



Study on precipitations of fluorine-doped silicon oxide

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Abstract

Precipitation on fluorine-doped silicon oxide film (SiOF) was observed while exposure to air for a prolonged period of time (>4 h). Most of the precipitates are less than 1 μm and clustered at wafer center. Under SEM view, the precipitation shows hexagonal shape, and mainly composed of Si and O. SIMS analysis showed that SiOF films without F precipitates showed leveling F% profile, whereas SIMS result for SiOF films with precipitations shows increasing gradient with depth. In this study, factors affecting the precipitation of SiOF film were investigated. Humidity in environment was found to be one of the essential elements for the onset of precipitation. Process optimization and control methodologies were also investigated for precipitation prevention to provide a more robust and stable SiOF film, hence ensuring the reliability of device performance.

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1. Introduction

In the manufacturing of ULSI devices, fluorine-doped silicon oxide film (SiOF) has been found to be very effective in the reduction of dielectric constant of the intermetal dielectric film, and has been adopted as one of the low- k dielectric materials to reduce RC delay effect and to 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 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 [1]. The dielectric constant of a film decreases with the increase in 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 becomes interactive with water from the air, consequently a degradation of film quality and increase of dielectric constant could be observed [2]. In addition to structural

instability of SiOF bonding reported elsewhere, one specific feature—precipitation of SiOF—was observed. Fluorine concentration would decay as a result of this precipitation phenomenon. For high fluorine content (> 4 at.%) of SiOF film, the as-deposited SiOF film may be a ‘metastable’ phase [3]. Interaction with water in ambient atmosphere during post-deposition period could further induce structural change as well as crystallization.

In the present study, precipitation behaviors of SiOF film deposited by PECVD using SiH_4 and SiF_4 after exposure to the ambient atmosphere were investigated. The interaction between water and SiOF films was suspected to be the main sources of film’s structural instability. The probable mechanisms contributing to the post-deposition structural relaxation of SiOF films were discussed. An in situ plasma-treatment method post film deposition was proposed and has been verified to be an effective method to eliminate the precipitation phenomenon.

2. Experimental

SiOF films were deposited on 200-V cm n-type silicon substrates in a remote plasma-enhanced chemical vapor deposition system using $\text{SiF}_4/\text{SiH}_4/\text{N}_2\text{O}$ mixture. The

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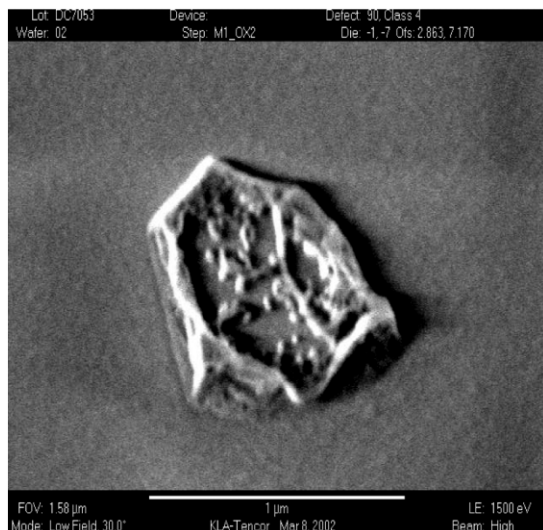


Fig. 1. SEM image of FSG precipitation.

reaction chamber was equipped by an inductively coupled plasma source. 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. The fluorine concentration in the film is expressed as fluorine atomic percentage from FTIR measurement. The plasma discharge was maintained using 13.56 MHz r.f. power at 200 W for all depositions. After deposition, SiOF films were exposed to the ambient atmosphere at room temperature. In the humidity experiment, SiOF films were humidified in an atmospheric pressure humidification vessel. 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 initiation of precipitation. SIMS analysis was conducted to investigate the concentration profile of precipitated SiOF film. Prior to the SIMS test, SiOF films were capped with PECVD SiO_2 2 kÅ to avoid contamination. XPS analysis was also conducted to verify the surface characters of plasma-treated SiOF films.

3. Results and discussions

3.1. Driving force of precipitates

The SEM image of precipitates is shown in Fig. 1. The precipitates is hexagonal in shape and $\sim 1 \mu\text{m}$ in size. Fig. 2 shows the wafer map of the precipitates. After the onset of precipitation, these precipitates showed up rapidly and densely clustered at wafer center. Its count increases and gradually saturated and could amount to as high as 10^4 . Fig. 3 shows the EDX analysis results of the precipitates. Within the detection limit, mainly Si and O are detected (F is supposed to be beyond tool detection limit). Fig. 4 illustrates the SIMS depth profile of the SiOF films capped with 2-kÅ PECVD silicon oxide prior to the appearance of precipitation. A leveling curve was observed in the concentration profile of fluorine, indicating that F is uniformly distributed throughout the SiOF film. Fig. 5 is the SIMS depth profiles of precipitated SiOF film capped with 2-kÅ PECVD silicon oxide. A concentration gradient of fluorine was found in the concentration profile, indicating uneven fluorine distribution within the precipitated SiOF film. From the fluorine concentration gradient of fluorine in Fig. 5, it is surmised that the fluorine on the SiOF surface participated in the formation of precipitates. As a result of fluorine consumption, the film

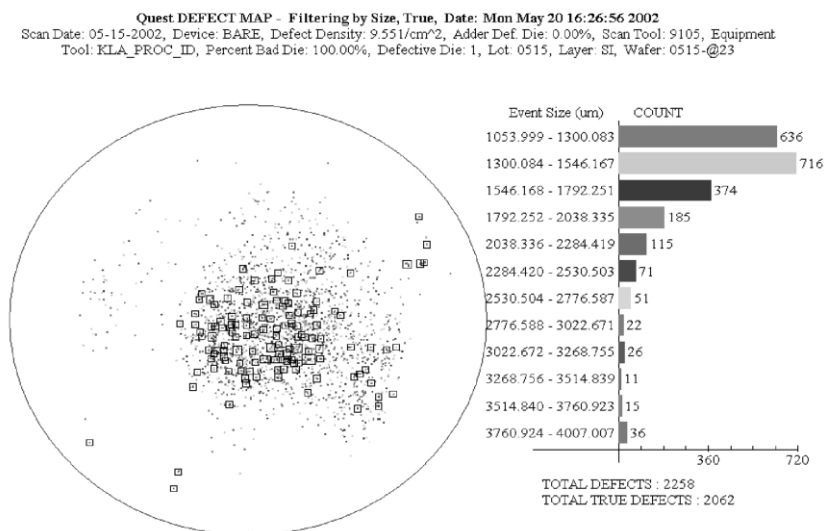


Fig. 2. Fluorine precipitation defect mapping (scan by KLA SP1).

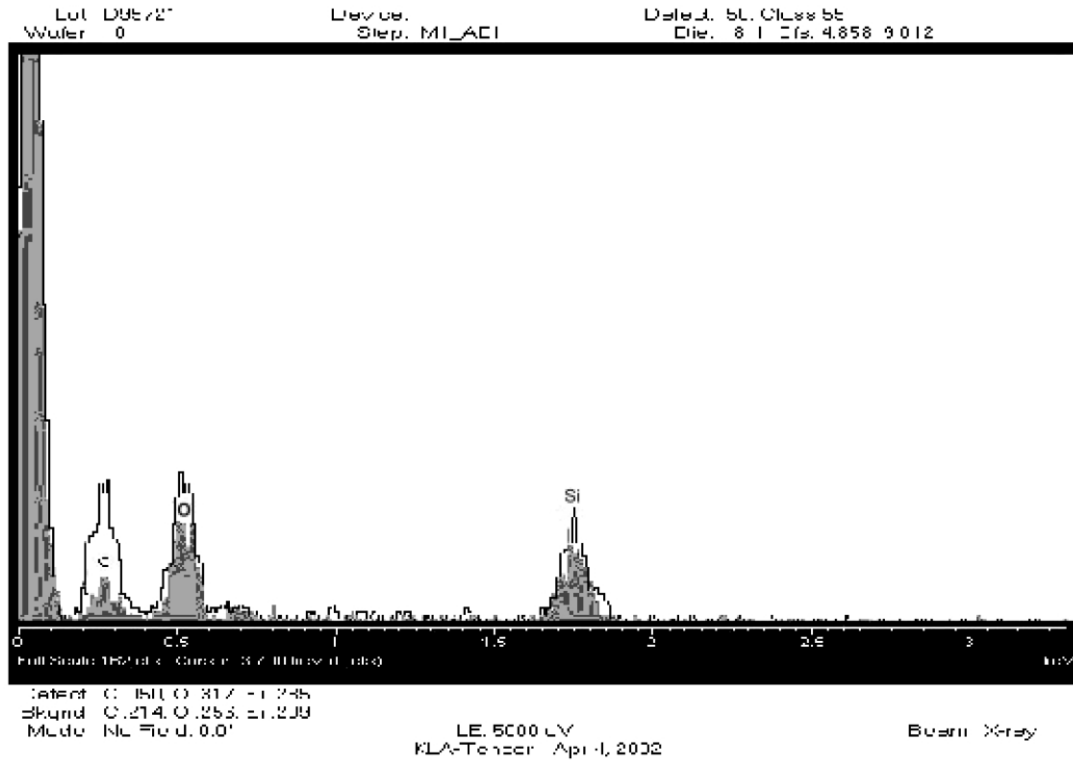


Fig. 3. EDX analysis result of FSG precipitation.

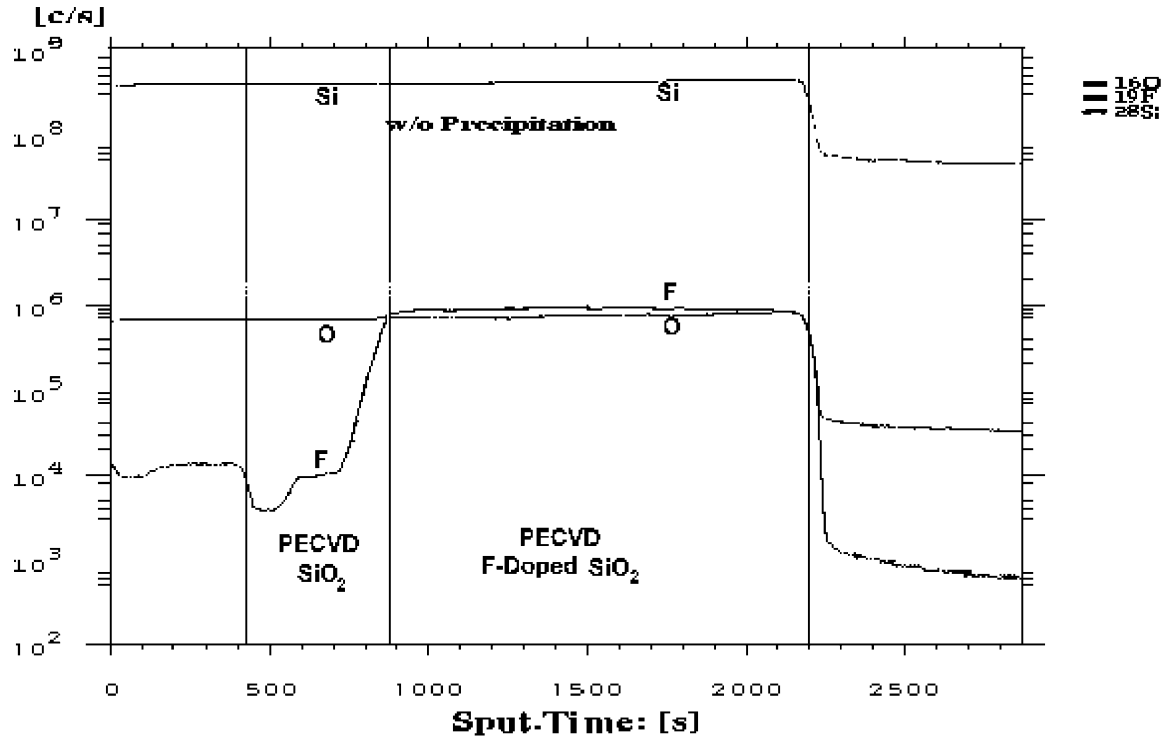


Fig. 4. SIMS F% profile for FSG film without precipitation.

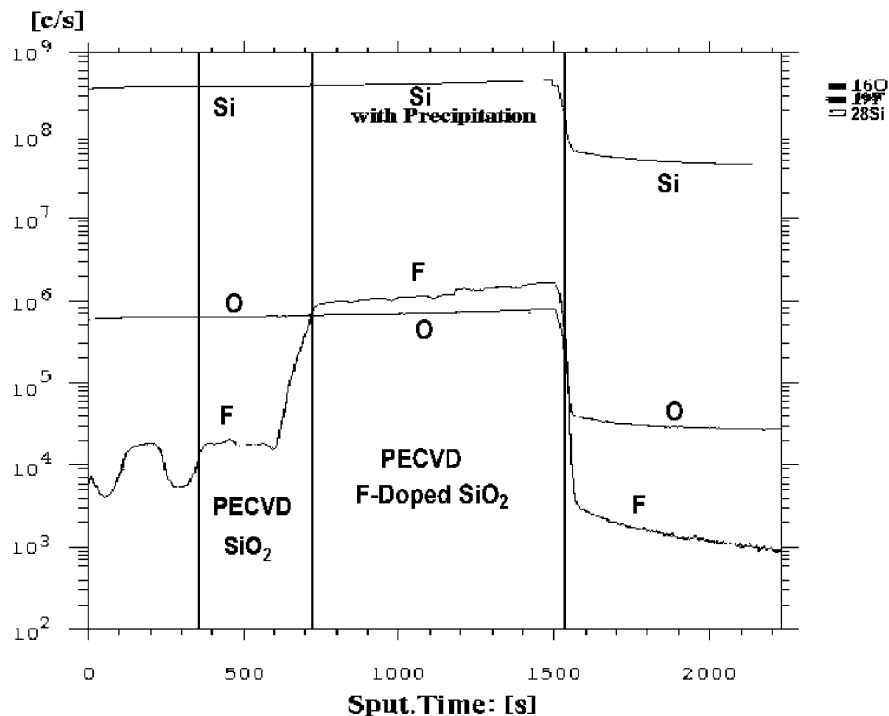


Fig. 5. SIMS F% profile for FSG film with precipitation.

surface is in any event like a ‘solute sink’, and a concentration gradient of fluorine was therefore formulated. When a concentration gradient is present, then there is a net flux in the direction of the gradient. Fluorine species from the bulk of SiOF film could diffuse to the film surface and formulate the precipitate.

Precipitation could be regarded as embodying fast crystallization. The rapidity of the precipitation process is a consequence of the high supersaturation at which it takes place. Low solubilities of such materials allow the development of high supersaturation. The high supersaturation ensures the initiation of primary nucleation for the precipitates [4]. The primary nucleation rate is usually very high. Nucleation is followed by crystal growth, the mechanism of which largely determines the crystal shape. The size of precipitates is usually small since the amount of mass that must be deposited before equilibrium is attained increases far more slowly than the number of crystals being formed. The equilibrium state of crystals, which gives the most compact shape of the crystal, is determined by the minimum overall energy of the crystal surface [5]. In the case of SiOF film, Pankov [6] reported that SiOF films with Si–F_x bond content of approximately 3.7 at.% corresponds to the energetically lowest state of the SiOF network and can be considered as an equilibrium value. The subsequent increase in the F content of the SiOF films results in ‘overequilibrium’ and causes structural instability and increased reactivity of the films during post-deposition period. In Fig. 6, comparison was made for the time period required for the appearance of precipitates for

SiOF film with various fluorine concentrations. PECVD (without the addition of SiF₄ reactant gas) SiO₂ film was also observed for reference. There is no appearance for the un-doped PECVD SiO₂ film throughout the observation, implicating that fluorine is the essential element for precipitation occurrence. In addition, it can be concluded that SiOF films with higher fluorine concentration showed relatively rapid formation of precipitates and could be interpreted as promoted by a stronger driving force. For the fluorine range (~4–6 at.%) discussed in this study, fluorine in the SiOF film seemed to be ‘supersaturated’ and in a state that is relatively unstable. Further reaction with environmental reagents or transformation in configuration could lead the SiOF film to an energetically stable state.

3.2. Effect of humidity with precipitation

Numerous studies have been focused on the interactions of moisture in atmospheric air with the SiOF films. Fluorine atoms incorporated in the SiOF film make it more open in structure. The replacement of divalent oxygen atoms by monovalent fluorine atoms increases the termination of Si–O–Si networks [7]. As a consequence, high-fluorinated films quickly absorb atmospheric water in large quantities during post-deposition, which effectively reduces activation barriers for both the hydrolysis and the structural relaxation processes. It is assumed that both moisture reactivity and structure relaxation processes in SiOF films during post-deposition period are strongly controlled by the inner energetics

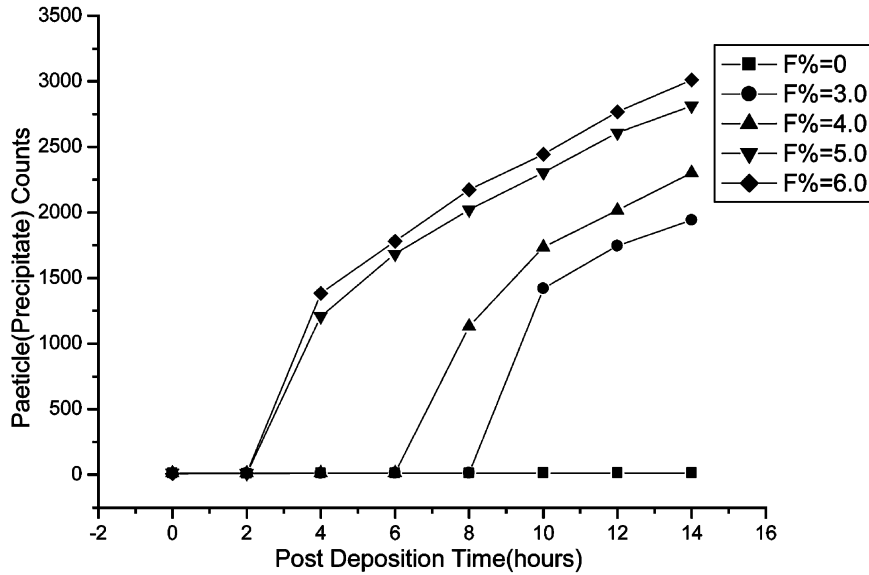


Fig. 6. Precipitation counts post-deposition for SiOF film with various fluorine concentrations.

of as-deposited film, whereas water absorption enables to reduce the activation barriers of the above processes [8]. Chemical reactions with environmental reagents, water molecules, for instance, could be accompanied by structural reconstruction. Since the precipitation of SiOF film takes place at the film surface, which is exposed to the ambient atmosphere, it is suspected that moistures, or water molecules in air, could possibly either participate in the precipitation reaction or at least catalyze the formation of precipitates. Fig. 7 shows the effect of humidity in environment on the initiation of precipitation. SiOF films of 5 at.% of fluorine concentration were subjected to exposure to atmosphere in closed ambient with controlled relative humidity (RH). The

result shows that precipitation could be observed even for as low as ~20% RH. However, the time it takes for the onset of precipitation varies for various humidity levels. An opposing trend could be deduced from the result. Higher humidity in air would accelerate the initiation of precipitation, implicating that water molecules in air do promote the precipitation of SiOF films.

3.3. Effect of postplasma treatment

To suppress the formation of precipitates on SiOF films, the effect of the plasma treatment post SiOF film deposition was investigated. Fig. 8 illustrates the post-deposition observation results for SiOF films in situ

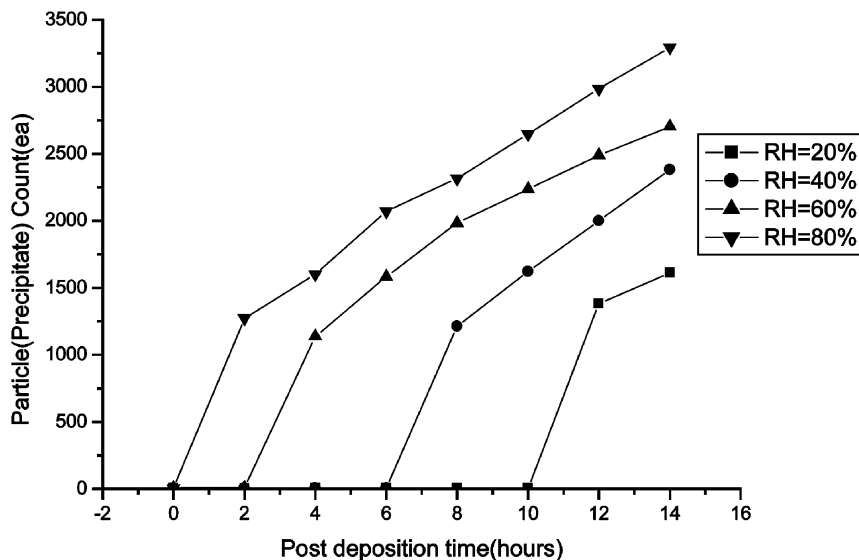


Fig. 7. Precipitation counts post-deposition for SiOF film with various RH in air.

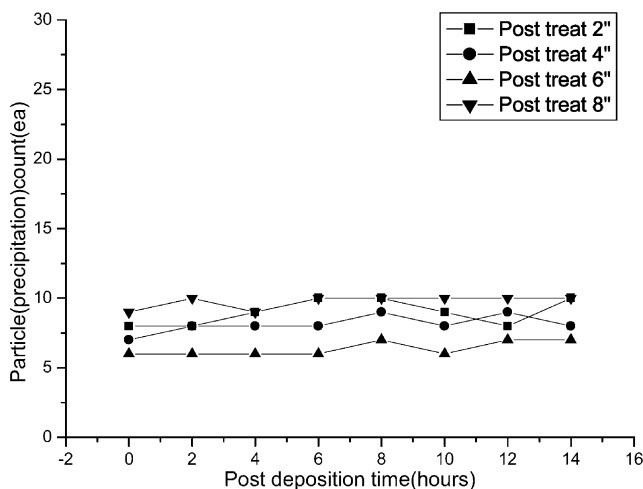


Fig. 8. Precipitation counts post-deposition for SiOF film with various plasma-treatment time.

plasma-treated on film surface in PECVD chamber and subsequently subjected to exposure to air. The results show no any precipitation observed for all the plasma-treated SiOF films, and for the 150 W plasma, post-treatment time as short as 2 s would be sufficient to suppress the initiation of precipitates. Fig. 9 shows the comparison of XPS surface analysis results between non-treated SiOF film and 2-inch-plasma-treated SiOF film, and Table 1 summarized the content of key elements. There is no obvious difference found between those with and without treatment, only slight increment

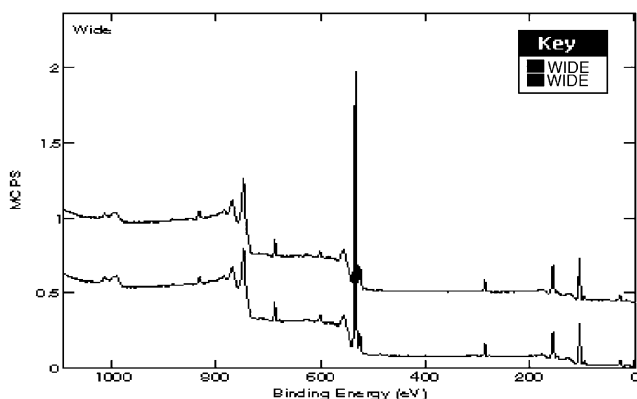


Fig. 9. XPS analysis for SiOF film with/without postplasma treatment (wide scan Mg K α).

Table 1

Percentage of elements from XPS quantification

Conditions	Take-off	F	O	N	C	Si
No treatment	0	3.8	55.5	0.5	8.8	31.4
	60	3.2	53.9	0.2	12.9	29.7
2-inch-N ₂ O treatment	0	3.1	57.1	0.1	7.4	32.2
	60	2.6	56.1	0.1	10.7	30.4

in the concentrations of oxygen and silicon for plasma-treated film. The binding energies of O 1s and F 1s after treatment slightly lower down to approximately 0.3 eV, which may be attributed to the effect of N₂O plasma treatment. It is likely that postplasma treatment changed both the chemical composition and the density of the films, resulting in both the depletion in fluorine concentration and the oxidation on film surface. This depletion in fluorine concentration leads to enhanced stabilization of dielectric constant and water absorption resistance.

4. Conclusions

In this study, preliminary investigations were made on the factors contributing to the precipitation phenomena of SiOF films. Supersaturated active fluorine species in the SiOF film participated in the surface reactions on SiOF films and results in the precipitation. Water molecules in air (humidity) would accelerate the initiation of precipitation. Postplasma treatment on SiOF film surface has been proven to be an effective method to suppress the precipitation occurrence.

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