X-ray Absorption Near Edge Structures of Silicon Nitride Thin Film by Pulsed Laser Deposition

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Silicon nitride thin film was fabricated by pulsed laser deposition using KrF excimer laser and a silicon nitride compact as a target. The deposition was carried out on Al\textsubscript{2}O\textsubscript{3} (0001) at 1173 K in N\textsubscript{2} gas pressure of 0.27 Pa. The X-ray diffraction did not provide any structural information of the deposited thin films except that it is composed of amorphous and/or micro-crystalline structure. X-ray absorption near edge structures (XANES) measurement of the film revealed that local arrangement of Si is not random. It should be composed of SiN\textsubscript{4} unit similar to the case of \textalpha-Si\textsubscript{3}N\textsubscript{4} crystal. Metallic Si component cannot be found in XANES.

Measurement of X-ray diffraction pattern was conducted to examine the quality of crystal in the deposited thin films. Then we made Si-K edge X-ray absorption near edge fine structures (XANES) measurement of the film. Si-K edge XANES measures electronic transition from Si-1s orbital to unoccupied bonds just above the Fermi energy. It is known to be sensitive to the local environment of the selected element, i.e., Si in this case.

1. Introduction

Silicon nitride has been utilized for structural components because it has high hardness, mechanical strength and high temperature oxidation resistance. It has also been used extensively in the semiconductor industry for several decades as insulating dielectrics. Recently, it is considered to be the first practical post-SiO\textsubscript{2} gate dielectric material for integrated silicon devices. It has also been used for passivation coatings as diffusion barriers of harmful impurities. For device process, many different deposition techniques have been studied. Both plasma enhanced chemical vapor deposition (CVD) and hot wire CVD with silane or silicon tetrachloride and ammonia gas mixtures have been successful\textsuperscript{1} and can be carried out at low substrate temperatures, which is a great advantage for the device process. However, because of the use of the reactive gases for the CVD deposition, these films contain high amount of bonded hydrogen which degrades the device performance occasionally.

In order to avoid such degradation, deposition without reactive gases is necessary. Pulsed laser deposition (PLD) does not give rise to contamination in principle because any reactive gases including hydrogen or halogen are not necessarily used. This method therefore has a potential for formation of high quality films without such impurities. The PLD has been greatly successful in the field of oxides thin film such as oxide superconductors\textsuperscript{2} and has achieved the deposition of some nitrides such as BN and AlN.\textsuperscript{3,4} Some research groups made PLD of Si\textsubscript{3}N\textsubscript{4} thin film and revealed the relationship between N\textsubscript{2} gas pressure and nitrogen content of the Si\textsubscript{3}N\textsubscript{4} thin films.\textsuperscript{5,6} However, any structural information are not known in the deposited thin films except for the fact that they were amorphous.

In this article, we report fabrication of silicon nitride thin film by PLD using a silicon nitride target in N\textsubscript{2} atmosphere.

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2. Experiments

Thin film was prepared on an \textalpha-Al\textsubscript{2}O\textsubscript{3} (0001) single crystal by PLD using an excimer KrF* laser source (\textlambda \textasciitilde 248 nm, pulse width \textasciitilde 25 ns, Lambda Physik COMPex205). Laser power was 600 mJ (approximately 0.2 J/mm\textsuperscript{2} at a target) and a pulse rate was 10 Hz. Amount of deposit was 10000 shots of laser pulses. A Si\textsubscript{3}N\textsubscript{4} compact without any sintering aids was used as a target. Because of poor sinterability, the compact was 60% in density. The distance between the target and the substrate was 70 mm. After evacuating the vacuum chamber to 4 \times 10\textsuperscript{-4} Pa, film deposition was carried out in high-purity nitrogen pressure of 0.27 Pa during deposition. Temperature of the substrate was kept at 1173 K for 3600 s before the deposition. The deposition was made for 1000 s. Film thickness was approximately 200 nm.

Quality of the film was investigated by X-ray diffraction using Cu-K\textalpha radiation and conventional \texttheta–2\texttheta scan (Rigaku, RINT 2000). The XANES spectra were obtained at BL1A beam line of UVSOR by total electron yield method. The beam line is equipped with a focusing premirror and a double crystal monochromator. The KTP (110) was used as an analyzing crystal for the monochromator. All measurements of XANES spectra were carried out in vacuo of 1 \times 10\textsuperscript{-4} Pa at room temperature. Measurement of the thin film was made on a sample after coating it by evaporated carbon to minimize charging. Spectra from reference samples were measured for
powders mounted on adhesive carbon tapes, α-Si$_3$N$_4$, crystalline-Si (Si) and amorphous SiO$_2$ (a-SiO$_2$) samples were obtained commercially. Cubic-Si$_3$N$_4$ (c-Si$_3$N$_4$) sample with a spinel structure was synthesized by a shock-compres-
sion technique as described in Ref. 7). Energy scale of XANES was calibrated with the first prominent peak of the Si-K edge of a-SiO$_2$. The experimental value for the peak energy of the Si-K edge XANES of a-SiO$_2$ in Ref. 8) was used as a reference.

3. Results and Discussion

X-ray diffraction of the PLD film did not show any peaks except some peaks due to the Al$_2$O$_3$ substrate. This result implies that the thin film is composed of amorphous structure or tiny crystalline phases. Any more structural information was not able to be acquired from the X-ray diffraction patterns.

Figure 1(a) shows the Si-K edge XANES spectrum of the deposited thin film. The spectrum is composed of a steep initial rise with a peak at 1844.0 eV and broad second shoulder peak (1860.7 eV). Figures 1(b)–(e) show the XANES spectra of four reference compounds. The Si-K edge XANES of a-SiO$_2$ was observed at 1846.7 eV in Fig. 1(e). The Si-K edge of α-SiO$_2$ was observed at 1846.7 eV in Fig. 1(e). The Si-K edge of Si metal showed three peaks at 1840.3, 1846.5 and 1850.0 eV in Fig. 1(b). The first peak (1840.3 eV) is lowest energy in these compounds. The peak energy of Si and α-Si$_3$N$_4$ (Fig. 1(c)) are 6.4 eV and 2.7 eV lower than the peak of a-SiO$_2$. They agree qualitatively with those in literature, i.e., 6-8 eV$^{9-11}$ for Si and 2.0 eV for α-Si$_3$N$_4$. Figure 2 shows theoretical XANES of two Si$_3$N$_4$ phases and SiO$_2$ (α-

![Fig. 1 X-ray absorption near edge structures of (a) the deposited thin film, (b) Si, (c) α-Si$_3$N$_4$, (d) c-Si$_3$N$_4$, and (e) α-SiO$_2$.](image)

![Fig. 2 Theoretical XANES of (a) α-Si$_3$N$_4$, (b) c-Si$_3$N$_4$, and (c) SiO$_2$ (α-quartz) as calculated by Ching et al.$^{12}$ by the first principles OLCAO method.](image)
provide different kind of structural information. Si-K edge extended X-ray absorption fine structure (EXAFS) to monitor the bond length and coordination numbers should be definitely the next step.

4. Conclusion

Silicon nitride thin film was prepared by PLD using a Si$_3$N$_4$ target. The thin film was deposited on Al$_2$O$_3$ (0001) at 1173 K. Nitrogen pressure of a vacuum chamber was kept at 0.27 Pa during the deposition. X-ray diffraction pattern showed that the thin film was composed of amorphous and/or micro-crystallites. Si-K edge XANES of the thin film was almost the same as that of α-Si$_3$N$_4$. No signature from the metallic Si can be found. The local structure in the deposited thin films is not completely random. It should be composed of SiN$_4$ units, although the Si–N bonds are once broken in the laser plume.

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