Evolution of Fluorine Content with Precipitate Formation in Fluorine-Doped Silicon Oxide

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Precipitates appear on fluorine-doped silicon oxide (SiOF) film when the film surface is exposed to atmospheric air. They are flake-type and hexagonal-shaped and show up rapidly after initiation, clustered at wafer center. It was found that the onset of precipitation is closely related to fluorine concentration of SiOF films, those with higher fluorine content exhibit high propensity of precipitation, along with more significant fluorine loss. In this study, the microstructural changes of SiOF films in the course of precipitation were examined. The Fourier transform infrared spectra of SiOF films showed the declined intensities of Si–F_n ($n = 1, 2$) bonding peaks at time after the formation of precipitates. In the surface analysis by X-ray photoelectron spectroscopy, the binding energy of F 1s reduced ∼0.5 eV after precipitation, indicating also decreased Si–F_n bonding on the surface layer of SiOF films. Meanwhile, analysis by thermal desorption spectroscopy indicated that the unstable fluorine content in the SiOF film is significantly reduced after precipitation.

1. Introduction

Fluorine-doped silicon oxide film (SiOF) has been found to be very effective in the reduction of dielectric constant over undoped oxide films and has been adopted as one of the low-*k* materials as interlayer dielectrics in ultralarge scale integrated (ULSI) circuit manufacturing to decrease the parasitic capacitance along the wiring, reducing RC delay effect and thus drive for higher device speed. The SiOF film is easily deposited by simply introducing a fluorine source gas into the plasma-enhanced chemical vapor deposition (PECVD) system for silicon oxide. The reduction of dielectric constant has been attributed to the incorporation of highly electronegative fluorine. The substitution of Si–F bonds for Si–O bond causes changes in the Si–O network to a less polarizable geometry.[1] The dielectric constant decreases with the increase of the fluorine concentration in SiOF films. Nevertheless, the incorporation of fluorine also worsens film stability. SiOF film is susceptible to moisture absorption. Films with high fluorine content become interactive with water from the atmosphere, and consequently degradation of film quality and increase of dielectric constant could be observed.[2] In addition to structural instability of SiOF film reported elsewhere, one specific feature — precipitation of fluorine-doped silicon oxide was observed. Such defects generated in semiconductor processing could induce film delamination and metal bridges, resulting in detrimental effect on device performance. Moreover, the microstructure and consequent dielectric properties of SiOF film could also be altered as a result of precipitation.

In this work, precipitation of SiOF film deposited by PECVD using SiH_4 and SiF_4 after exposure to the ambient atmosphere was studied to investigate its impact on the microstructure of SiOF films, especially on the behavior of fluorine which dominates the dielectric properties of SiOF film. The effects of the precipitation process on the properties of SiOF films are investigated by describing the evolution of fluorine concentration in the films. The fluorine concentration would decay as a result of the reduction of unstable fluorine after precipitation.
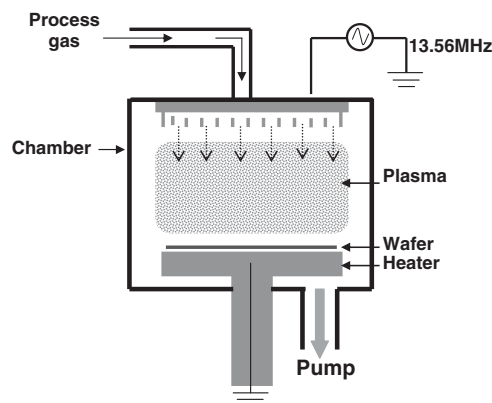

Fig. 1. Schematic of the plasma enhanced chemical vapor deposition reactor.

Table I. Key process parameters in this study.

Temperature (°C)	400
Pressure (Torr)	2
Plasma (W)	200
SiH_4 (sccm)	85
SiF_4 (sccm)	60–100
N_2O (sccm)	160
N_2 (sccm)	1000

2. Experimental Procedure

SiOF films were deposited on 200 mm n-type silicon substrates in a PECVD system using $SiF_4/SiH_4/N_2O$. Figure 1 shows schematic of the apparatus used for film deposition. Gas mixture was introduced from the top of chamber and excited with 13.56 MHz rf power by an inductively coupled plasma source. The detailed process conditions of film deposition were listed in Table I. Flow rates of SiF_4 were varied in a wide range from 60 to 100 sccm to obtain SiOF films of 400 nm thickness with different fluorine content. The SiOF film thickness was measured by an ellipsometer incorporating a He–Ne laser source using a Nano-Spec 9100. Surface morphology of the precipitates on SiOF film was characterized by Applied

Materials SEMVision integrated defect review scanning electron microscopy (SEM). The measurement of Fourier transform infrared spectroscopy (FTIR) was performed in the absorbance mode with a Bio-Rad Win-IR PRO. The bonding configuration of SiOF films were investigated by identifying the absorption peak positions in FTIR spectra ranging from 600 to 4000 cm^{-1}, measured by double-beam spectrometer. Each sample was scanned 64 times and the resulting spectra were averaged for accuracy concern. The resolution of IR spectrum was about 4 cm^{-1}. The concentration of fluorine was derived from the Si–F$_n$ ($n = 1, 2$) absorption band in FTIR within the range of 900–950 cm^{-1}. The plasma discharge was maintained at 200 W and the substrate temperature was kept constant at 400 °C for all depositions. After deposition, SiOF films were exposed to the ambient atmosphere at room temperature, 45% relative humidity (post-deposition period). X-ray photoelectron spectroscopy (XPS) analysis was conducted to verify the surface characteristics of SiOF films. The XPS spectra were obtained using a Thermo VG-310F spectrometer equipped with a spherical capacitor energy analyzer. An unmonochromatized Al Kα source (1486.6 eV) was used with anode voltage and power setting of 12 kV and 300 W, respectively. The spectra were performed at a 45° take-off angle, with a pass energy of 23.5 eV. Typical operating pressure was in the range of 10^{-10} Torr. Thermal desorption spectroscopy (TDS) analysis was conducted using FSM 900 to investigate the desorption species from SiOF film. A constant heating rate of 10 °C per min. from room temperature (25 °C) to 600 °C was used for this measurement. Throughout the experiment, the precipitates count inspection was performed by KLA SP1 bright field surface scanner system. An abrupt increase in particle count (from $\sim 10^1$ to $> 10^3$ order) in 1 h time interval was considered as the initiation of precipitation.

3. Results and Discussion

Figure 2(a) shows the SEM image of precipitates. Precipitation initiated spontaneously, forming hexagonal-shaped, $\sim 1 \times 1 \, \mu m^2$-sized flakes when SiOF films were exposed to the atmosphere. Figure 2(b) shows the mapping of the precipitate distribution on wafer. These precipitates rapidly showed up after the onset of precipitation and mostly clustered densely at wafer center. The precipitate counts increased rapidly then gradually saturated, and could amount to as high as $> 10^4$ at saturation.

It has been reported that the incorporation of fluorine creates FTIR absorption bands attributable to Si–F$_n$ bonds in the wave number between 900 and 1000 cm^{-1}.[3,5,10] The concentration of fluorine could be estimated from the Si–F$_n$ absorption band in FTIR, and the evolution of the Si–F$_n$ band indicates the changes of fluorine content in SiOF films. Figure 3 shows the FTIR spectra of SiOF films at (a) as-deposited, (b) post-deposition 5 h, (c) post-precipitation (exposed to the ambient atmosphere at room temperature, 45% relative humidity, at time after the precipitate counts had saturated) stages. The Gaussian fit to (a) and the individual peaks were also plotted on the same figure. The FTIR spectra in 750–950 cm^{-1} region consists of superimposed peaks of Si–O bending and Si–F$_n$. The absorption peaks contributing the band spectra in this region were deconvoluted assuming that this band consists of several
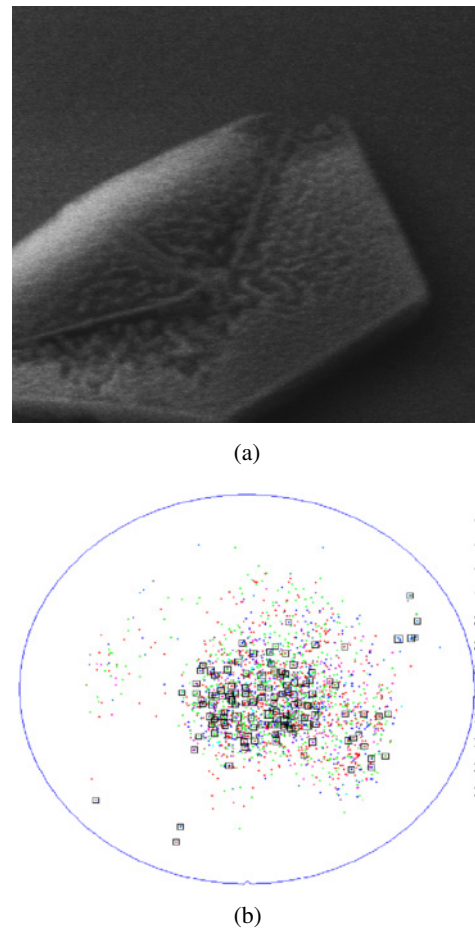

(a)

(b)

Fig. 2. (Color online) (a) SEM image of precipitates on the surface of SiOF films. (b) Wafer mapping of the precipitates distribution. The squares drawn on the scheme represent the location of aggregated precipitates.
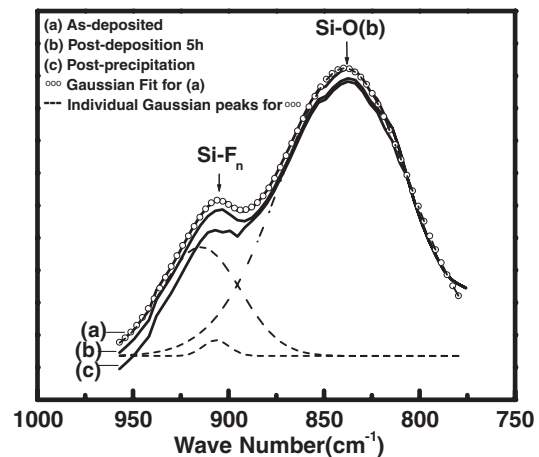

Fig. 3. FTIR spectra of SiOF films at (a) as-deposited, (b) post-deposition 5 h, (c) post-precipitation. Solid lines are the infrared spectra. The open circles are Gaussian fit to the spectra of (a), and the dashed line refer to each deconvoluted Gaussian peaks. [The Gaussian fits to (b) and (c) were not shown for clarity.]

peaks with Gaussian profile shapes. The peaks at 837 cm^{-1} was attributed to Si–O bending, while the peaks at 904 and 916 cm^{-1} were attributed to the symmetric silicon difluoride [Si(O–)$_2$F$_2$] stretching vibrational mode and the silicon monofluoride [Si(O–)$_3$F], respectively A sum of the three deconvoluted Gaussian peaks perfectly fits the spectrum of

as-deposited SiOF film. Since the absorbance of SiF$_n$ band is proportional to fluorine concentration and thickness, the ratio of the absorbance of SiF$_n$ to that of Si–O will be a measure of fluorine content independent of thickness. The fluorine content in this study were estimated by dividing the total absorbance of SiF$_n$ band integrated over each deconvoluted Gaussian peak by that for Si–O stretching peak ($\sim$1080 cm^{-1}).[11,12] This ratio was correlated to the known atomic percent level of fluorine measured by using XPS, and was in good accuracy within 10% uncertainty limit. It could be also observed in Fig. 3 that the intensity of Si–F$_n$ peak dropped after 5 h of exposure to air (post-deposition 5 h stage), and the precipitation led to further decline of the Si–F$_n$ peak (post-precipitation stage). The drop in fluorine content after 5 h of exposure to air could be attributed to the hydration or the interaction of fluorine with moisture, whereas the further decline of fluorine content at the post-precipitation stage implicates the participation of fluorine in the formation of precipitates.

As reported in our previous work,[4] since the onset of precipitation is closely related to fluorine concentration of SiOF films and precipitates showed up rapidly after its initiation, the time interval between the as-deposition and the appearance of precipitates varies for different fluorine concentrations. Figure 4(a) shows the variation of precipitate counts and fluorine content with time in the post-deposition period (post-deposition time) for SiOF films with two as-deposited fluorine levels (4 and 6 at. %). For SiOF films with 4 at. % of as-deposited fluorine content, the onset of precipitation occurred at about post-deposition 7 h, with a prominent drop of fluorine content. Nevertheless, for SiOF films with 6 at. % of as-deposited fluorine content, precipitation started within only post-deposition 4 h, accompanied also with a pronounced loss of fluorine content. Figure 4(b) re-plotted Fig. 4(a) and magnified the scale of fluorine content to trace the evolution of fluorine concentration in the post-deposition period. A gradual decrease of the fluorine content was observed in the post-deposition period, since the fluorine in SiOF is prone to react with moisture in the ambient atmosphere. Nevertheless, for either fluorine levels, a prominent drop of fluorine content occurred at the onset of precipitation, but the decline of fluorine content became no longer apparent afterwards. Moreover, SiOF films with higher fluorine content exhibit high propensity of precipitation, along with more significant fluorine loss. Figure 5 illustrated XPS surface analysis results of the (a) as-deposited and (b) post-precipitation SiOF films. The binding energy peak at 687 eV attributed to F 1s of Si–F species[6,7] reduced $\sim$0.5 eV after precipitation, which indicates the decrease of Si–F bonding at the surface layer of SiOF films. This result is consistent with that concluded from FTIR that the fluorine content of SiOF films will reduce after the precipitation process.

The microstructure of the SiOF films consists of the amorphous matrix, with incorporation of pores of irregular shape and size. The incorporated monovalent fluorine in SiOF films forms Si–F$_n$ bonds and terminates the Si–O–Si host network,[8] thus the degree of cross-linking decreases and the pore (void) size increases. Thermal gas evolution experiments are known to give information about the presence of pores (voids) in materials. The effusion peaks
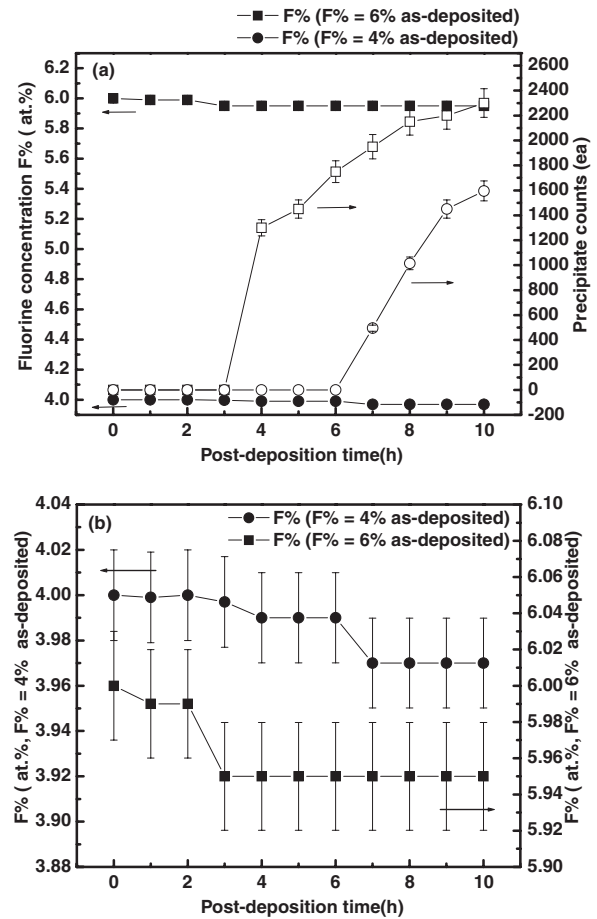

Fig. 4. (a) Precipitate counts (open symbols) as well as fluorine content (filled symbols) variation with post-deposition time for SiOF films of 4 and 6 at. % as-deposited fluorine levels. (b) The re-plot of Fig. 2(a), which magnified the scale of fluorine content.
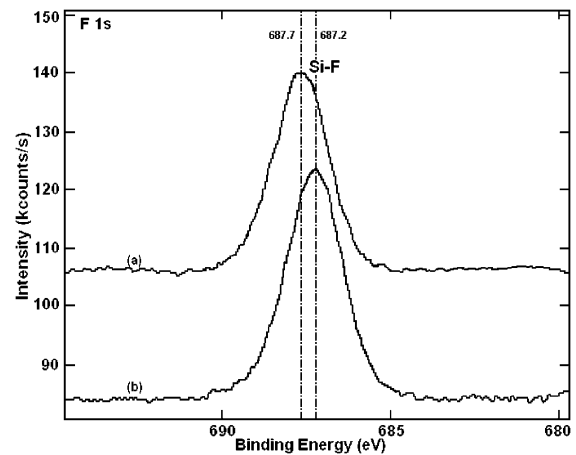

Fig. 5. XPS surface analysis result of the (a) as-deposited and (b) the post-precipitation SiOF films.

in the thermal desorption (TD) spectra are explained by the desorption of species from an interconnected void network and by gas species trapped in isolated voids which break up when the pressure inside the voids exceeds a certain value or when the film undergoes structural changes.[9] Figure 6 shows the TD spectra for the SiOF films with 6 at. % of as-deposited fluorine content at as-deposited, post-deposition 2 h, and post-precipitation stages. The mass fragments of (a) 18 m/z, (b) 19 m/z, and (c) 20 m/z correspond to the water,
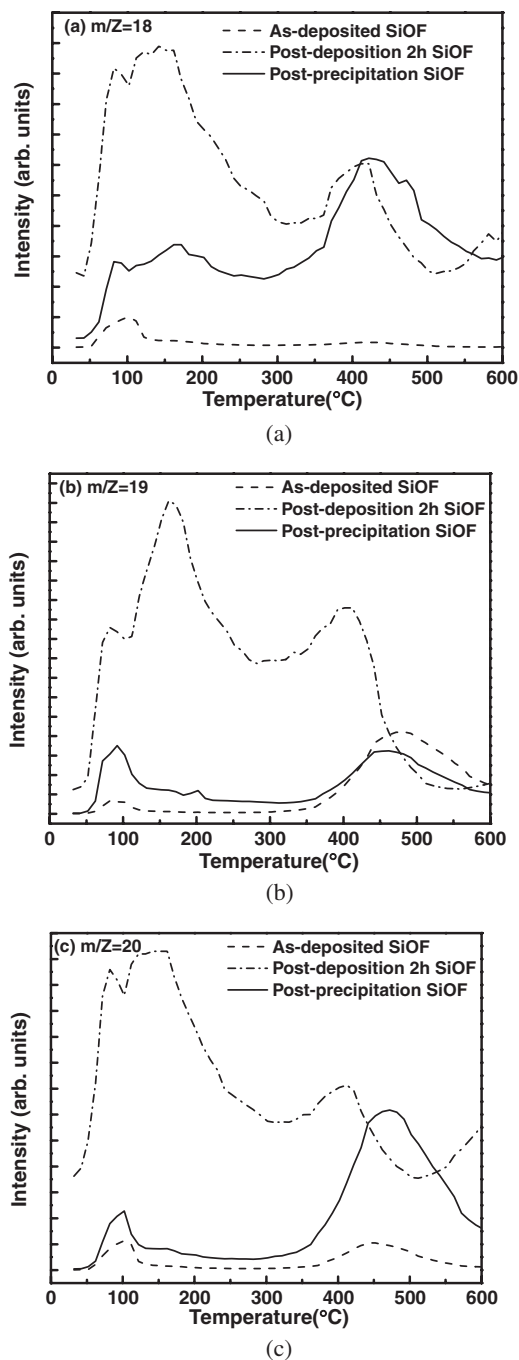
(a)

(b)

(c)

Fig. 6. TD spectra for the SiOF films with 6 at.% as-deposited fluorine content at as-deposited, post deposition 2 h, and post-precipitation stages. The mass fragments of (a) 18 *m/z*, (b) 19 *m/z*, and (c) 20 *m/z* correspond to the water, fluorine, and hydrogen fluoride.

are possibly from the hydrogen–fluoride molecules hydrogen-bonded to the Si–OH or Si–F bonds in the network. From these TD spectra, it can be concluded that the largest desorption peaks for either of these mass fragments are from SiOF films in the post-deposition period for 2 h, when the SiOF films have undergone significant moisture adsorption, and the precipitation is about to occur. After precipitation, the desorption of these mass fragments all diminishes, implicating that part of the unstable fluorine in SiOF film has been reduced through the precipitation process. The SiOF films with high as-deposited fluorine content (>4 at.%) is known to be a "metastable" phase,[10] and interaction with ambient environment during the post-deposition period could further induce structural changes as well as crystallization. In the present study, the precipitation of SiOF films seems to be a form of "structural relaxation", the oversaturated unstable fluorine in the SiOF film is likely to take part in the precipitation process, resulting in a prominent loss of fluorine content in SiOF film after precipitation.

4. Conclusions

Precipitation was observed on the surface of fluorine-doped silicon oxide film when exposing the films to ambient atmosphere for hours after film deposition. The FTIR spectra indicated that the precipitation led to the declining intensity of Si–F_n ($n = 1, 2, \ldots$) bonding. XPS surface analysis also showed the decrease of the Si–F bonding at the surface layer of SiOF films after precipitation. A prominent drop of fluorine content occurred at the onset of precipitation. TD spectra revealed that desorption of H_2O and fluorine-containing species from SiOF films reached maximum after the exposure to ambient atmosphere. Nevertheless, desorption of these mass fragments will diminish after precipitation, implicating that part of the unstable fluorine in the SiOF films has been reduced. The unstable fluorine in the SiOF film is likely to take part in the precipitation process, resulting in a prominent loss of fluorine content in SiOF film after precipitation.

fluorine and hydrogen fluoride, respectively. In Fig. 6(a), the water desorption peaks in the temperature range from 100 to 200 °C are ascribed to physically absorbed water, while those at around 400 °C are ascribed to water molecules hydrogen bonded to isolated Si–OH bonds. In Fig. 6(b), the broad desorption peaks at around 400 °C are ascribed to fluorine from the Si–F bond structure, and the desorption peaks at around 100 °C are related to fluorine atoms which are dissociated from adsorbed hydrogen–fluoride molecules. The desorption peaks at around 100 °C observed in Fig. 6(c) are ascribed to free hydrogen–fluoride molecules adsorbed in the SiOF network, and the desorption peaks at around 400 °C

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