

Effects of plasma treatment on the precipitation of fluorine-doped silicon oxide

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Abstract

Precipitates were observed on the surface of fluorine-doped silicon oxide (SiOF) films. These precipitates are flake-type and hexagonal in shape, showing up rapidly after initiation, and clustered at the wafer center. Post-deposition N₂O plasma treatment (post-plasma treatment) was found to be most effective in inhibiting the appearance of precipitates. In this paper, effects of post-deposition N₂O plasma treatment on the suppression of precipitates and stabilities of SiOF film were studied. X-ray photoelectron spectroscopy (XPS) analyses were conducted to investigate the changes in surface composition of SiOF films after N₂O plasma treatment. The surface morphology of the film was characterized by atomic force microscopy (AFM). Cross-sectional transmission electron microscopy (TEM) images showed that a surface layer of 150 Å was generated after N₂O plasma treatment. The changes on surface structures of SiOF films caused by N₂O plasma treatment and the consequent inhibition of precipitate formation were discussed.

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1. Introduction

With the advancement of ultra-large-scale integrated circuits (ULSI) technology, it is essential to reduce wiring capacitance and 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 [1]. Fluorine-doped silicon oxide film (SiOF) has been found to be very effective in the reduction of dielectric constants and has become 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 the reduction of the dielectric constant [2]. The dielectric constant decreases by increasing the fluorine concentration in the SiOF film. However, it also reduces film stability. The SiOF film is susceptible to moisture absorption. Films with high fluorine contents become interactive with water from air, and consequently result in degradation of film quality and low-*k* characteristics. Many researches have focused on the detrimental effects of water absorption on the properties of SiOF films [3–5]. In addition to the structural instability of SiOF bonding reported elsewhere, one specific feature—precipitation on the surface of SiOF film—was also observed.

Fig. 1(a) shows the SEM image of the precipitates on SiOF films. The wafer mapping of precipitates distribution is shown in Fig. 1(b). As investigated in our earlier report [6], precipitation initiated spontaneously forming hexagonal-shaped structure and clustered at the wafer center while the SiOF film was exposed to moist atmosphere. Fig. 2(a) is the cross-sectional transmission electron microscopy (TEM) image of precipitates on SiOF film. On high

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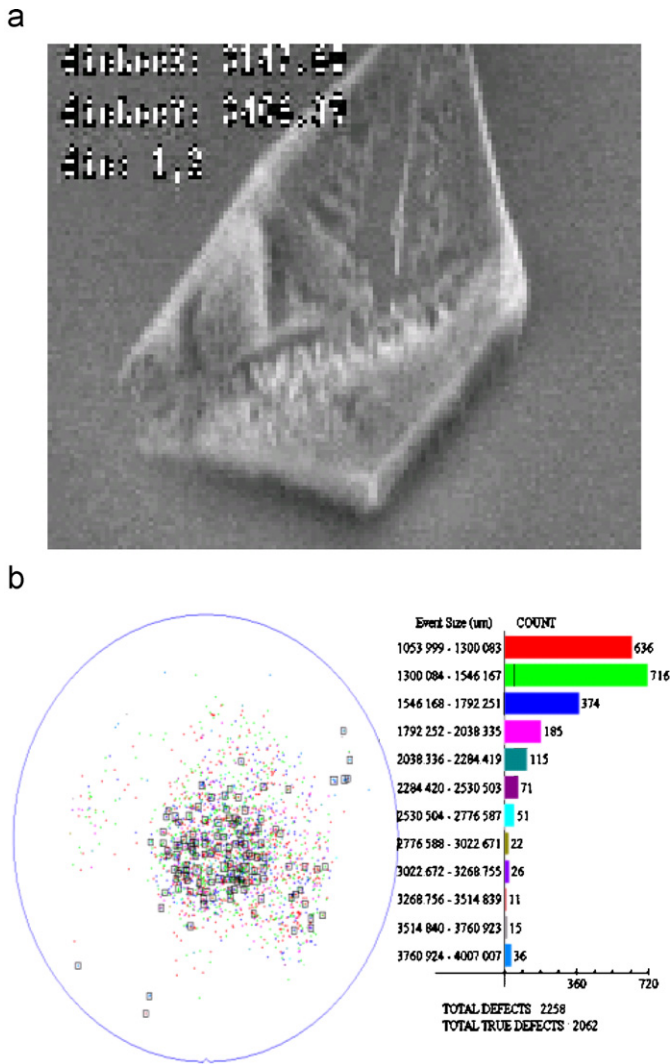


Fig. 1. (a) SEM image of precipitates on the surface of SiOF films and (b) wafer mapping of the precipitates distribution.

magnification the precipitate shows loosely connected porous structure. Fig. 2(b) demonstrates the EDX analysis spectra of the precipitate. Mainly Si and O are detected (F is supposed to be beyond tool detection limit). Such defects generated in semiconductor processing could induce film delamination and metal bridges, resulting in detrimental effects on device performance. A surface modification technique by employing the in situ plasma treatment method post film deposition was proposed and has been validated to be an effective method to eliminate the precipitate formation [6]. In this study, effects of post-plasma treatment on the surface characteristics and dielectric properties of SiOF thin films were investigated.

2. Experimental

SiOF films were deposited on n-type silicon substrates in a remote plasma-enhanced chemical vapor deposition

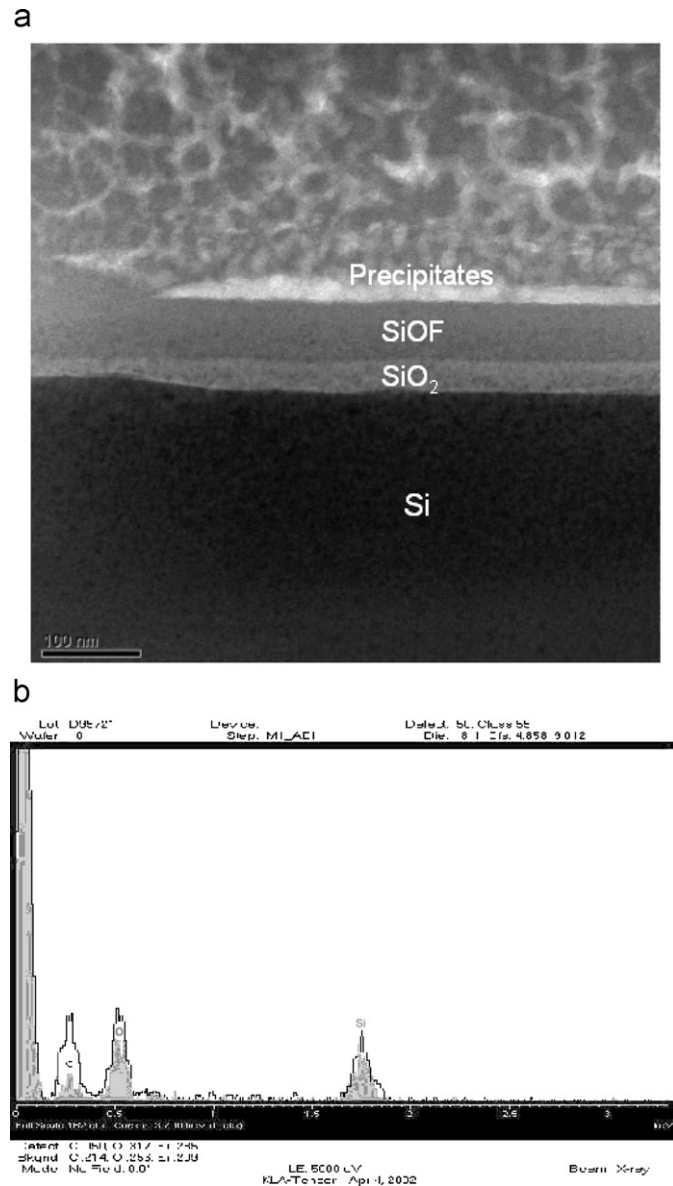


Fig. 2. (a) Cross-sectional TEM image of precipitates on the surface of SiOF films and (b) EDX analysis of precipitates.

system using SiF₄/O₂ gas mixture. The reaction chamber was equipped with an inductively coupled plasma source. The plasma discharge was maintained using 13.56 MHz rf power at 200 W to decompose the gas mixture and obtain SiOF films of 4K Å thickness. After deposition, SiOF films were exposed to the moist atmosphere at 25 °C, 45% relative humidity. The fluorine concentration of the as-deposited SiOF film is 9 at%, expressed as the fluorine atomic percentage from FTIR measurement. The post-plasma treatment was applied on N₂O gas and was maintained using 13.56 MHz rf power at 150 W. The surface roughness of SiOF films with and without post-plasma treatment was measured by atomic force microscopy (AFM). The scanning area of AFM surface images for each substrate is 10 × 10 μm². X-ray photoelectron

spectroscopy (XPS) was employed to investigate the difference in the distribution of surface elements that occurred at the exposed surface of plasma-treated SiOF films. The dielectric constants of SiOF films were investigated by measuring capacitance–voltage (C – V) characteristics using a metal–insulator–semiconductor (MIS) capacitor structure at 1 MHz. TEM analyses were performed to investigate the cross-sectional microstructures of the plasma-treated film surface. Throughout the experiment, the precipitate counts were measured by a wafer surface defect measurement tool (Tool-type KLA SP1). An abrupt increase in defect count (from 10^1 to $>10^3$) in 1 time interval was considered as the onset of precipitation.

3. Results and discussion

Fig. 3 illustrates the variation of precipitate counts with post-deposition time for non-plasma-treated and post-plasma-treated SiOF films with 6 at% of fluorine content. Non-plasma-treated (without post-plasma treatment) and in-situ post-plasma-treated SiOF films were subjected to an exposure to moist air. The results indicated that precipitates showed up on the non-plasma-treated SiOF films after 2 h, whereas no precipitation was observed for the post-plasma-treated SiOF films. In the post-plasma treatment, ion irradiation on the as-deposited SiOF films modified both topography and structure of the surface layer of the SiOF film. This modification is by the combined effects of sputtering, implantation, diffusion, and re-deposition processes [7]. Fig. 4 shows the TEM cross-sectional images of non-plasma-treated and post-plasma-treated SiOF films. A surface layer of 150 Å was formed after the post-plasma treatment. The AFM images

of surface topographies for non-plasma-treated and post-plasma-treated SiOF films are shown in Fig. 5. The measured root mean squares of surface roughness, taken from $10 \times 10 \mu\text{m}^2$ scans, for the as-deposited and

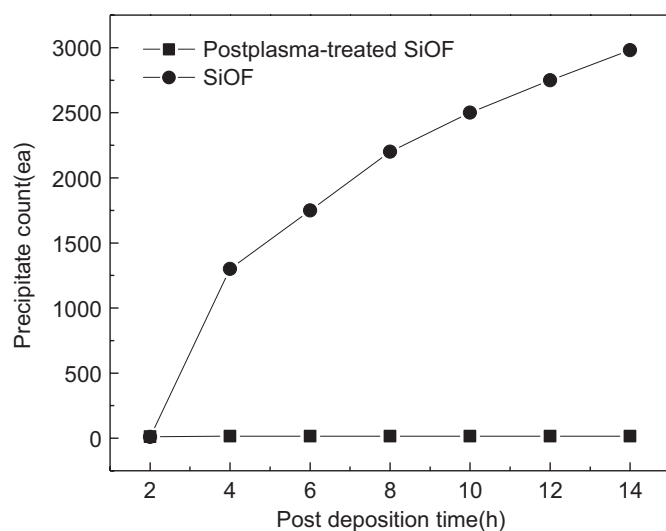


Fig. 3. Variation of precipitate counts with post-deposition time for SiOF films with 6 at% fluorine content. Non-plasma-treated and in-situ post-plasma-treated SiOF films were subjected to an exposure to moist air.

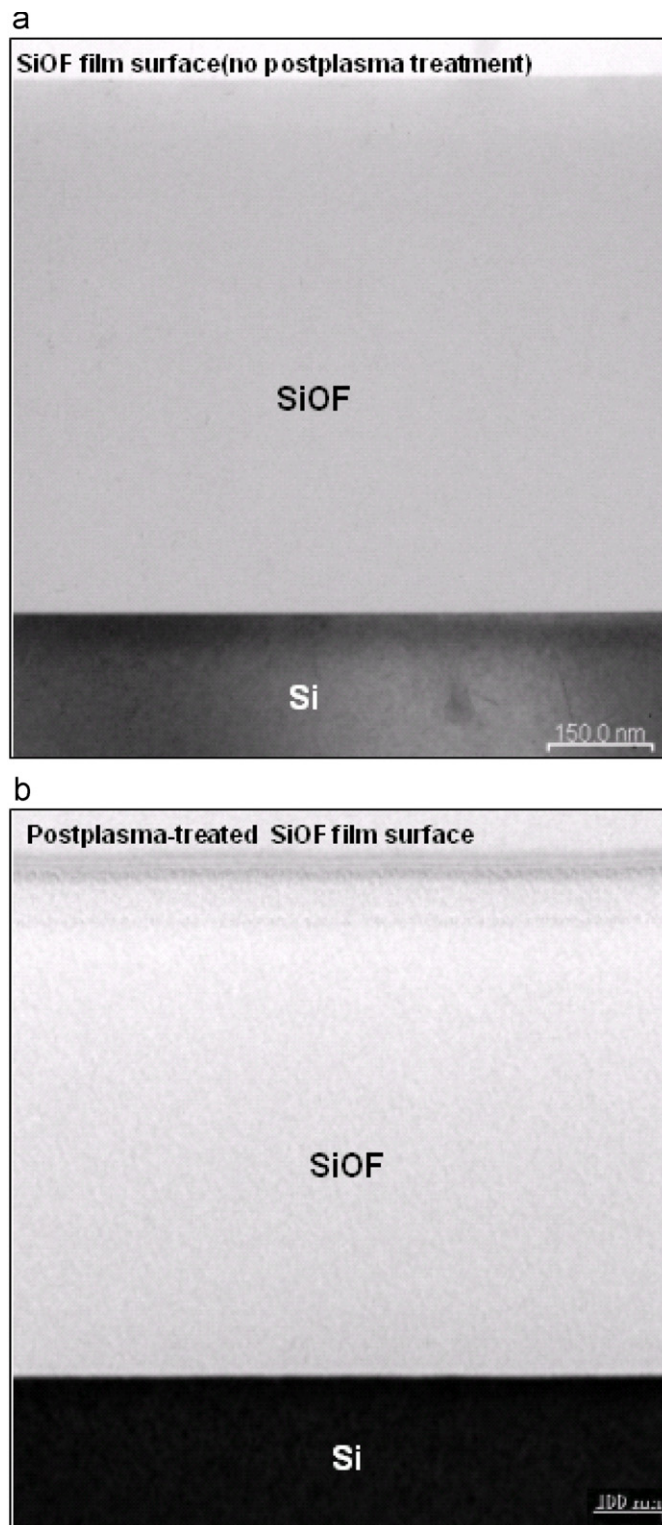


Fig. 4. TEM cross sectional images of (a) non-plasma-treated and (b) post-plasma-treated SiOF films. A surface layer of 150 Å was formed after the plasma treatment.

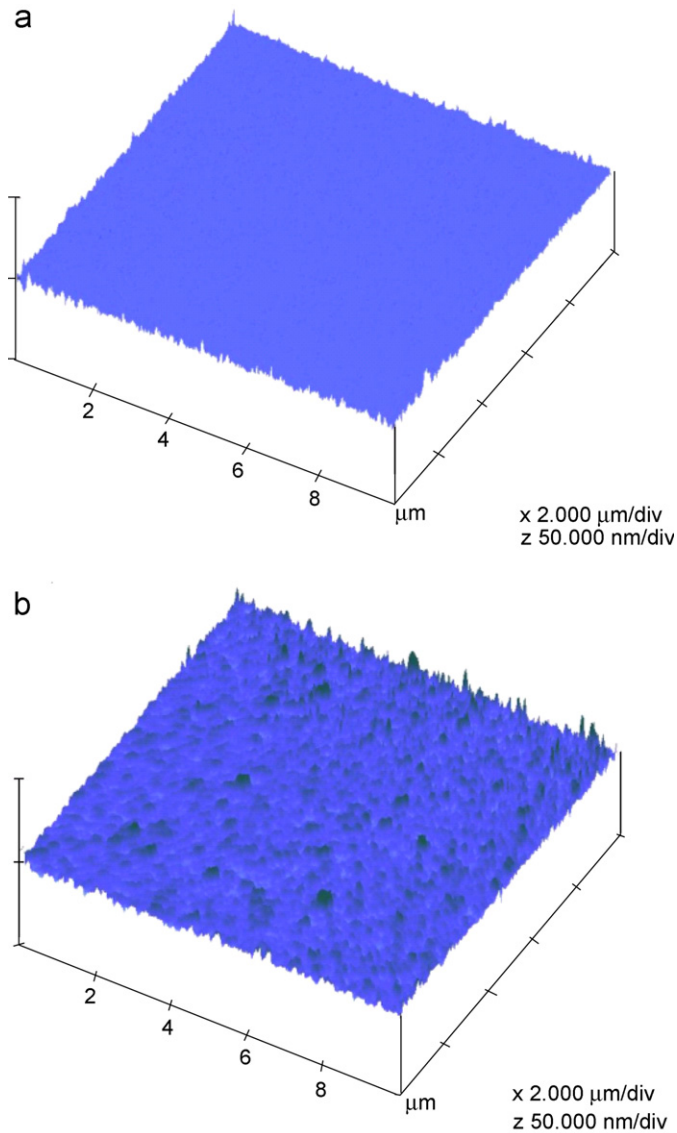


Fig. 5. AFM images of the surface topography for the non-plasma-treated and the post-plasma-treated SiOF films.

the post-plasma-treated SiOF film were around 1.21 and 2.23 Å, respectively. The surface roughness of the SiOF film increased as a result of the post-plasma treatment. This may be ascribed to the sputtering effects of N₂O plasma on the surface layer of the SiOF film during post-plasma treatment.

Fig. 6 shows the XPS spectra of post-plasma-treated and non-plasma-treated SiOF films. There is no significant difference between those with and without post-plasma treatment. The main bonding species were still kept after the plasma treatment. In Figs. 6(b) and (c), the binding energies of O 1s and F 1s after treatment lowered down to about 0.3 eV compared with the non-plasma-treated film. Table 1 summarizes the content of key elements. The concentration of oxygen and silicon increased whereas that of fluorine decreased

in the post-plasma-treated film. XPS result indicates that the chemical composition of the SiOF film at the surface changed from that of the as-deposited SiOF film. Oxidation and surface fluorine depletion occurred during the N₂O post-plasma treatment. Some fluorine atoms on the surface layer of SiOF films were replaced by oxygen atoms after post-plasma treatment. It is likely that the active radicals (e.g. O⁺) and ion-bombardment effects in the post-plasma treatment changed both the chemical composition and the density at the top surface of SiOF films [8], resulting in both depletion of fluorine concentration and oxidation on the film surface. In our previous study we reported that fluorine in the surface layer of SiOF films participated in the formation of precipitates [6], and fluorine species in the bulk of SiOF film could diffuse to film surface and form precipitates. The surface oxidation and densification due to plasma treatment plays an important role in blocking the diffusion path of fluorine from bulk to the surface, thus inhibiting the formation of precipitates.

Comparison of film properties for the as-deposited and the post-plasma-treated SiOF films is summarized in Table 2. More pronounced increase in the compressive stress of SiOF films was observed as a result of post-plasma treatment. Nevertheless, there is no noticeable difference in the overall film density and dielectric constant between the as-deposited and the post-plasma-treated SiOF films, even though the post-plasma treatment leads to the depletion of fluorine on the surface and densification of the film by ion bombardment. The post-plasma treatment is quite an efficient method not only in blocking the moisture [9] but also in inhibiting the precipitation formation. The dielectric properties and stabilities of SiOF films can be improved without degrading its low-*k* characteristics by N₂O post-plasma treatment.

4. Conclusions

Precipitates were observed on the surface of fluorine-doped silicon oxide films. The N₂O post-plasma treatment can effectively suppress the formation of precipitates. A surface layer of 150 Å was formed after the post-plasma treatment. Post-deposition treatment affects both chemical composition and film density of the surface layer of SiOF film. The post-plasma treatment will lead to oxidation, depletion of fluorine, and densification of the surface layer through active radicals (e.g. O⁺, •) and ion-bombardment effects in N₂O plasma. It is quite an efficient method to block the diffusion path of fluorine from bulk to film surface, thus inhibiting the formation of precipitates. The dielectric properties and stabilities of SiOF films can be improved without degrading its low-*k* characteristics by N₂O post-plasma treatment.

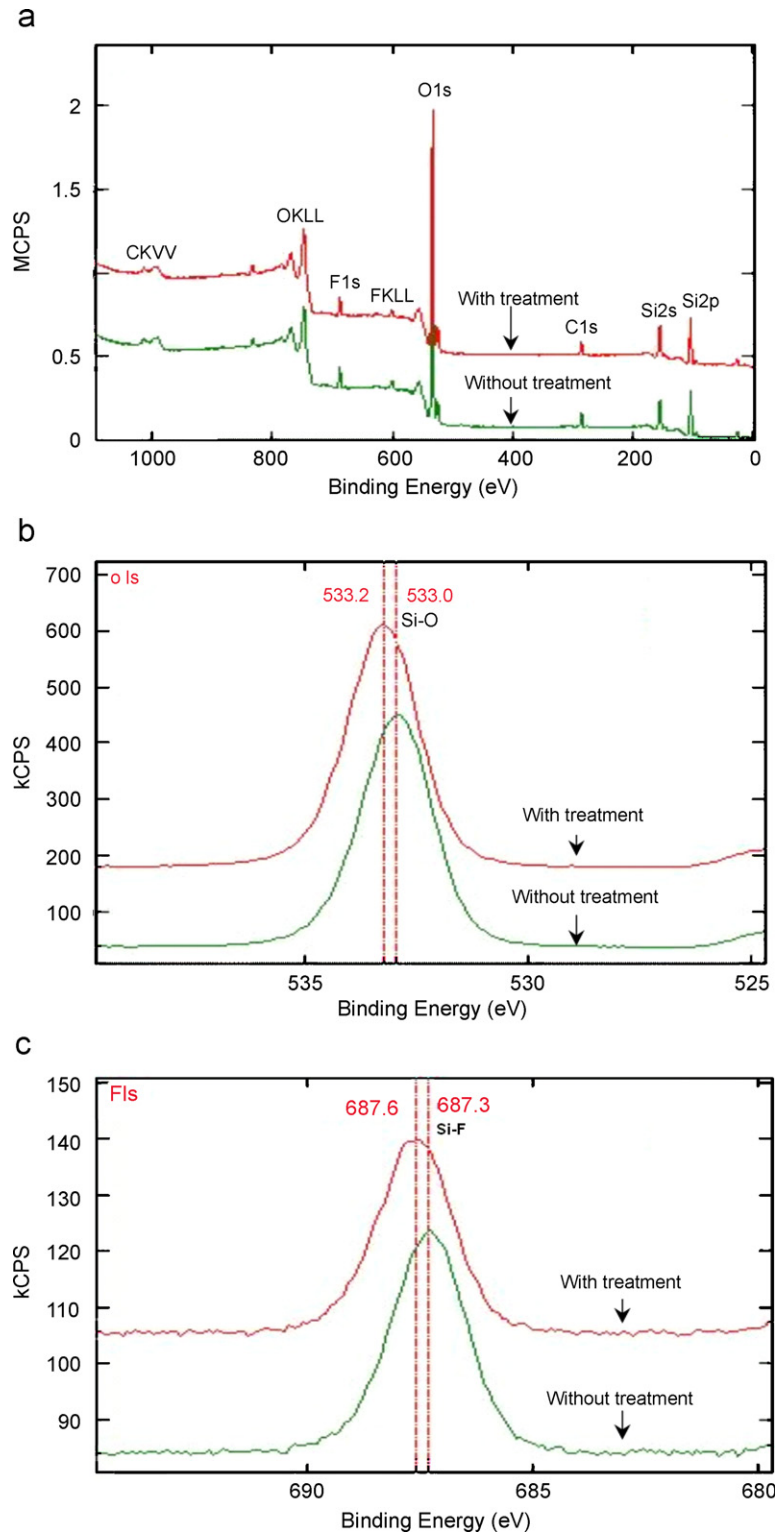


Fig. 6. XPS spectra of (a) wide scan (MgK α) (b) O 1s, and (c) F 1s for SiOF films with and without post-plasma treatment.

Table 1
Percentage of elements from XPS quantification (unit: %)

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
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

Table 2
Comparison of film properties for the as-deposited and the post-plasma-treated SiOF films

Conditions	Dielectric constant (<i>k</i>)	Refractive index (<i>n</i>)	Density ^a (g/cm ³)	Stress (MPa)
Non-plasma-treated SiOF	3.522	1.435	2.0995	−204.1
Post-plasma-treated SiOF	3.523	1.434	2.0953	−211.2

^aThe density is determined from the *n* value using Lorentz–Lorentz relationship $\rho = K(n^2 - 1)/(n^2 + 2)$, where $K = 8.046$.

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