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**Technical Note**

# Evaluation of Hindrance to the Growth of SiN Passivation Layer by Contamination of Fluoride Ions in Front Opening Unified Pod (FOUP)

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## ABSTRACT

We have investigated the hindrance to the deposition growth of silicon nitride (SiN) passivation layer from the contamination by airborne molecules in the front opening unified pod (FOUP). In particular, an artificial contamination of FOUP by fluoride ions as the source of the contaminants is utilized to elucidate the influence of contamination on the wafer surface. When the bare wafer surface is exposed to fluoride ions in the contaminated FOUP, the deposited thickness of the SiN layer is observed to decrease to a maximum of 11 Å from our experimental condition. On the other hand, there is no appreciable variation in the thickness of deposited SiN layer stored in the pre-cleaned FOUP. Based on the analytical results of wafer surfaces and FOUPs, we believe that the contamination of fluoride ions on wafer surfaces is originated from the contaminated surface of FOUP. Therefore, we conclude that it is necessary to clean and monitor the inside of FOUP on a regular basis, especially after wet or dry etching processes, which generates gaseous impurities.

***Keywords:*** Airborne molecular contaminants (AMC); Cleanroom contamination; Front opening unified pod (FOUP); Fluoride ion; SiN layer.

## INTRODUCTION

Airborne molecular contaminations (AMCs) are becoming a prominent issue in the manufacturing process of semiconductors because of the very large scale of integrated circuits and increased silicon wafer size (Den *et al.*, 2006). Sometimes, a certain concentration level of airborne molecules could have a negative effect on the production yield and safety of workers in cleanrooms. AMCs could result in physical and electrical defects in semiconductors, mainly due to chemical reactions with deposited gaseous molecules acting at the surface of wafers (Iwamoto and Ohmi, 1997; Hsu, 2001; Kamoshima *et al.*, 2008). Therefore, semiconductor manufacturing companies are attempting to analyze and monitor AMCs in cleanrooms to ensure production yield and worker safety. Some AMC-induced defects at the wafer surface may result in a decrease of the deposited film thickness, which could occur during direct manufacturing processes such as cleaning, deposition, and etching, in particular when exposed to moisture, fine particles, and various types of chemicals (Frickinger *et al.*, 2000; Tokunaga *et al.*, 2003; Hu *et al.*, 2005; Hu *et al.*, 2009). Furthermore, the wafers could also be contaminated by residual components in a carrier box called front opening unified pod (FOUP), which is used for the transportation of wafers (Nguyena *et al.*, 2009). This is a matter of great concern, because more than a dozen of processed wafers are loaded, unloaded, stored, and transported in FOUPs at every manufacturing step. Therefore, increasing attention has been drawn to the problems faced by the contaminations and the cleaning and purging steps of FOUP (Hu *et al.*, 2006; Hu *et al.*, 2007; Yoo *et al.*, 2012).

In this study, we have examined the influence of internal contamination of FOUPs on wafer surfaces of deposited

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layers. Especially, this study has focused on the effect of fluoride ions on deposited SiN layers that are extensively used for passivation. There are a lot of fluoride ions such as hydrogen fluoride (HF) and fluorine ammonium ($NH_4F$) for wet etching process (Kikyuama *et al.*, 1991; Spierings, 1993; Iliescua *et al.*, 2005; Lin *et al.*, 2010), and sulfur hexafluoride ($SF_6$), tetrafluoromethane ($CF_4$), trifluoromethane ($CHF_3$), difluoromethane ($CH_2F_2$) and nitrogen trifluoride ($NF_3$) for dry etching (Jansen *et al.*, 1996; Layadi *et al.*, 1999; Chang and Chang, 2006), which are presently used at every etching step. It is considered that these ions might be the reason for hindrance to the growth of deposited films due to the highly corrosive reaction with incoming species. Based on the background mentioned above, this study is aimed at finding out the relationship between the contamination of fluoride ions in FOUPs and the growth of SiN layer on wafer surfaces.

## METHODS

Fig. 1(a) shows the schematic diagram of experimental setup for the artificial contamination. Pre-cleaned FOUP and wafers were used to estimate the effect of AMCs on SiN layer growth. In pre-cleaning process, FOUP was washed by FOUP clean equipment (UPC12500, HUGLE), which was used in semiconductor manufacturing process. As for the washing conditions, the spraying was continued for 25 seconds using ultrapure water (UPW) and the drying was kept for 250 seconds with nitrogen gas purge. In order to elucidate the influence of internal contamination of FOUP upon the deposited film thickness, this pre-cleaned FOUP was artificially contaminated by standard hydrogen fluoride (HF) solution (Titrisol, Merck). A Teflon beaker with 20% HF solution were placed in FOUP, and left for 30 minutes for gaseous diffusion (González-Aguirrea *et al.*, 2013).

Automated sampling system (ProFAST-200H, WITHTECH Inc., Fig. 1(b)) was developed and introduced to evaluate a degree of contamination in FOUP. The quantitative and qualitative analyses of contaminated materials were performed by two monitoring systems connected to the sampling system: (1) acidic gas monitoring system and (2) ammonium ions monitoring system. The acidic gas monitoring system (Navi-MG200, WITHTECH Inc., Fig. 1(c)) consisted of an ion chromatography, and the ammonium

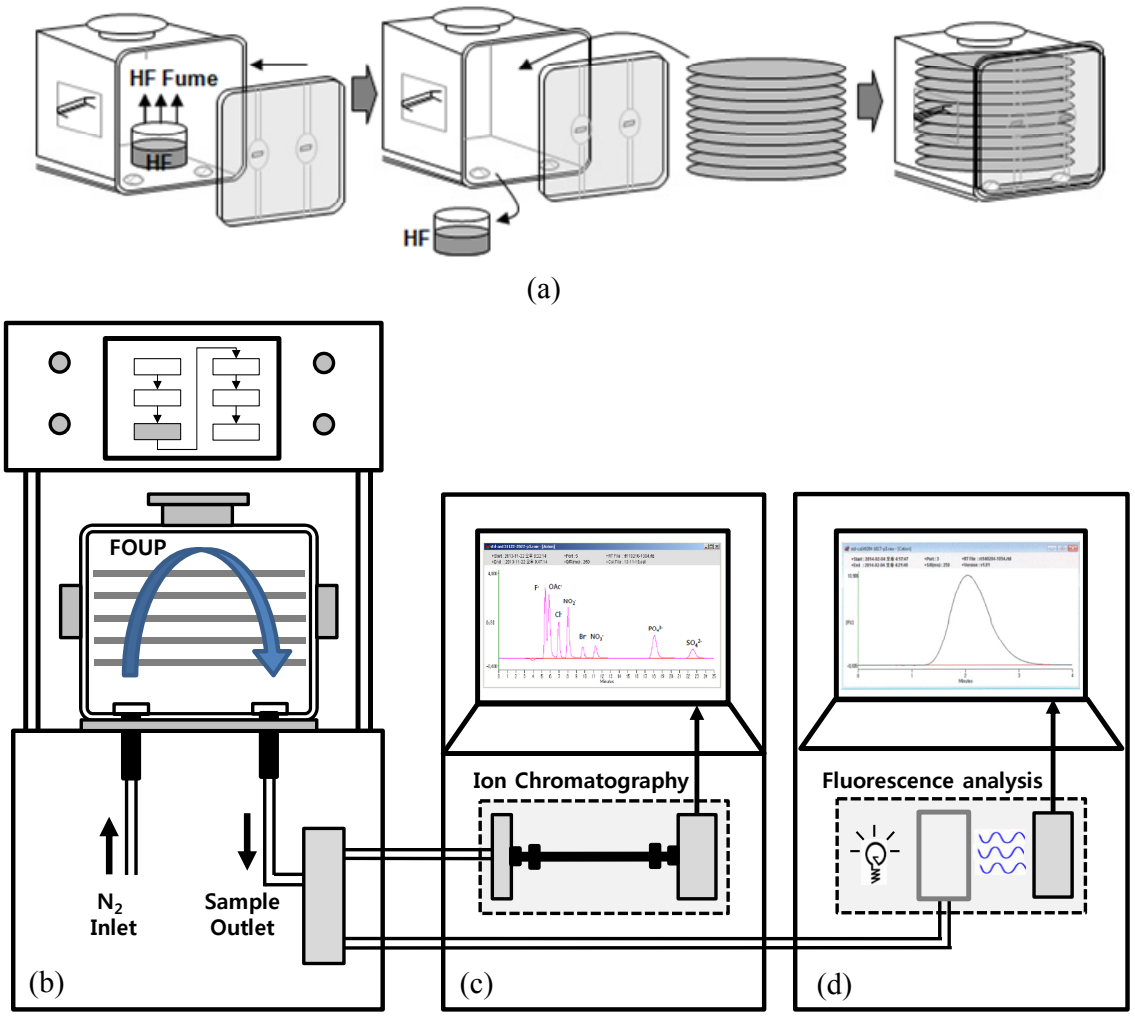


**Fig. 1.** Schematic diagram for artificial contamination of the inside of FOUP (a), and automated sampling system (b) connected with the analyzers for ion chromatography (c) and fluorescence analysis (d).

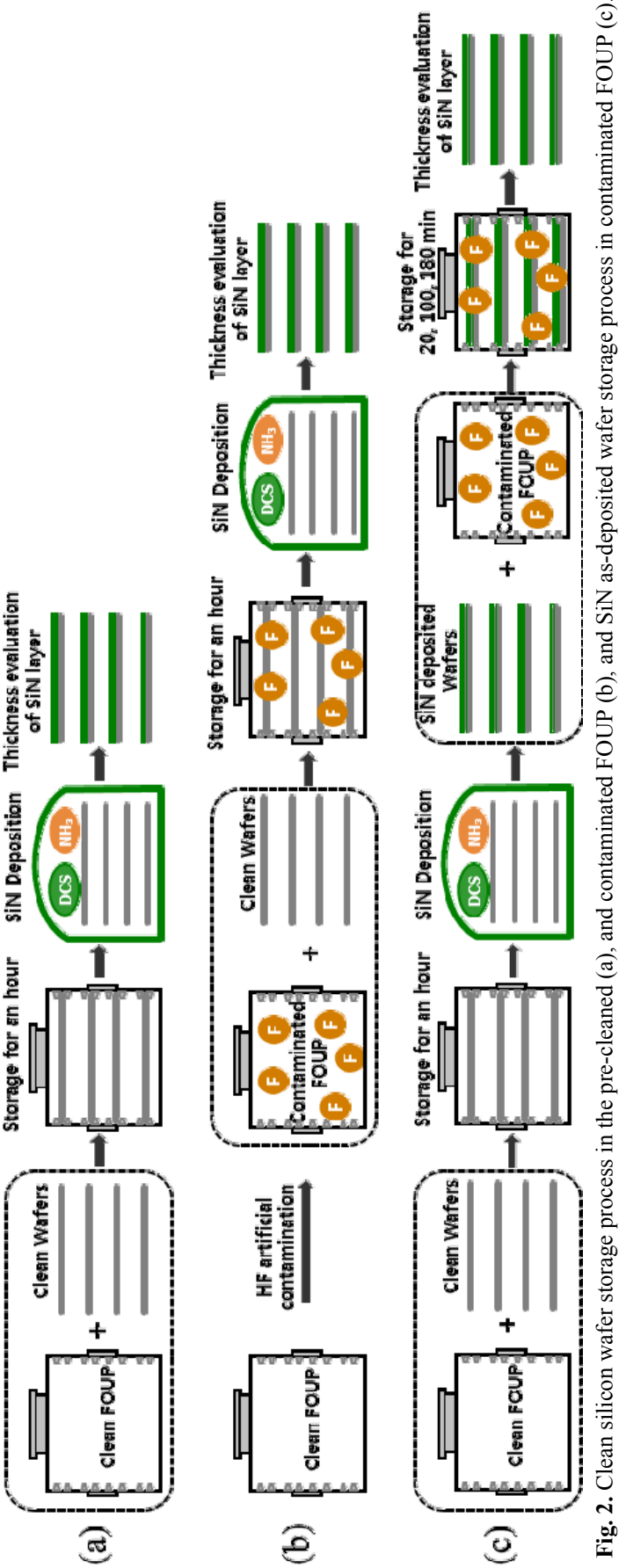


**Fig. 2.** Clean silicon wafer storage process in the pre-cleaned (a), and contaminated FOUP (b), and SiN as-deposited wafer storage process in contaminated FOUP (c).

ions monitoring system (Navi-WF301, WITHTECH Inc., Fig. 1(d)) was based on a fluorescence analysis. The internal air of both pre-cleaned FOUP and contaminated FOUP was collected with nitrogen gas purge to absorbent for 10 minutes and sent to the monitoring systems.

Fig. 2 shows the schematics of storage process of wafers prepared for the study of the contamination effects on the SiN deposition in this work. Some of pre-cleaned bare wafers were stored in pre-cleaned FOUP for one hour and then chemical vapor deposition (CVD, PRODUCER-SE, AMAT) step with dichlorosilane ($SiH_2Cl_2$) and ammonia ($NH_3$) gases was processed for the formation of SiN layer with various film thicknesses (Fig. 2(a)). In Fig. 2(b), pre-cleaned bare wafers were loaded and left for one hour in contaminated FOUP, and also CVD step was processed for the formation of SiN layer with various film thicknesses. Deposited film thicknesses between wafers stored in pre-cleaned FOUP and contaminated FOUP were measured and compared. Additionally, some of SiN as-deposited wafers with same thickness (92 Å) after CVD process in Fig. 2(a) were transferred to contaminated FOUP and stored as intervals of 20, 100, and 180 minutes (Fig. 2(c)). Film thickness and surface morphology of all SiN deposited wafers were obtained using transmission electron microscope (TEM, JEM-3000F, JEOL) and scanning electron microscope (SEM, S-5500, Hitachi), respectively.

The chemical analysis on the samples prepared in Fig. 5 was done by X-ray photoelectron spectroscopy (XPS, Quantum2000, ULVAC-PHI) to check the presence of fluoride ions and to confirm the fact that fluoride ions on contaminated wafer could affect the formation of SiN layer. We divided clean wafers into two groups, and stored one group in pre-cleaned FOUP and the other group in contaminated FOUP for an hour. Then, some of these wafers were taken out from each FOUP to analyze their surfaces. After SiN layer deposition with consistent thickness, their surfaces were also measured using XPS. Additionally, it was used to analyze inner surfaces of pre-cleaned FOUP and contaminated FOUP so as to check if the contamination by fluoride ions was originated from FOUP.

## RESULTS AND DISCUSSION

Fig. 3 shows the concentration of detected fluoride ions from a pre-cleaned FOUP and artificially contaminated FOUPs. We prepared four artificially contaminated FOUP and one pre-cleaned FOUP, and measured the inside concentration of each FOUP. The experimental error ranges were observed between 0.1 and 11.6% for these contaminated FOUPs. The fluoride ion concentration of contaminated FOUP was about 6,420 ppb which was 400 times higher than that of the pre-cleaned FOUP. A small amount of nitrate and ammonium ions were also detected in both the pre-cleaned and the contaminated FOUP. It appeared that the primary reason for the presence of these ions was due to an inflow of ambient air into FOUPs during cleaning.

Fig. 4 shows SiN film thickness and thickness difference for two different FOUPs: pre-cleaned and the contaminated. SiN deposition was conducted for three wafers and the thickness was measured at 3 points (top, center and bottom parts of wafers). From this measurement, 9 data were collected from each measuring point, ranging from 0.7 to 9.1% in the experimental error. It was observed that the SiN thickness on the wafer stored in the contaminated FOUP decreased by 6 to 11 Å. Furthermore, it should be noted that the thickness difference increased (up to 11 Å) as deposited film thickness increased (up to 800 Å). This behavior suggests that thinner SiN layers might be more strongly affected by residual fluoride ions in FOUP. Although there are many studies on various patterns of defects caused by AMCs or molecules in cleanroom environment (Iwamoto and Ohmi, 1997; Nguyena *et al.*, 2012), very little is known about the investigations for the relationship between contamination and layer growth.

Fig. 5 shows the XPS results for the clean silicon wafer stored in pre-cleaned FOUP and contaminated FOUP for

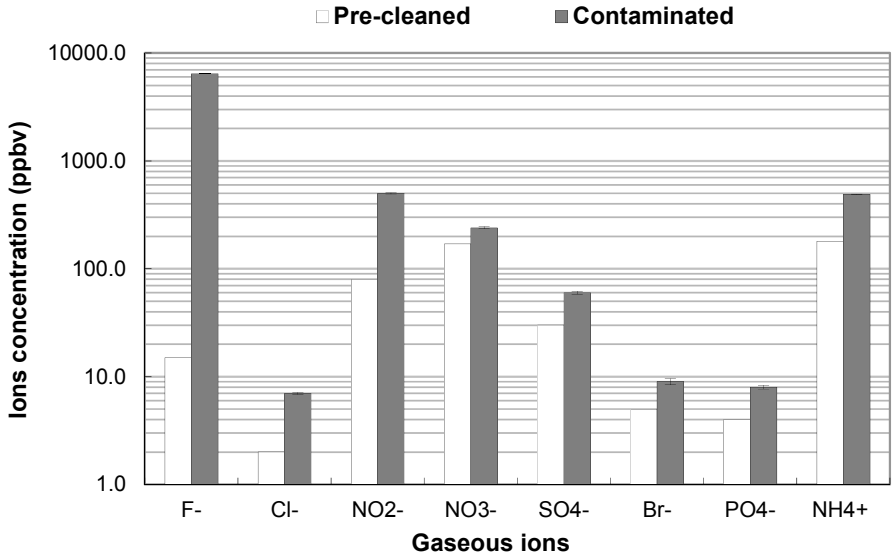


**Fig. 3.** Concentration of gaseous ions detected in the pre-cleaned (□) and contaminated (■) FOUP.

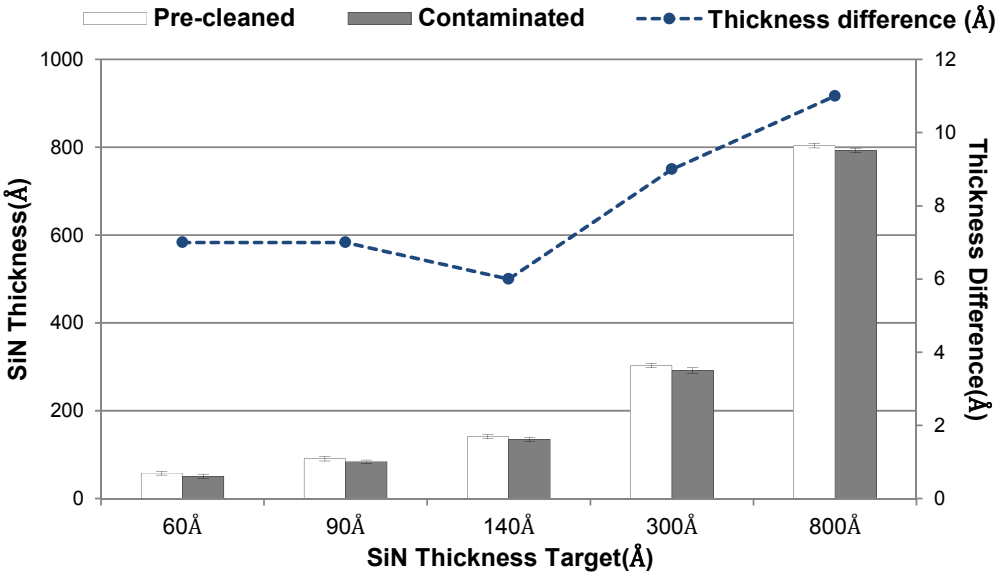


**Fig. 4.** Thickness of SiN deposited film layer of wafers stored in the pre-cleaned (□) and the contaminated (■) FOUPs, and thickness difference ratio (--●--) of SiN layers stored in the contaminated FOUP.

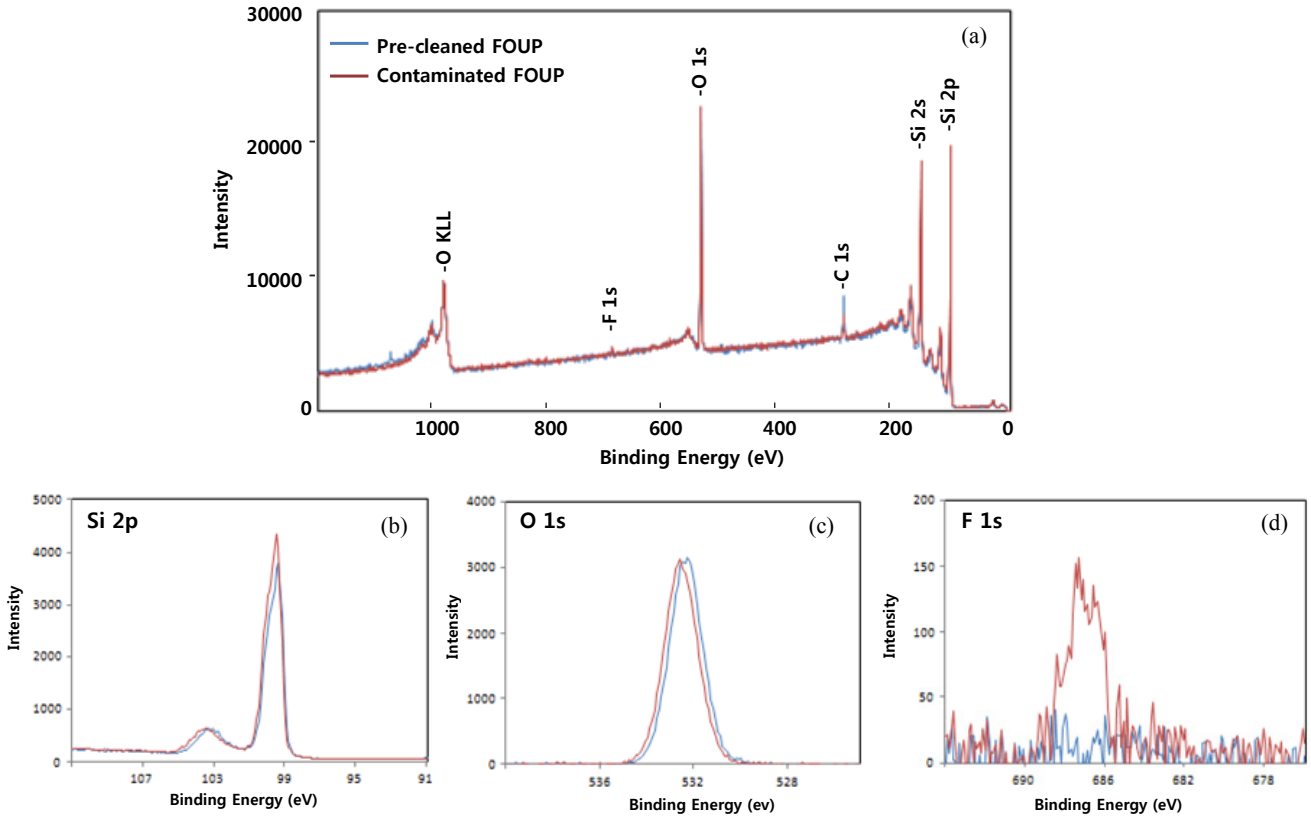


**Fig. 5.** XPS spectra of clean silicon wafers stored in each pre-cleaned FOUP and contaminated FOUP for an hour (a), and magnified spectrums of silicon (b), oxygen (c) and fluoride (d) detection.

an hour. The silicon and oxygen elements were detected on silicon wafer surfaces for these two FOUPs. Oxygen was detected due to the existence of native oxide on wafer surfaces. When the peaks of fluoride detection (F1s) were partially magnified with a range of 660–700 eV, it turned out that fluoride was observed only for the case of silicon wafer stored in contaminated FOUP.

We have also obtained the XPS spectra of SiN-deposited wafers (Fig. 6). The spectra showed the existence of carbon, nitrogen, oxygen, and silicon elements. Besides, very small amount of fluoride was detected and assumed to be arisen from contamination. It was considered that among these

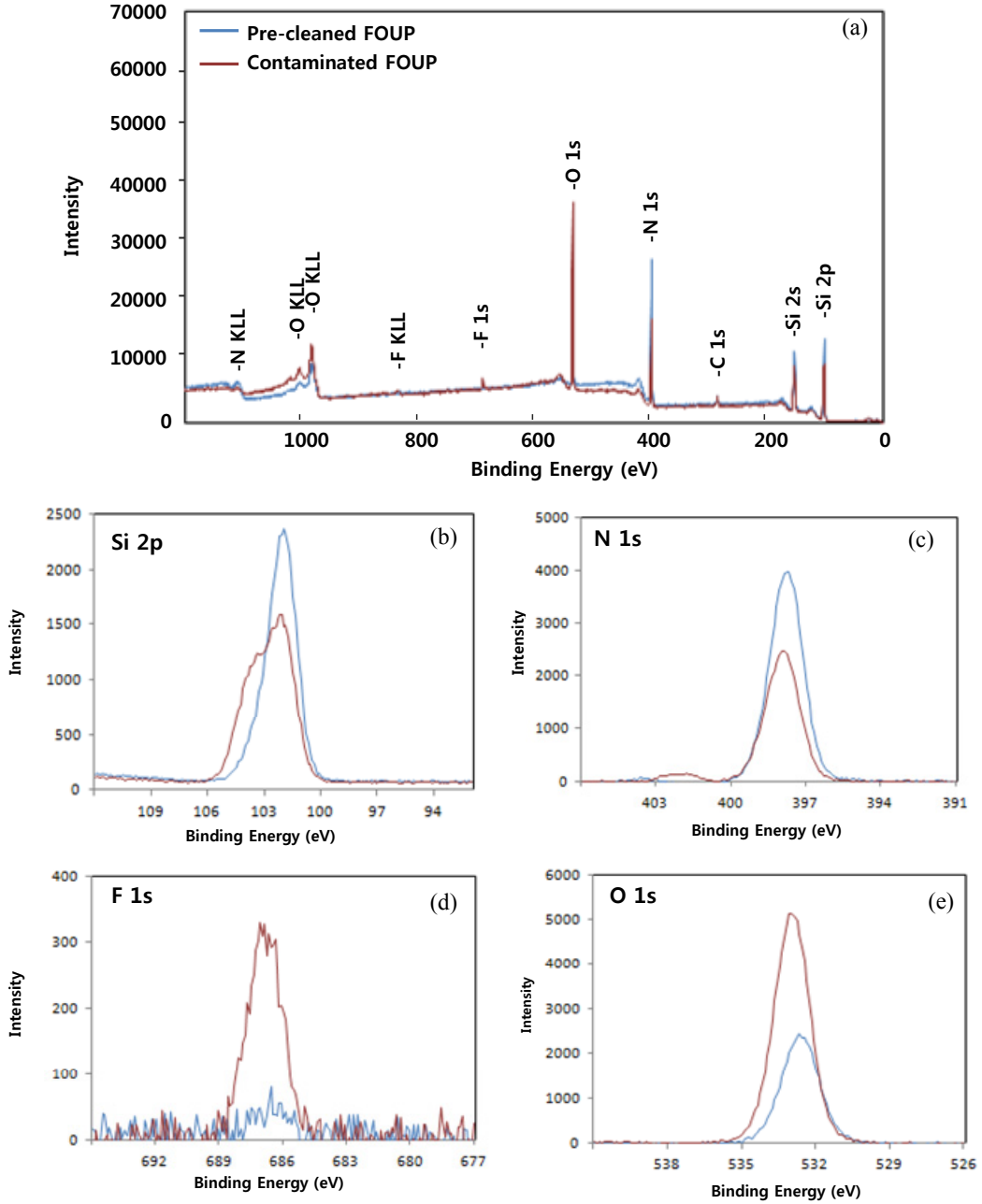


**Fig. 6.** XPS spectra of SiN as-deposited wafers stored in each pre-cleaned FOUP and contaminated FOUP for an hour (a), and magnified spectra of silicon (b), nitrogen (c), fluoride (d) and oxygen (d) detection.

elements, the carbon appeared when the wafer was contaminated by exposure to atmosphere during transfer for XPS experiments. It was found that carbon, nitrogen, and oxygen peaks were all observed in both pre-cleaned FOUP and contaminated FOUP (Figs. 6(a), 6(c) and 6(e)). However, fluoride was detected only in contaminated FOUP (Fig. 6(d)), which was similar to the case of clean silicon wafers.

Fig. 7(a) exhibits XPS survey for inner surfaces of pre-cleaned FOUP and contaminated FOUP, indicating that silicon, carbon, oxygen and fluoride were observed. It was assumed that the carbon and oxygen was attributed to the material of FOUP, which was composed of polycarbonate. Almost the same amount of carbon was detected in pre-cleaned FOUP as well as in contaminated FOUP (Fig. 7(b)). However, the fluoride was only detected in contaminated FOUP, which indicated that the contamination of wafers was due to the contaminated FOUP (Fig. 7(c)).

Based on these XPS results, it is reasonable to speculate that contamination of clean silicon wafer surfaces by fluoride ions might have been derived from the inner surface of contaminated FOUP. Consequently, it was also considered that this contamination hinders the growth of SiN layer deposited on contaminated wafers. And chloride, which is included in dichlorosilane ($SiH_2Cl_2$) to deposit SiN layer, is not observed on wafer surfaces and it seems it is exhausted

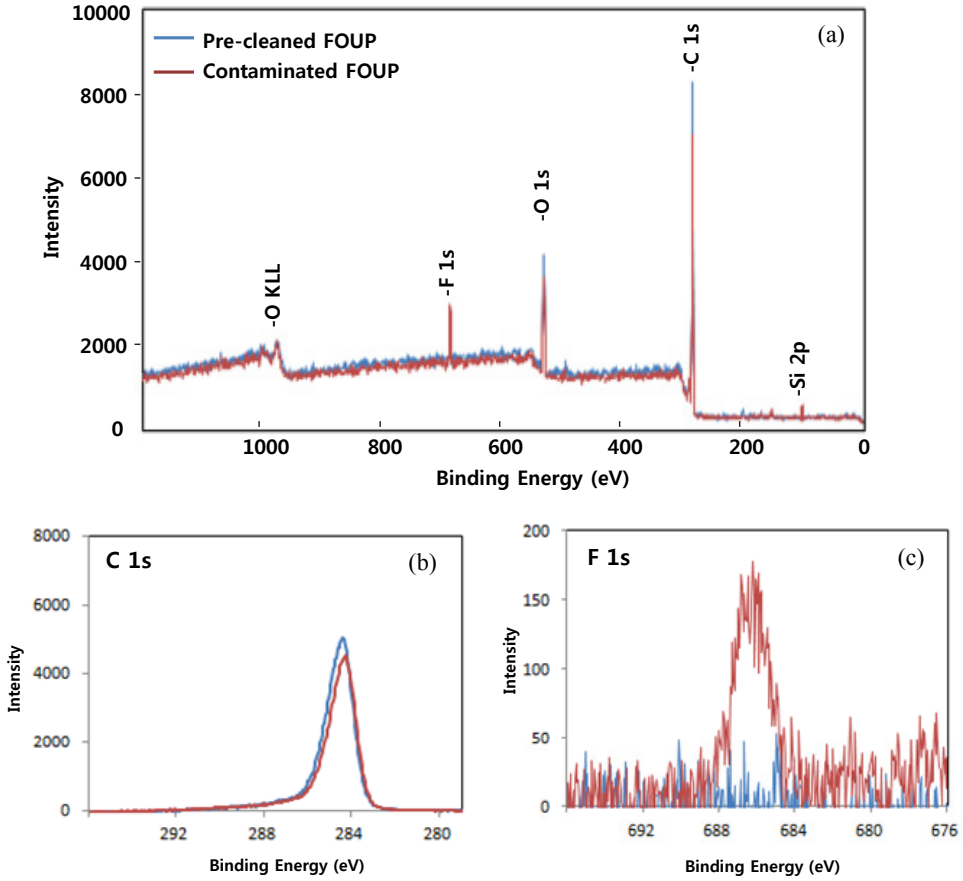


**Fig. 7.** XPS spectra of inner surface of pre-cleaned FOUP and contaminated FOUP (a), and magnified spectra of carbon (b) and fluoride detection.

judging by the fact that it is not detected. There were two more gases used in CVD process for SiN deposition such as dichlorosilane ($SiH_2Cl_2$) gas and ammonia ($NH_3$) gas. From these two gases, the disilane ($Si_2H_2$) gas was produced by chemical reaction. This gas reacted with fluoride ion on the wafer surface, which subsequently generated the silicon tetrafluoride ($SiF_4$) gas. The production of silicon tetrafluoride ($SiF_4$) gas might bring about a shortage of silicon component on the wafer surface.

Several wafers coated by SiN layers with the same thickness of 92 Å were also stored in the contaminated FOUP and were sequentially extracted after a storage time of 20, 100, and 180 min. Afterwards, the morphologies and thicknesses were measured using SEM and TEM, respectively. The images of the surface morphology and layer thickness according to the storage time in the contaminated FOUP are shown in Fig. 8. Recently, similar results have previously been reported. Hua *et al.* (2014) reported the crystal defects on an aluminum-bonding pad due to the fluorine-induced corrosion, and Wu *et al.* (2012) also found the metal corrosion on the patterned wafer. Although the observed areas were not so wide, it was possible to recognize the crystal-like defects and corrosion parts in our case. The thickness and surface of the SiN layer have not been changed at all with the storage time, even when the wafer had been stored for 180 minutes in the contaminated FOUP. This indicated that the thickness decrease of the deposited SiN layer was caused by contamination of the bare wafer surface by fluoride ions rather than by contamination of the SiN deposited surface.

Based on the results above, it should be noted that the concentration of fluoride ions at the bare wafer surface hampered the growth of deposited layers. The contamination by fluoride ions at the inner surface of FOUPs could be induced by the transferred and stored wafers after each etching step. The residual fluoride ions in FOUP might have been released into the surface of every transferred wafer. In the long run, it is suggested that the cleaning and purging steps, and gaseous ion monitoring of FOUPs are necessary after every etching process to improve the production yield by preventing any defects at the wafer surface.

## CONCLUSIONS

We investigated the hindrance to the growth of a SiN layer, which was due to residual gaseous impurities in FOUP. An artificial contamination in FOUP was utilized to prove the concept of hindrance. The concentration of residual fluoride ions in the contaminated FOUP was 6,420 ppbv, which was 400 times higher than that in the pre-cleaned FOUP. A hindrance in the growth of SiN layer did not occur if bare wafers had been stored in the pre-cleaned FOUP before the SiN deposition process. Otherwise, when the bare wafer

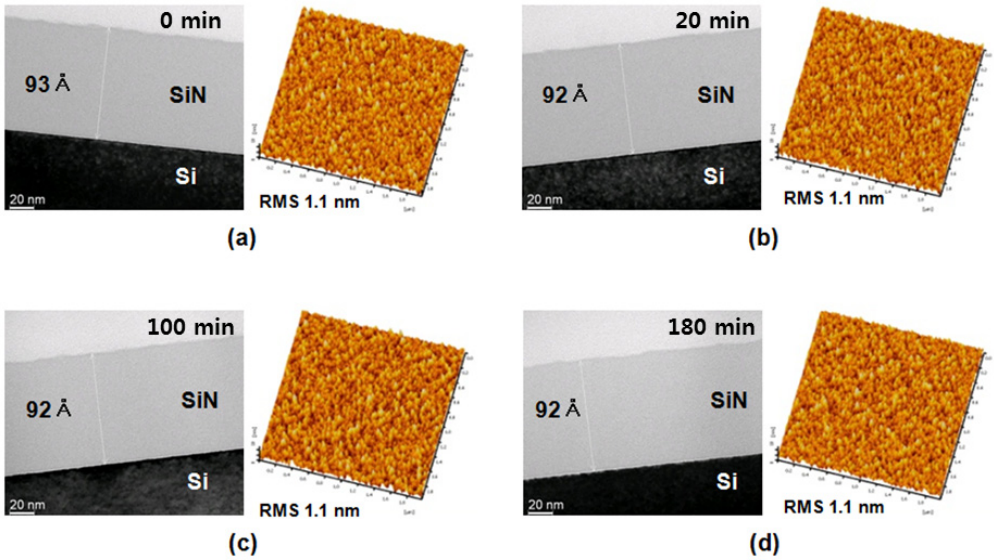


**Fig. 8.** Variation of SiN layer thickness and morphology depending on storage times of 0 (a), 20 (b), 100 (c) and 180 (d) minutes in the contaminated FOUP.

was stored in the contaminated FOUP, the thickness difference of SiN layer gradually increased from 6 Å to 11 Å as deposited layer thickness increased. According to the analytic results on wafer surfaces stored in pre-cleaned and contaminated FOUP, and on inner surface of each FOUP, the fluoride component was only found on wafer surfaces stored in the contaminated FOUP and on inner surface of contaminated FOUP. It indicated that contamination of fluoride ion in clean silicon wafers was originated from the inner surface of FOUP. In order to observe the effect of fluoride ion contamination on the surface state of the wafers, SiN as-deposited wafers in clean condition were stored in the contaminated FOUP. The thickness of these SiN layers did not decrease, irrespective of the storage time in the contaminated FOUP, even when the wafer had been exposed for 180 minutes to a high concentration of fluoride ions. This result indicated that the fluoride ions could not directly affect the SiN layer but the bare wafer surface during the CVD process. It appeared that some of the remaining fluoride ions at the surface of wafer diffused into the inside of FOUP during transportation and storage of these wafers. Then, the residual fluoride ions in FOUP migrated to the bare surfaces of the other cleaned wafers. These migrated fluoride ions could inhibit the formation of SiN layer from dichlorosilane ($SiH_2Cl_2$) and ammonia. This study provides evidence that the cleaning and monitoring processes are essential, and should be applied not only to the processed wafers but also to FOUPs after each chemical etching step.

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