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# Precipitates formation and its impact on the structure of plasma-deposited fluorinated silicon oxide films

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**Abstract**

Fluorine-doped silicon oxide (SiOF) films prepared by plasma enhanced chemical vapor deposition would generate precipitates on the film surface during exposure to air. The chemical and structural changes of SiOF films during the precipitation process were investigated under various fluorine-doping concentrations in SiOF films. Film composition depth profiles characterized by secondary ion mass spectrometer (SIMS) indicate uneven fluorine distribution within SiOF film after precipitation. During the precipitation process, the Fourier transform infrared (FTIR) spectra of SiOF films showed the decreasing trend in the intensities of Si–$F_n$ ($n=1$, 2...) bonding peak, whereas an opposing trend in Si–OH bonding as well as the shoulder peak of Si–O stretching mode were observed. Moreover, the formation of the precipitates lead to lower refractive index, a relief in compressive residual stress, and higher wet etch rate of SiOF films. The structural changes of SiOF films due to the formation of precipitates were extensively discussed.
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*Keywords:* Fluorine-doped silicon oxide; Precipitation; Defects; Si–F bond

## 1. Introduction

With the progress of ultralarge scale integrated (ULSI) technology, it is essential to reduce wiring capacitance and to minimize the signal delay as the space between metal lines decreases to the sub half-micron level. It is well accepted that low-k materials are inevitable at the sub-0.13 μm technology nodes. Fluorine-doped silicon oxide film (SiOF) has been found to be very effective in the reduction of dielectric constant and has become the most desirable because of its good thermal stability, similarity to silicon oxide, and easy integration into existing silicon processing. The SiOF film is easily deposited by simply introducing a fluorine source gas into the plasma-enhanced chemical vapor deposition system for silicon oxide. The incorporation of highly electronegative fluorine causes changes in the Si–O network to a less polarizable geometry and results in a reduction of the dielectric constant. The dielectric constant of a film decreases with the increase of the fluorine concentration in the film. However, it also reduces film stability. SiOF film is susceptible to moisture absorption. Film with a high fluorine content become interactive with water from the air, and consequently results in a degradation of film quality and increase of dielectric constant. Many researches have focused on the detrimental effects of water absorption on the properties of SiOF films [1]. In addition to structural instability of SiOF bonding reported elsewhere, one specific feature-precipitation of fluorine-doped silicon oxide was also observed.

Fig. 1 shows the SEM images of the various growing stages of precipitates from SiOF films. As investigated in our earlier report [2], precipitation initiated spontaneously forming hexagonal-shaped structure while SiOF film was exposed to ambient atmosphere. Such defects generated in semiconductor processing could cause detrimental effect on device performance. In this study, effects of the precipitation behavior on the bonding configurations as well as the film characteristics were investigated, and the resulting film

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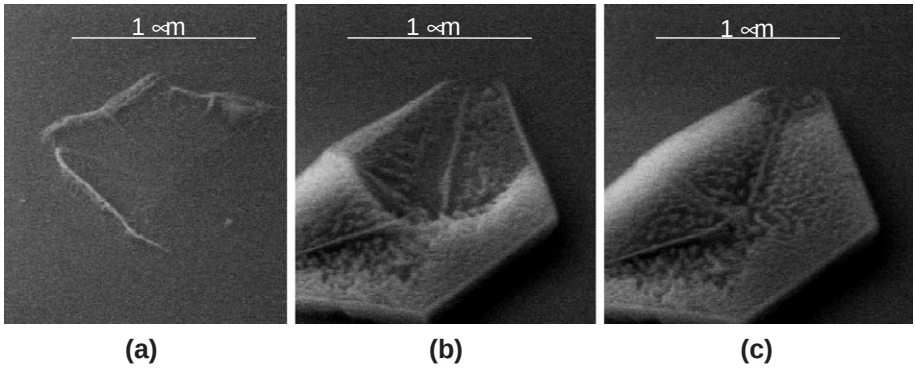


Fig. 1. SEM images showing various stages of the growth of precipitates from SiOF films: (a) precipitate initiation, (b) precipitate formation, and (c) precipitate completion.

property changes after the precipitation of SiOF films were discussed.

## 2. Experimental

SiOF films were deposited on 200 V cm *n*-type silicon substrates in a remote plasma enhanced chemical vapor deposition system using $SiF_4/O_2$ gas mixture. The reaction chamber was equipped by an inductively coupled plasma source. The plasma discharge was maintained using 13.56 MHz rf power at 200 W to decompose the gas mixture for all depositions. Flow rates of $SiF_4$ were varied in a wide range from 60 to 100 sccm to obtain SiOF films of 4 kÅ thickness with different fluorine content. After deposition, SiOF films were exposed to the ambient atmosphere at 25 °C, 45% relative humidity. SIMS analysis was conducted to investigate the changes of fluorine concentration profile before and after the precipitation of SiOF film. Samples subjected to SIMS analysis were capped with PECVD $SiO_2$ 2 kÅ to avoid contamination and further reaction with atmospheric air. The fluorine concentration in the film is expressed as fluorine atomic percentage from FTIR measurement. The chemical bonding configuration of the SiOF films were investigated by identifying the absorption peak positions in FTIR spectra ranging from 4000 to 600 $cm^{-1}$, 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 film thickness and

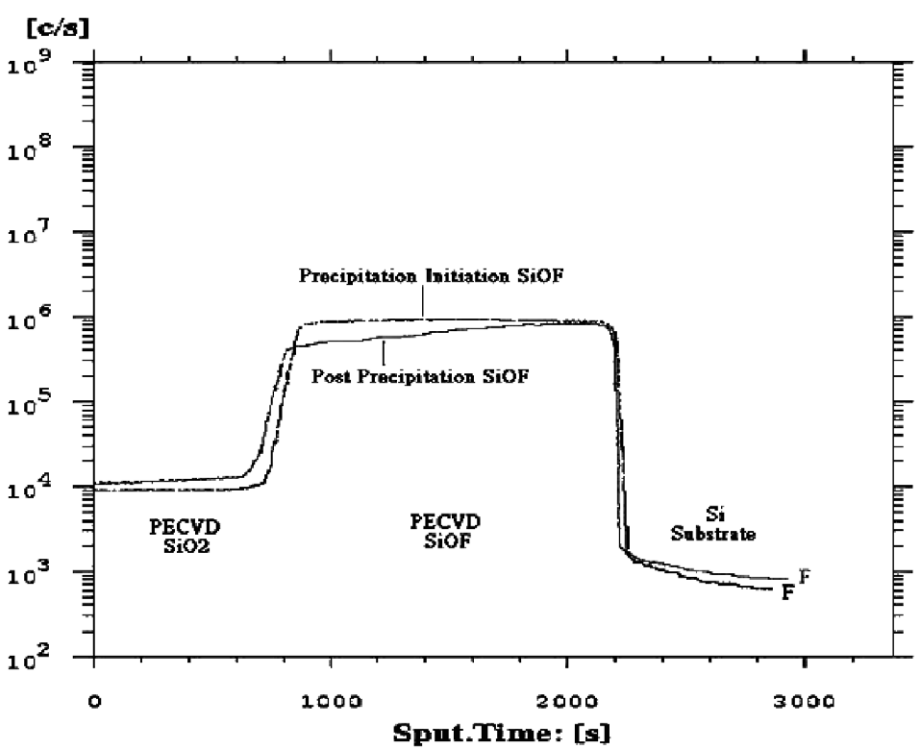


Fig. 2. SIMS F% profiles of SiOF film at precipitation initiation and post precipitation stages.

refractive index were determined by a spectroscopic ellipsometer at a 74.9° incident angle. The chemical wet etching rate of oxides was tested using 10 : 1 $NH_4F$ buffered HF oxide etcher (10 : 1 BOE) solution. To monitor the wet etch rate, film thickness was measured before immersing the samples into the 10 : 1 BOE chemical solution for 2 min. After the immersion, the samples underwent standard cleaning process, and then post-etch thickness measurement. The thin film stress is calculated by subtracting the original radius of curvature of the wafer to obtain the net radius of curvature change due to the thin film process. Throughout the experiment, the precipitates count was measured by particle measurement tool (Tool type KLA SP1). An abrupt increase in particle count (from $\sim 10^1$ to $> 10^3$ order) in one time interval was considered as the start of precipitation.

## 3. Results and discussions

In Fig. 1, the growth of the precipitates on SiOF film was divided into three stages:(a) precipitate initiation, (b) precipitate formation, and (c) precipitate completion (post precipitation). The whole process of growth (from initiation to completion) often takes less than 1 hour. The following analysis on SiOF film properties was conducted from the as-deposited SiOF film to these three stages of precipitate growth to monitor the changes in film structure and bonding configuration throughout the precipitation process. As reported in our previous work [2], since the onset of precipitation is closely related to fluorine concentration of SiOF films and the relative humidity in ambient atmosphere, the interims between as-deposited and the initiation of precipitation on SiOF film surface vary significantly for

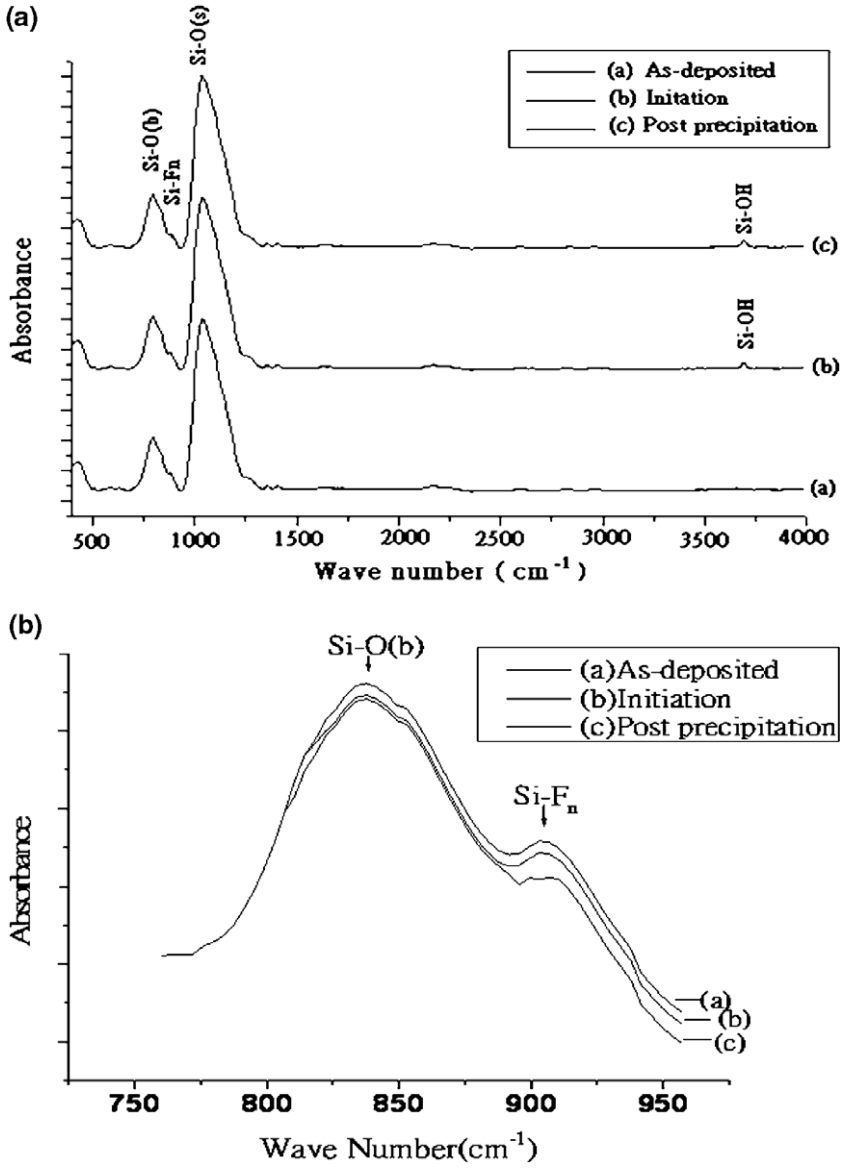


Fig. 3. FTIR spectra of SiOF film with 4 at.% fluorine concentration during precipitation.

various fluorine concentrations (from ~3 hours for 9 at.% SiOF film to ~8 hours for 4 at.% SiOF film under 45% relative humidity). Fig. 2 compares the fluorine concentration depth profiles from SIMS analysis for SiOF films at precipitate initiation stage and post precipitation stage. A relatively flat profile of fluorine was observed for the SiOF films at the precipitate initiation stage, indicating that F is uniformly distributed throughout the SiOF film. Nevertheless, rather surprisingly a sloped profile of fluorine showed up for the precipitated SiOF film, indicating that fluorine concentration increases with sample depth. The uneven distribution of fluorine within the precipitated SiOF film implicated that fluorine on the SiOF film surface participated in the formation of precipitates. The top surface of SiOF film evidently acts as a sink for fluorine, and the formation of precipitates on film surface apparently provides the driving force for fluorine species to diffuse from the bulk of SiOF film to the film surface.

To clarify the effects of precipitation on SiOF film structure, the changes in the FTIR spectra of SiOF films at these three stages were investigated, focusing on the OH stretching vibration bands (wave number ~ 3670 $cm^{-1}$), the band due to silicon fluoride sites (Si–$F_n$, $n=1, 2\ldots$, wave number ~900 to 1000 $cm^{-1}$), and the Si–O–Si stretching vibration band (wave number ~1080 $cm^{-1}$). Fig. 3 shows the evolution of FTIR spectra during precipitation of the SiOF films with 4 at.% of fluorine concentration. From the as-deposited to the precipitate initiation stage, only slight increment in Si–OH peak was observed. The shape and position of the Si–O stretching vibration peak along with the Si–$F_n$ peaks remain almost unchanged. In the post precipitation stage, there is still virtually no change in the Si–O stretching vibration peak, however, a slight reduction of Si–$F_n$ peaks and further increase in Si–OH peak intensity could be observed. Fig. 4 shows the evolution of FTIR spectra during precipitation of the SiOF films with 9 at.% of fluorine concentration. The Si–O stretching vibration peak shifts towards lower wave number and slightly broadens from the as-deposited to the precipitate initiation stage. Slight increment in Si–OH and reduction in

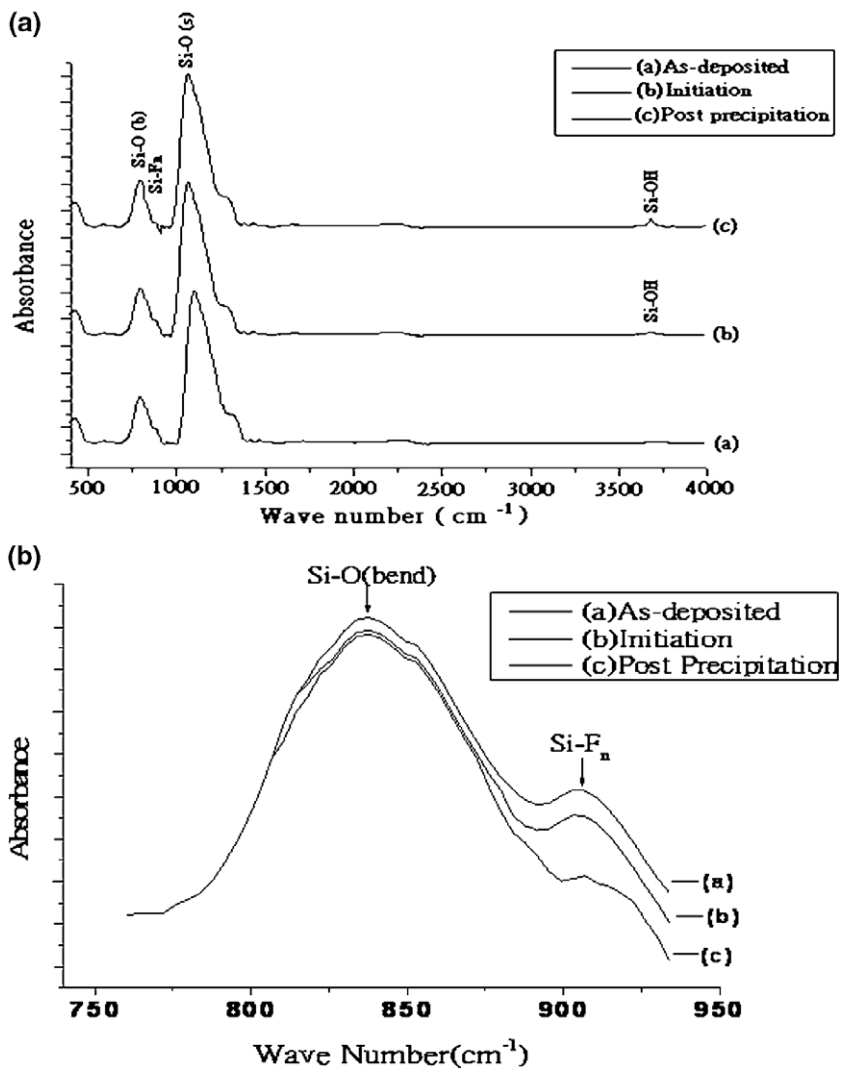


Fig. 4. FTIR spectra of SiOF film with 9 at.% fluorine concentration during precipitation.

Si–$F_n$ peak intensities could also be observed. In the post precipitation stage, an increase in the intensity of the shoulder peak (~1155 $cm^{-1}$) of Si–O stretching vibration, along with prominent increases in Si–OH as well as decreases in Si–$F_n$ peaks were observed.

The reduction in the peak intensity of Si–$F_n$ indicates the loss of fluorine, such result coincides with that obtained from the SIMS analysis, and could be attributed to either the hydration or the participation in the formation of precipitates. The Si–O stretching vibration peak of SiOF film is known to shift to higher wave number with increasing fluorine concentration due to the large electro-negativity of fluorine. Incorporated fluorine forms polarized Si–$F_n$ bonds and will distort Si–O–Si bond shifting Si–O–Si stretching band to a higher wave number [3]. In this case, the shift of the Si–O–Si toward lower wave number on the contrary could be due presumably to the weakening of Si–$F_n$ bonds. For the emerging shoulder peak of Si–O–Si stretching mode, Chou et al. reports to be indicative of the increased porosity of an oxide film [4]. Si–$F_n$ bonds also terminate the Si–O–Si structure resulting in the chain-like SiOF network with reduced density and increased moisture reactivity. However, the network of high-fluorinated SiOF films is far from the equilibrium state and will attempt to relax during post-deposition period in order to toward the minimum energetic state. It is assumed high-fluorinated films absorb atmospheric water during post-deposition period, which effectively reduces activation barriers for both the hydrolysis and structural relaxation processes [5]. For SiOF films with either fluorine concentration, the increased Si–OH peak intensities indicate continuous absorption of water or increased water absorbability due to the possibly the "relaxation" in the film structure throughout the precipitation process.

The changes in refractive index of SiOF films with various fluorine concentrations throughout the precipitation process were illustrated in Fig. 5. There was scarcely any change in the refractive index for SiOF film from the as-deposited to the precipitate initiation stage. However, precipitation leads to prominent drop of the refractive index, especially for samples with high fluorine concentration (9 at.%). The refractive index of PECVD silicon oxide film is known to be mainly dependent on three film properties, including the amount of polarizable species, the Si/O ratio, and the film density [7]. For the respective SiOF films with various fluorine doping levels in this study, the fixed $SiF_4/O_2$ flow rate ratio allows us to assume that the Si/O ratio in the films is approximately the same and that the refractive index depends only on the fluorine doping level. The RI of SiOF film is known to decrease with the increase of fluorine concentration and is ascribed to the decrease in film density along with decreasing film electronic polarization [6]. Nevertheless, throughout the precipitation process for SiOF films with each fluorine doping level, the loss of fluorine does not bring about the increase of

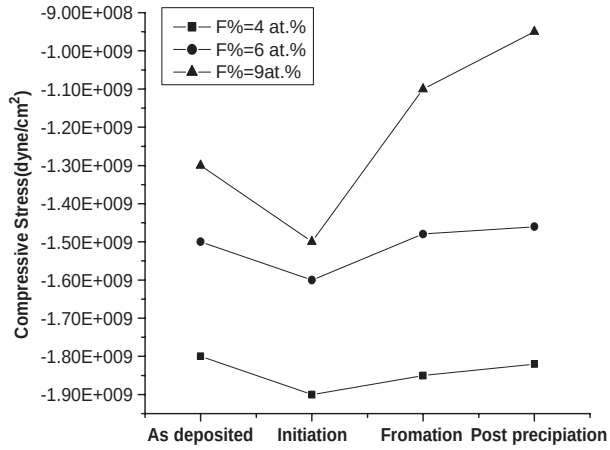


Fig. 6. Variation of compressive stress during the precipitation process of SiOF film.

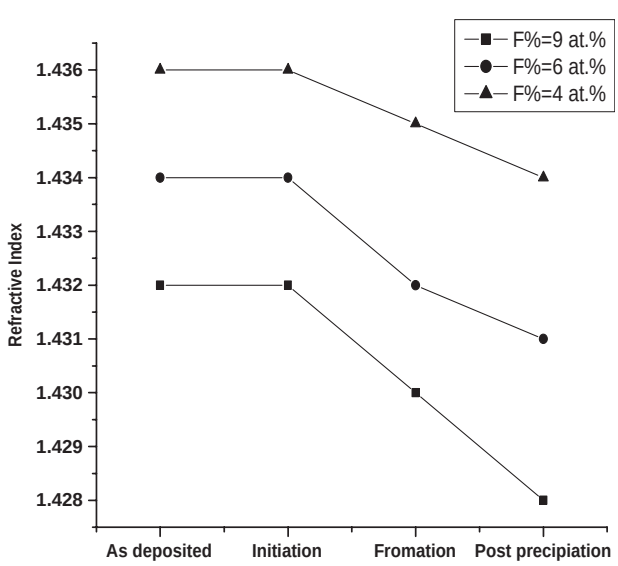


Fig. 5. Variation of the refractive index during the precipitation process of SiOF film.

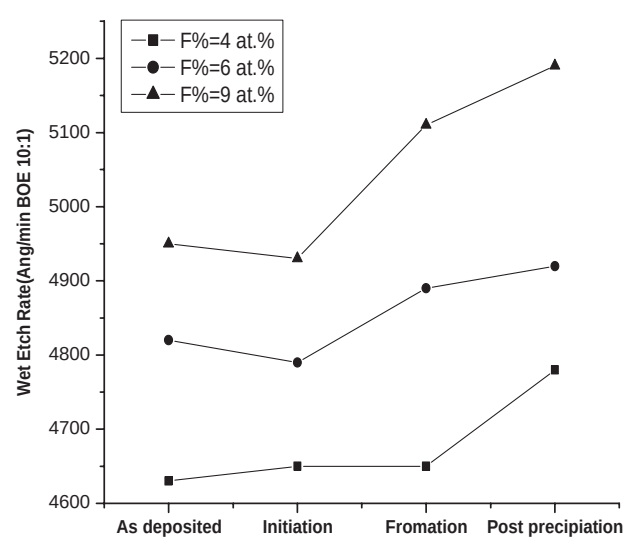


Fig. 7. Variation of wet etch rate during the precipitation process of SiOF film.

refractive index. By contrast, the refractive index also declines after precipitation. The plausible explanation for the drop of refractive index for the precipitated SiOF film is the loss of film density post precipitation. According to the Lorentz–Lorentz model and the Gladstone–Dale model, there is a linear relationship between the RI and film density [7]. The apparent drop in refractive index could be implicating the corresponding loss in film density.

Fig. 6 illustrates the changes in SiOF film stress throughout the precipitation process. The stress investigated here should contain both intrinsic and extrinsic, resulting mainly from changes in film microstructure or impurity, and the interactions between the film and the environment. The compressive stress initially increases and then gradually dropped as a result of precipitation. Films with high fluorine concentration would undergo more violent stress changes. Fig. 7 compares the wet etch rates of SiOF films for the as-deposited and the three stages of precipitation. Samples at each stage were subjected to the BOE wet etching. The thickness loss after wet etching is considered as the wet etch rate. As-deposited samples showed comparable wet etch rate as that of samples at the initiation stage of precipitation, whereas samples in the post precipitation stage exhibit higher wet etch rate performance. Kim and Choi reported that the physical absorption of water will lead to the increase in compressive stress upon exposure to humid air [8]. This explains the increase in the intensity of compressive stress at the initiation stage of precipitation. However, the significant relief of stress accompanying the precipitation should be ascribed to the change in structure or configuration. The wet etch rate of PECVD silicon oxide is known to be very sensitive to film porosity and to the presence of non-relaxed bonding angles. In SiOF films, the additional factor appears due to the presence of highly electronegative fluorine atoms in the Si–O–Si bonding network leading to the electron shift toward the F atom with the resulting weakening of the Si–O bonding. The weakening of the Si–O bond is likely to increase with increased fluorine concentration resulting in the corresponding increment of wet etch rate. Since the precipitation is spontaneous and could be deemed as a kind of “structural reconstruction” to the energetically lowest state, the less compressive stress and the increase in wet etch rate should not be caused by the strained bonging configuration and is more likely to be attributed to the change in structure of SiOF films, i.e., the increased porosity of the film structure. The relief in compressive stress would result in a corresponding increase in water diffusion rate and hence a higher dissolution rate (wet etching rate) in the BOE solution [9]. In addition, film porosity provides a higher surface area for holding water molecules and easy access for it to reach the reaction sites, and would also contribute to the high wet etch rate.

## 4. Conclusions

Precipitates were observed on the surface of high-fluorinated SiOF film during exposure to air. Effects of precipitation on SiOF film properties were investigated. SIMS analysis indicates uneven fluorine distribution within SiOF film after precipitation. Precipitation of SiOF film would lead to reduced refractive index, a relief in compressive film stress, high wet etch rate, and consequently increased porosity and deterioration of film structure.

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