_y films were deposited in the electron cyclotron resonance (ECR) chemical vapor deposition system with SiH_4, O_2, and CF_4 as reaction gases.[3] The CF_4, in contrast to SiF_4 or $FSi(OC_2H_5)_3$ used in other reports,[1] is an indirect fluorinating source. The incorporation of fluorine comes from the unvolatile silicon fluoride, which has a similar formation mechanism as the etching of oxide by fluorocarbon plasma, therefore, the concentration and stability of fluorine in F_xSiO_y must strongly relate to the process temperature. In this letter, we clarify the influences of deposition temperature on thermal stability, moisture resistance, and other properties of F_xSiO_y film.

F_xSiO_y films ($SiH_4/O_2/CF_4$=8/85/10 sccm, MW 300 W, 3 mTorr) were deposited on *N*-type Si (100) 4 in. wafers to a thickness around 240 nm. With temperature (T) at 25, 100, 200, and 300 °C. After they were annealed in nitrogen ambient at various temperatures (400, 500, 600, 700, and 800 °C) for half an hour, the thermal stability of these films was analyzed by Fourier transform infrared spectroscopy (FTIR). From FTIR spectrum, variation of the Si–OH peak around 3650 cm^{-1} with time was monitored as the moisture absorption. The variation of film stress with time was measured, which also reflects the moisture absorption in the film. The refractive index was investigated by ellipsometry and the dielectric constant (k) was measured using metal-insulator-semiconductor (MIS) structure at 1 MHz.

Figure 1 shows the thermal stability of F_xSiO_y films. Note that for all the films deposited at various temperatures, the ratio of Si–F (~930 cm^{-1}) over Si–O (stretching mode, ~1080 cm^{-1}) peak intensity does not degrade at 400 °C after half an hour annealing. However, for the 25 °C deposited film, the ratio starts to decay at 500 °C. On the other hand, the film deposited at 100 °C can stand T above 500 °C and only slightly degrade during 600 °C annealing. The film deposited at 200 °C can stand T above 600 °C and the film deposited at 300 °C even can stand T above 700 °C, without outgassing of fluorine. Therefore, thermal stability of fluorine is shown to strongly depend on the deposition temperature.

It is assumed that the formation of Si–F bonds in F_xSiO_y film, with the addition of CF_4, is mainly by two reactions:[3] (1) homogeneous reaction in the plasma; the active F and O atoms react with SiH_4, which results in the

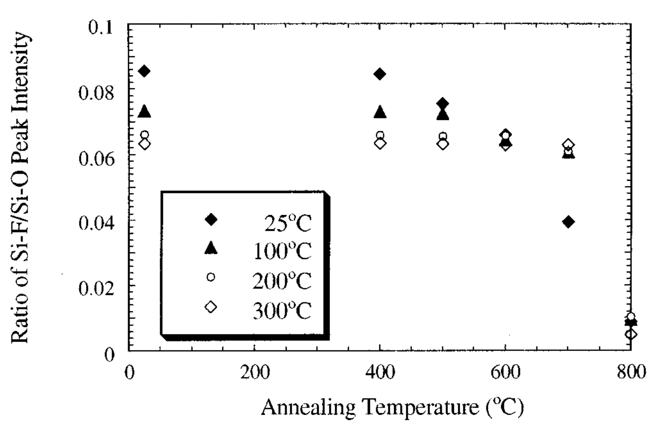

FIG. 1. Variations of Si–F/Si–O peak intensity from FTIR spectrum with different annealing temperatures, for F_xSiO_y films deposited at 25, 100, 200, and 300 °C.

TABLE I. Changes of F_xSiO_y film dielectric constant, refractive index, Si–F/Si–O intensity ratio, Si–F absorbance peak position, density, and mechanical stress due to deposition temperature.

Deposition temperature (°C)	Dielectric constant (k)	Refractive index (*n*)	Si–F/Si–O ratio (FTIR)	Si–F peak (cm^{-1})	ρ^a (g/cm^3)	Stress (MPa)
25	3.17	1.375	0.08552	932.48	1.8418	−74.2
100	3.35	1.406	0.07329	933.39	1.9763	−97.3
200	3.44	1.429	0.06603	934.31	2.0742	−150.4
300	3.51	1.434	0.06336	934.47	2.0953	−203.8

[a]The density of F_xSiO_y (ρ) is determined from an n value using Lorentz–Lorentz relationship:[8] $\rho = K(n^2-1)/(n^2+2)$, where $K=8.046$. The density of thermal SiO_2 is 2.212 g/cm^3.

formation of F_xSiO_y species and deposition and (2) heterogeneous reaction on film surface; the active fluorine is absorbed (physical and chemical) on the deposited film and the unvolatile fluoride will remain in the film during the subsequent deposition. At the same time, the volatile fluoride results in the simultaneous etching. This can be realized from the fact that there will be low deposition rate at high CF_4 flow rate.[3] Therefore, the bonding strength of fluorine in these unvolatile species buried in the film will determine the stability during subsequent thermal cycles. At low deposition temperature, there will be weak bonding or physical adsorbed fluorine buried in the film. Besides, low surface migration energy of the deposited species at low temperature also leads to a less dense network. Upon thermal cycles, these easy-going −F bonds will break and diffuse out. Oppositely, most of the weakly bonded fluorine (fluoride) will be volatile and the film structure will become denser during the high temperature deposition. Therefore, the remaining −F bonds can stand a harsher thermal stress. This reflects in the shift of the Si–F absorbance peak position in the FTIR spectrum. The increase of Si–F peak vibration frequency with the increase in deposition temperature is assumed due to the increase of average bonding strength, as shown in Table I. We can provide a desired thermal tolerance (500–700 °C) for back-end processes simply by adjusting the deposition temperature.

Deposition temperature also affects other properties of F_xSiO_y film, as summarized in Table I. Both of dielectric constant and compressed stress increase with the increasing process temperature, which will result in a higher transmission delay and metal interconnection cracking problems. Therefore, within allowed tolerance for thermal stability, low deposition temperature is preferred.

To investigate the moisture resistance of F_xSiO_y, the follow-up recording of moisture absorption by FTIR spectrum was made, as shown in Fig. 2(a). Except for the 300 °C deposited film, the peak intensity of Si–OH (~3650 cm^{-1}) in the F_xSiO_y films all increases during the 168 h air exposure (25 °C, humidity 42%). Variation of film stress with air-exposure time more distinctly reflects the absorption of moisture, as shown in Fig. 2(b). Note that only 300 °C deposited film did not swell (more compressed) with exposure time. Lower deposition temperature and higher fluorine concentration[3] both lead to a less dense network of oxide, which will enhance the water absorption. Here it is shown that, to get water resistance, the deposition temperature must be greater than 300 °C.

The outgassing of water had been shown to arise reliability problems.[4–7] However, the high deposition temperature, which results in a higher k and higher stress, is also undesirable. Here we find that ECR-SiO_2 (SiH_4/O_2 = 2/85 sccm, 300 W, 3 mTorr) even deposited at room temperature, does not absorb moisture and swelling, as shown in Figs. 2(a) and 2(b). After capping by a thin ECR-SiO_2 layer (40 nm), the moisture absorption of F_xSiO_y film deposited at lower temperature can be prevented. Therefore, the necessity of high deposition temperature for moisture resistance (300 °C) is avoidable.

In summary, using the indirect fluorinating precursor CF_4, the concentration and stability of fluorine in F_xSiO_y

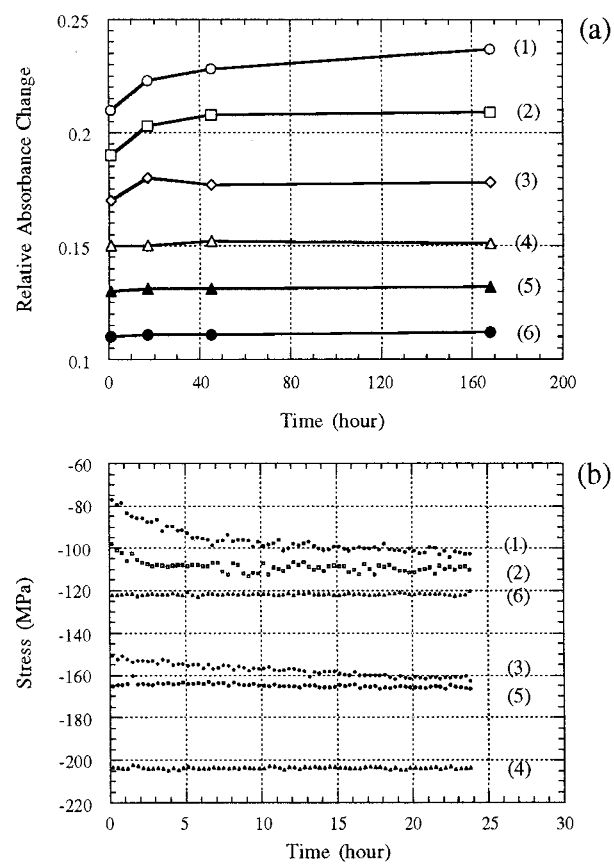

FIG. 2. Variations of (a) Si–OH (~3650 cm^{-1}) peak intensity from FTIR spectrum and (b) mechanical stress with time, in clean room air (25 °C, humidity 42%), for F_xSiO_y (250 nm) deposited at (1) 25 °C, (2) 100 °C, (3) 200 °C, (4) 300 °C, (5) ECR-oxide (250 nm), and (6) ECR-oxide/F_xSiO_y/ECR-oxide (40/240/40 nm) deposited at 25 °C.

film will strongly depend on the deposition temperature. Higher temperature deposition can improve thermal stability but result in a higher *k* and compressed stress. Therefore, within allowed tolerance for thermal stability, low deposition temperature is preferred. The thermal stability (500–600 °C) provided by 100 and 200 °C deposited film is enough for currently used back-end processes. On the other hand, to get a moisture resistance, the deposition temperature must be greater than 300 °C. However, capping a thin ECR-SiO_2 (40 nm) layer (even deposited at room temperature) on F_xSiO_y is shown to prevent water absorption. In this way, high temperature deposition can be avoided.

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