Depth Profiling of Perhydoropolysilazane Thin Film Using Multi Anode XPS Technique

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The depth profiling of perhydoropolysilazane(PHPS) thin films on Si wafers were investigated by multi anode x-ray photoelectron spectroscopy (XPS) which has four x-ray anodes such as Mg, Zr, Ag and Ti . As the excitation energy of x-ray become higher, the information depth is more deepened. So it is possible to non-destructive depth profiling analysis of PHPS films by using multi anode XPS. It was found that the PHPS films to convert to silica occur not only on surface but also in sample inside by means of thermal treatment.

1. Introduction

PHPS has characteristic that convert to the silica reacting with oxygen and moisture in air as equation in Fig.1. So it has been attracted to many industrial fields as silica thin film forming techniques for oxygen gas barriers coating, hard coating, electric insulation coating and antireflection coating etc. The silica coating film obtained from PHPS has different composition depending on depth and different reaction speed to convert to silica by means of different treatment condition[1]. So the depth profiling analysis of PHPS is very important to industrialization for many fields.

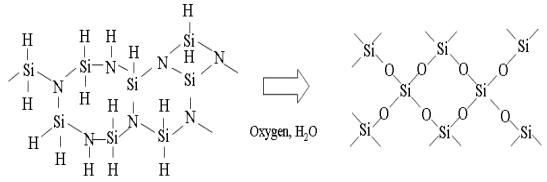

Fig. 1 The reaction scheme of PHPS.

Generally, the depth profiling analysis using XPS is done by a method combined with Ar ion sputtering. However in the case of depth profiling analysis of insulator such as metal oxides, the surface charging and reduction reaction are occurred during Ar ion bombardment. As the result the changing of XPS spectra appears in some metal oxides. Therefore it is very difficult to estimate the chemical state of specimen[2].

Whereas the depth profiling analysis by using high energy light source such as synchrotron radiation (SR-XPS) was reported[3]. Because of the excitation energy of light source can be changed by using synchrotron radiation, the kinetic energy of emitted photoelectron can be changed intentionally. Thus it can be non-destructive depth profiling analysis by using SR-XPS. In this study, we investigated the depth profiling of PHPS film by using multi-anode XPS, which has four x-ray anodes and excitation energy of x-ray can be changed intentionally as using synchrotron radiation.

2. Experimental

2.1 Sample preparation of PHPS thin film

Xylene solution of PHPS (AZ Electronic Materials Japan NL110) was used as the coating solution for PHPS films. PHPS thin films on Si(100) single-crystal substrate were prepared by spin coating at a spinning condition of 1000rpm for 30sec. After that the PHPS films were heated in air for 30min at 80℃, 140℃, 200℃ and 250℃.

2.2 XPS and FT-IR measurement

The XPS measurement was performed by using a ULVAC-PHI model PHI-5500. Because of the use of four x-ray anodes such as Mg, Zr, Ag and Ti, the kinetic energy of the photoelectron is changed. Thus the information depth is deepened in order of Mg, Zr, Ag and Ti. The Infrared spectra were obtained by PerkinElmer Japan model Spectrum one and a bare Si(100) single crystal substrate was used as the reference.

3. Results and discussion

First, we examined of relationship between information depth and a kind of x-ray anodes by using Si wafer. Fig.2 shows the Si1s spectra when ZrL α , AgL α , TiK α and TiK β were used. In the case of ZrL α used, which was the lowest energy in the above x-ray anodes, the peaks of Si1s were almost depending on SiO_2 (spectrum A). When

excitation energy of x-ray is higher, the lower binding energy peaks from Si substrate were increasing and the peaks from SiO_2 were decreasing. Whereas, in the case of using TiK β which was the highest energy in the above x-ray anodes, the peak depending on SiO_2 was not detected(spectrum C). Thus it was understood that the non-destructive depth profiling analysis was able to be done by using multi anode XPS.

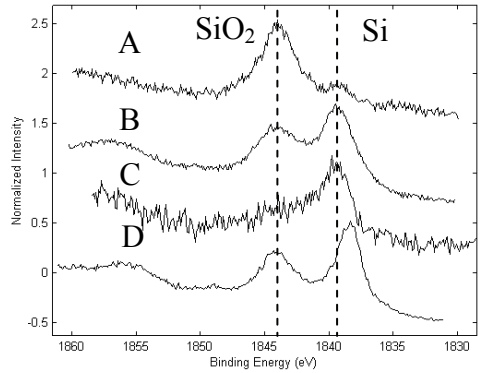

Fig. 2 The Si1s spectra of Si wafer obtained by multi anode XPS.
(A:ZrL α , B:AgL α , C:Tik β , D:Tik α)

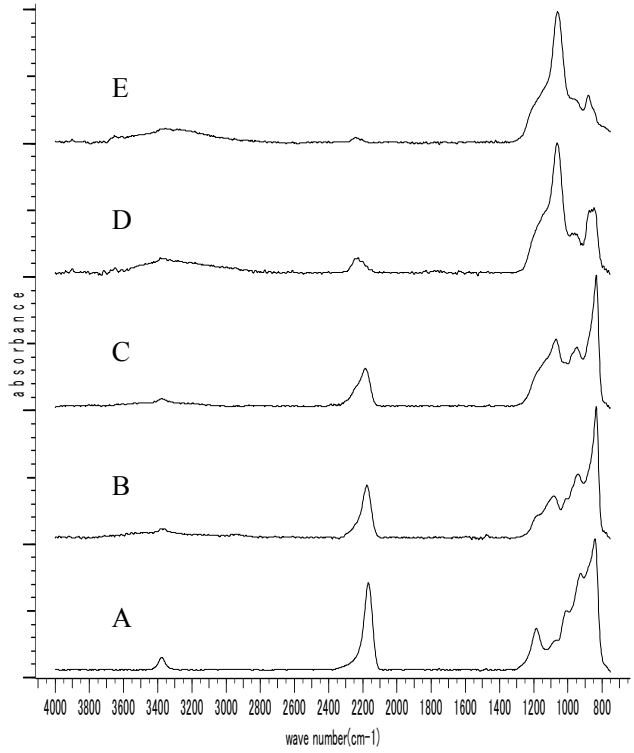

Fig. 3 The changes of FT-IR spectra of PHPS after thermal treatment.
(A: non-thermal treatment, B:80℃-30min, C:140℃ -30min, D:200℃-30min, E:250℃-30min)

Fig.3 shows the changes of FT-IR spectra of PHPS films on Si wafer, which were treated at various temperatures. The N-H stretching bands at around 3370cm^{-1}, 1190cm^{-1}, Si-H stretching bands at around 2260cm^{-1}, and Si-N bands at around 900cm^{-1} were decreased as thermal treatment temperatures were increased. Whereas Si-O bands at around 1060cm^{-1} were increased. These results indicated that PHPS films were converted to silica by thermal treatment.

Fig.4 shows the changes of Si2p spectra, which were obtained from the same samples as Fig.3. The binding energy of Si2p spectra of non-thermal treatment specimen (spectrum A) were at around 101.9eV which were depending on Si-N bond and the peak at around 103eV and 99eV which were depending on SiO_2 and Si were not detected in all x-ray anodes. Therefore the influence of Si substrate can be ignored in the sample made for this study. The peak shifts of Si2p depending on the increasing thermal treatment temperatures were observed not only when using MgK α which was the lowest excitation energy but also when using TiK α which was highest excitation energy. These results indicated that the PHPS film converted to silica occurs not only on surface but also in sample inside.

In conclusion, we report the result of depth profiling analysis of PHPS film after various treatments by using multi anode XPS.

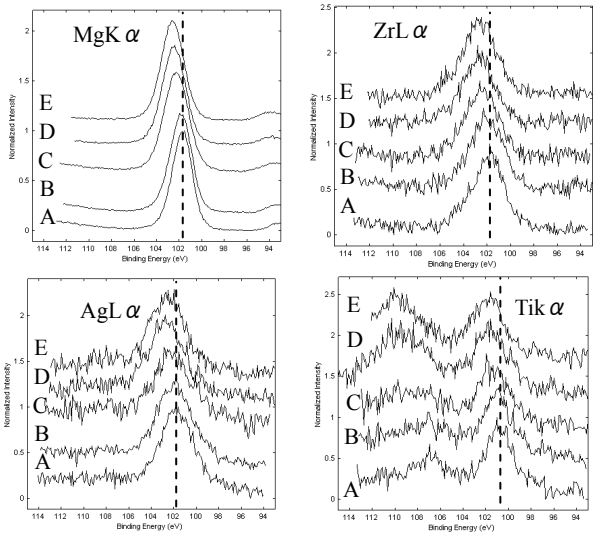

Fig. 4 The changes of Si2p spectra of PHPS after thermal treatment.
(A: non-thermal treatment, B:80℃-30min, C:140℃ -30min, D:200℃-30min, E:250℃-30min)

4. Acknowledgements

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5. Reference

[1] Yasuhiro NAGANUMA, Satomi TANAKA, Chihiro KATO, Toyohiko SHINDO, J. Ceram. Soc. Japan **112**, pp.599-603 (2004).
[2] Satoshi HASHIMOTO, J. Surf. Sci. Soc. Jpn. **25**, pp.198-204 (2004).
[3] Hiroyuki YAMAMOTO, Yuji BABA, Teikichi SASAKI, Surf. Sci. **349**, Issue1, pp.L133-L137 (1996).