High-Quality Nitrogen-Doped Fluorinated Silicon Oxide Films Prepared by Temperature-Difference-Based Liquid-Phase Deposition

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In this study we investigate the properties of nitrogen-doped fluorinated silicon oxide films deposited on silicon using hydrosilicofluoric acid and ammonium hydroxide aqua as sources by the temperature-difference-based liquid-phase deposition method. The deposition rate increases with the concentration of ammonium hydroxide aqua and the deposition temperature. Fluorine and nitrogen atomic concentrations increase with the concentration of ammonium hydroxide aqua. In the study, the F atomic concentration of the deposited films can range from 5.1% to 9.8%. The dielectric constant of the film is a function of the concentration of ammonium hydroxide aqua and the deposition temperature. At a deposition temperature of 40 °C, the dielectric constant can drop to 3.06 with 0.5 M NH_4OH incorporation. It is suitable for intermetal dielectric application. The films also exhibit good passivation to moisture.

I. Introduction

Advances in ultra-large-scale integrated circuits (ULSI) have led to the necessity for an intermetal dielectric (IMD) with the dielectric constant (k) as low as possible to overcome the limitation of signal delay. As a candidate for low-k IMD material, fluorinated silicon oxide (SiOF) has received extensive interest due to its easily integrated properties and various available precursors.[1,2] In addition, the incorporation of F in metal oxide semiconductor (MOS) structures can improve radiation hardness and hot-carrier-effect immunity.[3,4]

Many deposition techniques for low-dielectric-constant SiOF films have been investigated. The dielectric constant can be below 3.2 when the F content of SiOF films prepared by conventional methods, such as plasma-enhanced chemical vapor deposition (PECVD) techniques, is higher than 4.2%.[5,6] But they are subject to several problems, such as thermal stress, dopant redistribution, material interaction, and substrate warpage due to the high deposition temperature. To remove these problems, low-temperature methods are being developed to grow SiOF films.

Liquid-phase deposition (LPD) is a low-temperature technology for depositing oxide films using hydrosilicofluoric acid (H_2SiF_6) and boric acid (H_3BO_3) as sources.[7] A high concentration of F can be obtained (1.85–6.2 atom %) in the LPD SiO_2 films.[8,9] The role of H_3BO_3 is to consume the hydrofluoric acid (HF) in the solution and drive the deposition of SiO_2 films. On the other hand, the temperature-difference-based liquid-phase deposition (TD-LPD) process entails preparation of the deposition solution of H_2SiF_6 saturated with SiO_2 at a lower temperature (~0 °C), and deposition of SiOF films at a higher temperature (15–40 °C) without the incorporation of H_3BO_3.[10,11] The concentration of F can reach 8.6 atom %. The dielectric constant is about 3.4. The temperature difference controls the deposition rate of LPD SiOF. The higher F concentration of the deposited films is from the higher F concentration in the deposition solution due to the absence of H_3BO_3.

Usually, SiOF films with higher F concentration show higher moisture absorption and a lower breakdown field.[2,12] To improve these drawbacks, we try to prepare a SiOF film doped with nitrogen. Oxynitride exhibits a lower leakage current and higher breakdownfield.[13] Oxynitride is also an excellent diffusion barrier for impurities and exhibits good passivation to moisture and contaminants.[14]

In this paper, we investigate the properties of nitrogen-doped TD-LPD SiOF films by adding ammonium hydroxide aqua (NH_4OH) into the TD-LPD growth solution.

II. Experimental Section

The deposition system contains a Teflon vessel and a temperature-controlled water bath, which offers a uniform temperature environment with an accuracy of ±0.1 °C. The substrate used in this work is p-type, boron-doped, (100)-oriented silicon with a resistivity of 15–25 Ω cm. The preparation procedures of the growth solution used to deposit LPD films are (1) dissolution of high-purity (99.99%) silica gel in a H_2SiF_6 aqueous solution (3.886 mol/L), (2) stirring for 17 h at 5 °C, (3) filtration to remove undissolved silica gel from the treatment solution, and (4) addition of NH_4OH (3 mL, 0.1–1.0 M) to the treatment solution (24 mL) at 23, 30, 35, and 40 °C, respectively.

The properties of the films prepared at various deposition temperatures were investigated. The thickness and refractive index of LPD SiOF were measured by ellipsometry using a Gaertner model L116C autogain ellipsometer at a wavelength of 632.8 nm. The thickness was also examined by scanning electron microscopy (SEM). Metal oxide semiconductor (MOS) capacitors with LPD SiOF films as a dielectric were prepared for electrical characterization. The area of the aluminum electrode was 7.065×10^{-4} cm^2. A high-frequency (1 MHz) Hewlett-Packard 4280A capacitance–voltage meter with a 30 mV signal amplitude was used for the capacitance–voltage

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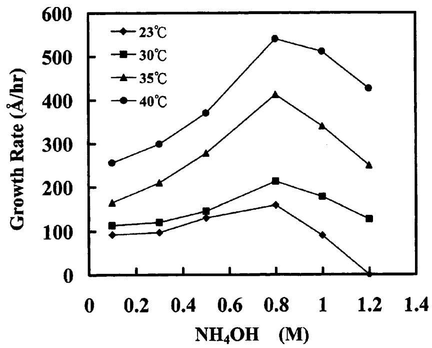

Figure 1. Deposition rate of TD-LPD SiOF films as a function of deposition temperature and NH_4OH concentration.

($C-V$) measurement. An HP4156A semiconductor−parameter analyzer was used for current−voltage ($I-V$) characterization. The compositions of LPD SiOF films were further investigated by X-ray photoelectron spectroscopy (XPS) using an ESCA 210 instrument and secondary ion mass spectroscopy (SIMS) using a CAMECA IMS-4F instrument. The composition was examined by XPS, which can provide information about the chemical bonds of the films. The inaccuracy of XPS is 5%. The error bars are indicated in the related figures. The structure of the film was examined by a SIMS depth profile. SIMS is more sensitive to the chemical species; its limit of detection can reach parts per million (ppm). The thickness of the samples used for XPS and SIMS examinations was several angstroms, which is much thicker than the transition region at the interface. That is to say, the results of the surface investigation technique XPS were from the upper stable layer.

III. Results and Discussion

A very smooth surface morphology of a TD-LPD SiOF thin film can be examined by SEM observation under our experimental conditions. The basic chemical reaction of TD-LPD SiOF deposition was proposed as follows:[7]

$$H_2SiF_6 + 2H_2O \Leftrightarrow 6HF + SiO_2 \ (\Delta H < 0) \qquad (1)$$

The addition of silica gel (SiO_2) will shift the equilibrium of reaction 1 from right to left, and a SiO_2-saturated H_2SiF_6 growth solution is obtained. Moreover, H_2SiF_6 can dissolve more silica gel at a lower temperature because reaction 1 is an endothermic reaction. In this study, the preparation temperature of the deposition solution was fixed at 5 °C. The growth solution becomes supersaturated as the solution temperature increases from the preparation temperature of 5 °C to the deposition temperature from 23 to 40 °C. Then, NH_4OH with various concentrations is added to the deposition solution fixed at a temperature of 23, 30, 35, or 40 °C. The role of NH_4OH in the TD-LPD SiOF deposition is proposed as follows:

$$NH_4OH \Leftrightarrow NH_4^+ + OH^- \qquad (2)$$

$$HF \Leftrightarrow H^+ + F^- \qquad (3)$$

$$H^+ + OH^- \Rightarrow H_2O \qquad (4)$$

The concentration of OH^- ions in the growth solution increases with the concentration of NH_4OH. The H^+ of HF from H_2SiF_6 neutralizes the OH^- from NH_4OH and drives reaction 1 from left to right to enhance the deposition rate. Figure 1 shows that the deposition rate of TD-LPD SiOF films is a function of the deposition temperature in the range of 23−40 °C and the molar concentration of NH_4OH in the range of 0.1−1.2 M. In the range of NH_4OH concentration from 0.1 to 0.8 M, the deposition rate increases with the molar concentration of NH_4OH and the deposition temperature. The deposition rate can be controlled well within 90−540 Å/h. At a concentration of NH_4OH higher than 0.8 M, the deposition rate decreases dramatically. They are from the supersaturated clouded solution from SiO_2 precipitation due to too much NH_4OH addition.[15] A hazy surface morphology is obtained. The deposition rate even drops to 0 Å/h deposited at 23 °C with 1.2 M NH_4OH concentration.

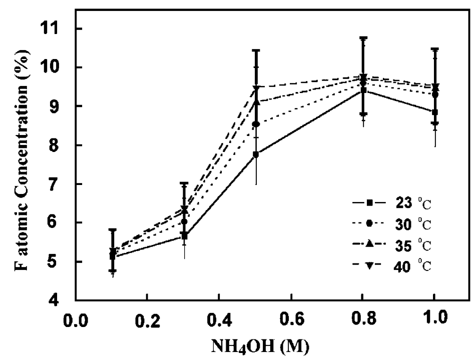

Figure 2. F atomic concentration of TD-LPD SiOF films as a function of deposition temperature and NH_4OH concentration. ■, ●, ▲, and ▼ error bars for 23, 30, 35, and 40 °C, respectively.

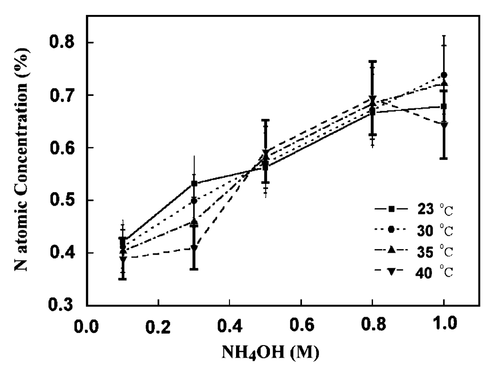

Figure 3. N atomic concentration of TD-LPD SiOF films as a function of deposition temperature and NH_4OH concentration. ■, ●, ▲, and ▼ error bars for 23, 30, 35, and 40 °C, respectively.

The F atomic concentration of TD-LPD SiOF films examined by XPS increases with the NH_4OH concentration in the range of 0.1−0.8 M and with the deposition temperature in the range of 23−40 °C as shown in Figure 2. The increase of deposition temperature or NH_4OH concentration will drive reaction 1 from left to right according to Le Chatelier's principle. The F atomic concentration in the growth solution increases according to reactions 2−4, and therefore, the F atomic concentration increases in the TD-LPD SiOF films. At a NH_4OH concentration higher than 0.8 M, the F atomic concentration of the deposited films decreases with the temperature slightly. They are also from the clouded solution due to SiO_2 precipitation by too much NH_4OH addition. The F is incorporated into the SiO_2 precipitation. In the study, the F atomic concentration of the deposited films ranges from 5.1% to 9.8%. The result indicates that the F concentration of the films prepared by TD-LPD with NH_4OH incorporation is higher than that of the films prepared by conventional LPD (1.85−6.2%)[8,9] and TD-LPD (8.6%).[10,11]

Figure 3 shows the nitrogen atomic concentrations of TD-LPD SiOF films measured by XPS as functions of the molar concentration of NH_4OH and the deposition temperature. The N atom is from the NH_4^+ dissociated from NH_4OH. Basically,

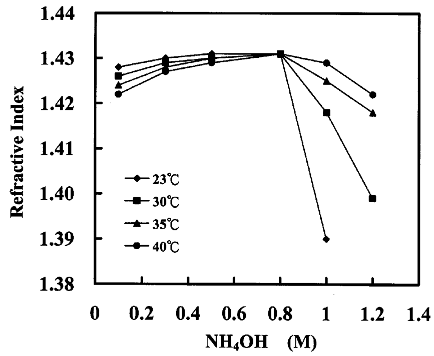

Figure 4. Refractive index of the TD-LPD SiOF films as a function of deposition temperature and NH_4OH concentration.

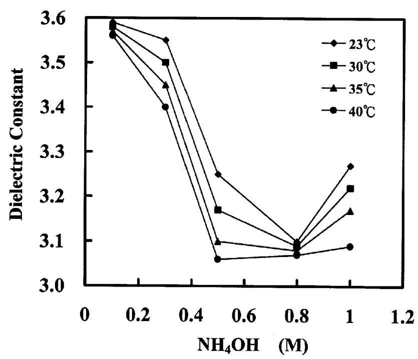

Figure 5. Dielectric constant of TD-LPD SiOF films as a function of deposition temperature and NH_4OH concentration.

it has the same tendency as F incorporation. Higher NH_4OH concentration or higher deposition temperature drives both reactions 1 and 2 from left to right and induces higher N atom concentrations in TD-LPD SiOF films. The N concentration is much lower than the F concentration in the solution for the SiOF film deposition. A 6 M F concentration resulted for 1 M SiO_2 formation from reaction 1, but only 1 M N resulted from reaction 2.

However, it has a tendency opposite that of F concentration shown in Figure 2 in the range of 0.1−0.3 M NH_4OH. The N concentration of SiOF films decreases with increasing deposition temperature. The deposition rate increases with the deposition temperature as shown in Figure 1. At the limited concentration of NH_4OH, the N concentration in the film decreases with the deposition temperature. Also, the NH_4OH concentration is higher than 0.8 M, and the N atomic concentration of the deposited films decreases with the temperature slightly. N is also incorporated into the SiO_2 precipitation in the clouded solution by too much NH_4OH addition.

The refractive index of TD-LPD SiOF films is almost independent of the molar concentration of NH_4OH and the deposition temperature as shown in Figure 4. In general, the refractive index of a SiO_2 film increases with the number of Si−N bonds[16,17] and decreases with the number of Si−F bonds.[5] The refractive index is almost kept at 1.43 with the NH_4OH concentration in the range of 0.1−0.8 M owing to the compensation effect of F and N. The drop of the refractive index with NH_4OH concentration higher than 0.8 M is attributed to the hazy morphology deposited by the clouded solution.

Figure 5 shows the dielectric constant of LPD SiOF films as a function of the concentration of NH_4OH from 0.1 to 1.0 M and the deposition temperature from 23 to 40 °C. Figures 2 and 3 show that F and N concentrations increase with the NH_4OH molar concentration and the deposition temperature.

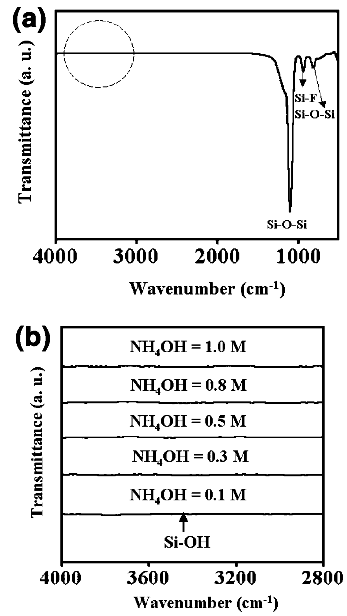

Figure 6. (a) Typical FTIR spectrum of an about 800 Å thick TD-LPD SiOF:N film and (b) FTIR spectra of TD-LPD SiOF:N films with various concentrations of NH_4OH incorporation.

However, they also show that the increase of the F concentration is much higher than that of the N concentration. Therefore, the dielectric constant of LPD SiOF films is dominated by the F concentration and decreases with the concentration of NH_4OH from 0.1 to 0.8 M and the deposition temperature from 23 to 40 °C. At a deposition temperature of 40 °C, the dielectric constant can drop to 3.06 with 0.5 M NH_4OH incorporation. The increase of the dielectric constant with NH_4OH concentration higher than 0.8 M is attributed to the F and N concentration decrease in the deposited films by the clouded solution.

Figure 6a shows the typical FTIR spectrum of an about 800 Å thick TD-LPD SiOF:N film. The absorption peaks at around 1090 and 810 cm^{-1} are due to the stretching and bending vibrations of Si−O−Si bonds. The absorption peak at 930 cm^{-1} is from the Si−F stretching vibration. The absorption band of Si−OH bonds was not observed in the range of 3200−3700 cm^{-1}.[9,18] The FTIR spectra of TD-LPD SiOF:N films with various concentrations of NH_4OH incorporation are shown in Figure 6b, which shows the absorption band from 2800 to 4000 cm^{-1}. Obviously, the band of Si−OH bonds was not observed in the TD-LPD SiOF:N films deposited at 40 °C with various concentrations of NH_4OH incorporation. These results show that the TD-LPD SiOF:N films exhibit good passivation to moisture as oxynitride films do.[14]

The lower dielectric constant TD-LPD SiOF films can be obtained at a deposition temperature of 40 °C. The electrical characteristics of those samples were examined. Figure 7a shows the *C*−*V* characteristics of TD-LPD SiOF films deposited at 40 °C with the NH_4OH concentration in the range of 0.1−1.0 M. The *C*−*V* curves show that the deep depletion capacitance is slightly lower than the inversion capacitance. This is because the film has a two-layer structure.[19,20] This is examined by the SIMS depth profile as shown in Figure 8 for a typical TD-LPD SiOF film deposited at 40 °C with a thickness of about 1850 Å. The profiles of Si, H, O, F, and N are indicated. F is distributed uniformly throughout the film. The nitrogen is accumulated at the interface of SiOF/Si, which is similar to the deposition by CVD.[15] Therefore, multilayers of N-doped SiOF/F-doped SiON/SiO_x/Si is the equivalent structure of a nitrogen-doped TD-LPD SiOF film and is shown in Figure 9.

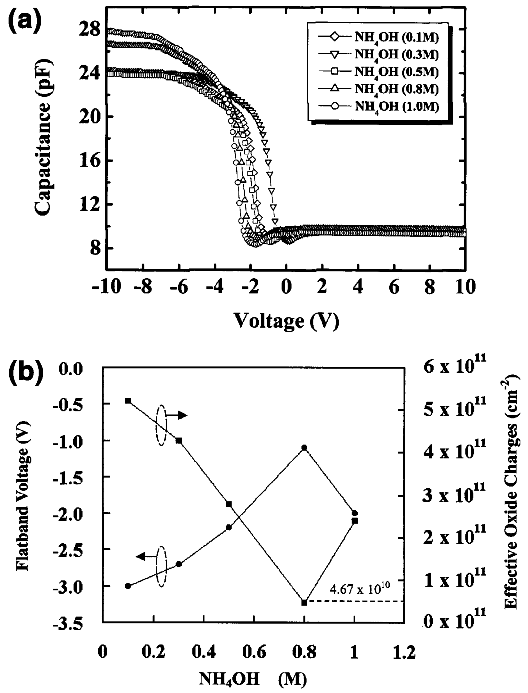

Figure 7. (a) High-frequency (1 MHz) *C*−*V* curves and (b) flat-band voltage shift and effective charges of TD-LPD SiOF films deposited at 40 °C as a function of NH_4OH concentration.

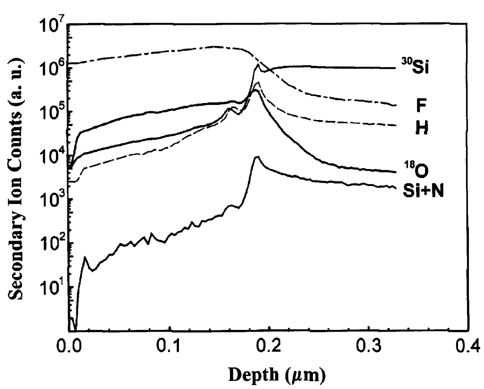

Figure 8. SIMS depth profile of a typical nitrogen-doped TD-LPD SiOF film deposited at 40 °C.

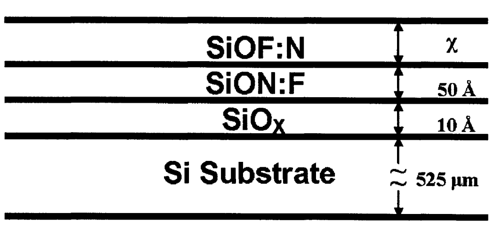

Figure 9. Multilayer structure model of a nitrogen-doped TD-LPD SiOF film.

The flat-band voltage shift and effective oxide charges as a function of the molar concentration of NH_4OH are shown in Figure 7b. These results show that the effective positive charges decrease with increasing concentration of NH_4OH from 0.1 to 0.8 M in the TD-LPD SiOF films. This is from the decrease of the traps by higher N[21] and F[2] concentrations in the SiOF films with the concentration of NH_4OH. At a concentration of NH_4OH of 0.8 M, the effective oxide charges could reach 4.67×10^{10} cm^{-3}. The effective oxide charges increase with the concentration of NH_4OH higher than 0.8 M due to many defects contained in the hazy films deposited by the clouded solution.

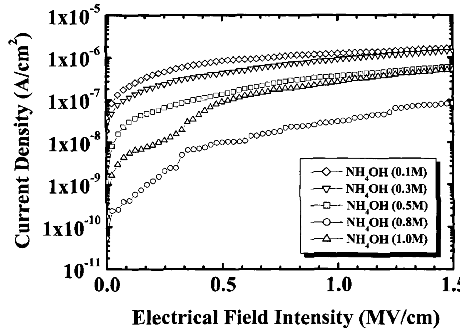

Figure 10. *J*−*E* relationship of TD-LPD SiOF films deposited at 40 °C as a function of NH_4OH concentration.

Figure 10 shows the *J*−*E* characteristics for the films deposited at 40 °C as a function of the electrical field with the NH_4OH concentration range of 0.1−1.0 M. The breakdown fields of all the deposited films exceed 1.5 MV/cm, which is significantly large for intermetal dielectrics. The leakage current density decreases with the NH_4OH concentration. The improvement of leakage current with the NH_4OH concentration is due to the increase in the number of Si−F[2] and Si−N bonds, which passivate and neutralize Si dangling bonds of LPD SiOF films.[22,23] The leakage current density of the film is on the order of 10^{-8} A/cm^2 under 1.5 MV/cm and on the order of 10^{-10} A/cm^2 under 0.2 MV/cm with the NH_4OH molar concentration fixed at 0.8 M. The leakage current density increases approximately linearly with voltage at very low electric fields. The ohmic behavior is due to the hopping conduction mechanism of trapped electrons by dangling bonds.[24] The Schottky mechanism dominates at high electric fields.[25] It can be concluded that the TD-LPD SiOF film nitrided by NH_4OH shows excellent electrical quality in terms of *C*−*V* and *I*−*V* measurements. At a concentration of NH_4OH of 1 M, the film contains many defects due to the supersaturated clouded solution, and the electric properties of the films are degraded.

IV. Conclusions

High-quality and low-dielectric-constant nitrogen-doped SiOF films can be grown on Si by the TD-LPD method with NH_4OH incorporation. In this study, the growth rate can be controlled well within 90−540 Å/h and the refractive index can be kept at about 1.43 corresponding to the NH_4OH concentration range of 0.1−0.8 M and the temperature range of 23−40 °C. F and N concentrations of the nitrogen-doped TD-LPD SiOF films are functions of the NH_4OH concentration and the deposition temperature. The effective oxide charges can reach 4.67×10^{10} cm^{-2}, and the leakage current density can be on the order of 10^{-8} A/cm^2 under 1.5 MV/cm at a concentration of NH_4OH of 0.8 M. The dielectric constant can be about 3.06. The low dielectric constant is from the higher F concentration in the silicon oxide films due to the incorporation of NH_4OH. The good passivation to moisture is from the N incorporation. The high electrical properties are from both N and F concentrations in nitrogen-doped TD-LPD SiOF films. The nitrogen-doped SiOF films by the TD-LPD method with NH_4OH incorporation are suitable for IML application.

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