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S-E-6

Structure Investigation of Amorphous Silicon Nitrides by Si•K-EXAFS

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Hitachi, Ltd. has been constructed 1.8~14keV, soft X-ray to X-ray, beam line for EXAFS studies in the Photon Factory. The beam line is equipped by specially designed double crystal monochromator and EXAFS measuring system. The beam line is able to obtain EXAFS spectra of Si•K X-ray absorption edge. Using the beam line and synchrotron radiation (SR), EXAFS spectra of amorphous thin films of silicon nitrides formed by CVD methods has been measured and the radial atomic structures are investigated.

1. INTRODUCTION

The structures of amorphous thin films of the silicon compounds are indispensable for research works on the semiconductor devices. The relations between the methods of thin film formation and the atomic structures of the thin films are very important to improve the electric properties of the semiconductor devices.

Most of the thin films utilized in the LSI fabrication processes have amorphous atomic structures. The oscillations observed in the absorption coefficient above the X-ray edge are analyzed and interpreted in the terms of the average radial structure. The oscillations are today named EXAFS (extended X-ray absorption fine structure). There have been several difficulties to obtain the EXAFS spectra of silicon compounds.

To obtain the precise EXAFS spectra of silicon compounds, double crystal monochromator and ionization chambers are newly developed to use even in an ultra-high vacuum of 10^{-8}torr. EXAFS spectra of the two modifications of the crystalline α- and β-Si_3N_4 were obteined by the fluorescent yield measurement and also ones of thin films by LP-CVD and ECR-CVD by the transmission measurement.

2. SPECIAL FEATURE OF MEASUREMENT SYSTEM

The special double crystal monochromator and ionization chambers have been developed to use in the ultra-high vacuum of 10^{-8}torr. The thickness of the X-ray window is reduced from usual 400μm to 75μm and the transmission intensities of X-rays with Si•K edge energy has improved as strong as 3000 times.

2.1 X-RAY OPTICAL SYSTEM OF BEAM LINE

The EXAFS measurement system was installed at the beam line BL-8B of the Photon Factory. The length between the X-ray source point of the storage ring to a sample is 31m. The X-ray optical system of BL-8B is shown schematically in Fig.1. The bent cylindrical mirror is located at down-

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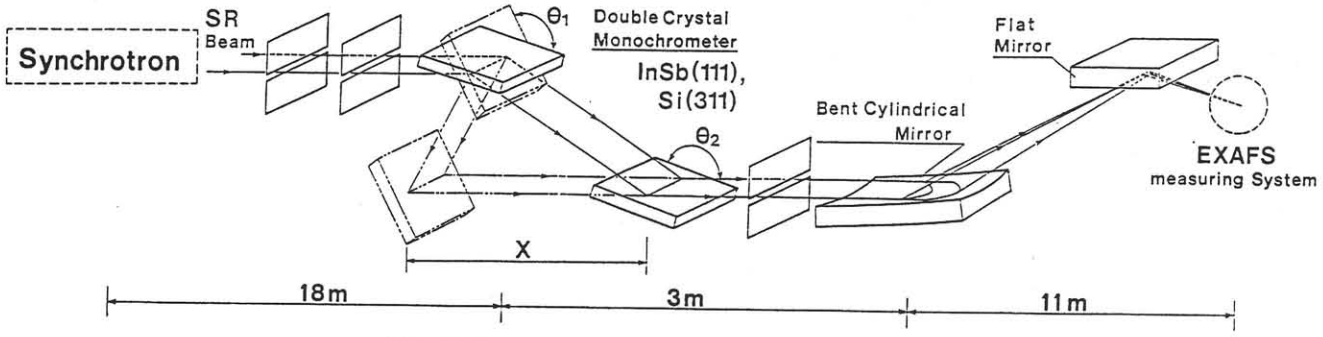

Fig.1 Schematic Illustrations of X-ray Absorption Spectrometer using SR

stream of the monochromator in order to reduce the thermal load of the first monochromator crystal. Flat mirror is located just upstream of the EXAFS measurement system to eliminate the harmonics and multiple reflections generated at the monochromator.

SR beam with a size of 25(H)×1(V)mm² at the slit position upstream of monochromator is reduced to FWHM size of 2.5(H)×0.7(V)mm² at specimen position. Critical energy of the bent cylindrical mirror is set at about 14 keV. The critical energy of the flat mirror is adjusted by the angle and usually set at 2.8keV to measure Si·K EXAFS spectra.

2.2 DOUBLE CRYSTAL MONOCHROMATOR

Energy range of 1.8～2.8keV(7.0～4.4Å) is required to measure Si·K-EXAFS spectra. Soft X-rays of the energy range exibit extremely high coefficients of mass absorption and are strongly absorbed by the usual X-ray transmission window to isolate the clean ultra-high vacuum of the storage ring and low vacuum of the measurement system.

Specially designed motors and rotary encoders to set the monochromator crystal angles are adopted to use in the high vacuum. The insulators of the motors and encoders are replaced to Teflon and polyimids to reduce the sublimations from the insulators. The ball bearings are also replaced to usual grease lubricant to fomblin oil which has very small vapor pressure of ~10^{-14}torr at 25℃. These components of the monochromator enable 1/28,800th of a degree of rotation angular resolution even in high vacuum of 10^{-8}torr. The thickness of X-ray window between the storage ring and the monochromator is then reduced to 75μm because there is almost no pressure difference and the vacuum of the monochromator is enough clean.

2.3 IONIZATION CHAMBERS AND Si(Li) DETECTORS

The EXAFS measurment system is illustrated schematically in Fig.2. Two ionization chambers are for incident and transmission intensities (Io,It). Si(Li) and secondary electron detectors are for fluo-

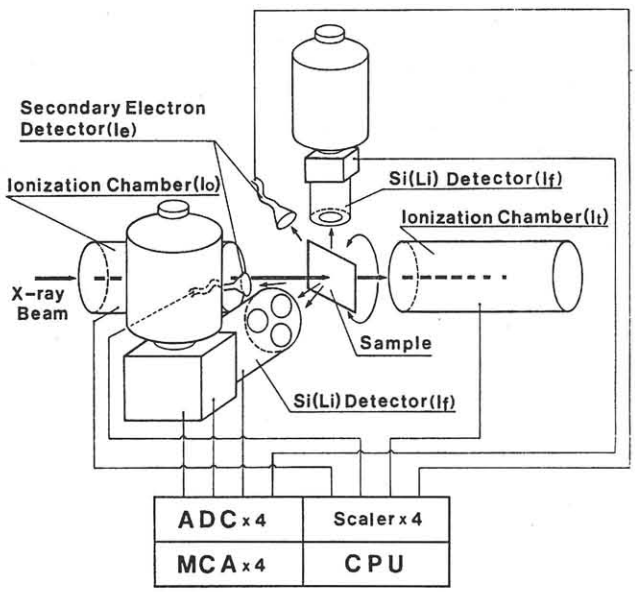

Fig.2 Schematic Illustrations of EXAFS Measurement System

rescent yield (If) and secondary electron yield (Ie), respectively.

In order to obtain precise EXAFS spectra, ionization chambers and Si(Li) detectors are newly developed. The working gas pressures of the ionization chambers are regulated by the PI (proportional-integral) controllers. Neon with the pressures of 40torr for Io and 70 torr for It are usually employed for working gas at Si·K-EXAFS measurement. 80 mm^2 (ϕ 10) Si(Li) elements are utilized for detector. Three Si(Li) elements are mounted in the horizontal Si(Li) detector. The saturation counting level is improved by employing three systems of counting equipments.

3. STRUCTURE INVESTIGASTION OF SILICON NITRIDES

Energy of the monochromatized beam is calibrated by the Si, P and S K-absorption edges using a disc of the mixture. Calculated energy resolution of BL-8B is about 0.4eV at the Si·K-absorption edge (1.84keV).

3.1 MEASUREMENT OF EXAFS SPECTRA

Powders of the standard α- and β-Si_3N_4 crystalline samples are ground and mounted on a diamond plate to measure fluorescent yields. Silicon nitride thin films are prepared by LP-CVD method on the silicon wafer and ECR-CVD method on the Kapton film with thickness of 7.5 μm. The thickness of the thin film sample is adjusted about 1.0 μm. Samples are heated at 800℃ for LP-CVD and 150℃ for ECR-CVD.

Energy scanning step of the near absorption edge region is set 0.25eV and 1~4eV for EXAFS region. Total measured energy point μ(E) is about 400 with the energy range of 1.78~2.8keV. Measured EXAFS spectra of the thin films prepared by LP- and ECR-CVD methods are shown in Fig.3

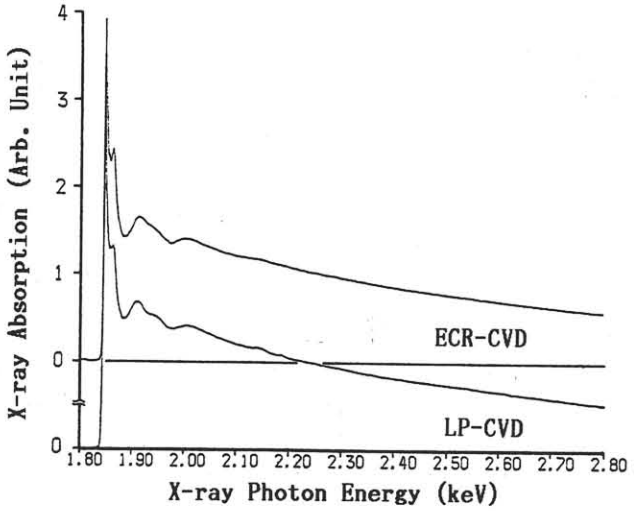

Fig.3 EXAFS of Silicon Nitride Thin Film

3.2 DIFFERENTIAL PROFILE OF ABSORPTION EDGE

Absorption edge profile of Si·K-edge is featured by the steep peak of absorption coefficients. The profiles of absorption edge of thin film prepared by LP-CVD and ECR-CVD resemble each other. But the differential profiles, $\partial \mu(E)/\partial E$ is different between the thin films. Observed $\partial \mu(E)/\partial E$, ∂-XANES (X-ray Absorption Near Edge Structure) spectra are shown in Fig.4.

The energy of steepest absorption is same between the films, but width of energy is different each other. The profile of ECR-CVD thin film is almost same as the standard crystalline α- and β-Si_3N_4 sample.

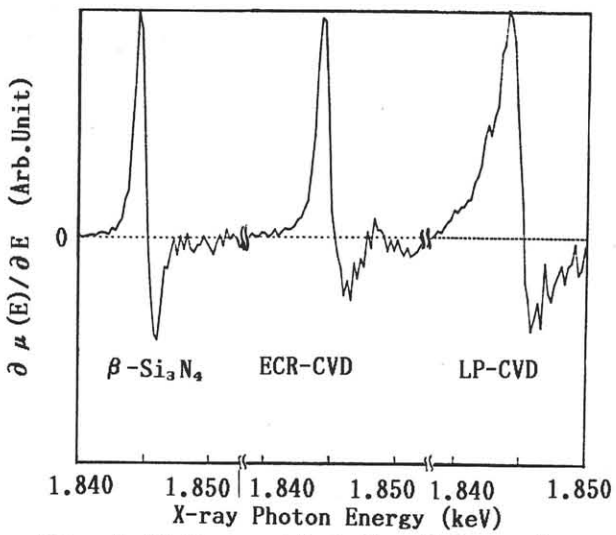

Fig.4 Differential Profiles of Si·K Absorption Edges

3.3 RADIAL STRUCTURE

The measured EXAFS spectra are analyzed through the conventional method as following.

$$(\mu(E)-\mu_0(E))/\mu_0(E)=\chi(k)=$$
$$\Sigma_j 4\pi \int \rho |f_j(k)| \exp(-2r/\lambda) G_{ij}(r) \cdot \sin(2kr+\phi_{ij}(k))dr \quad [1]$$

where $|f_j(k)|$ and $\phi_{ij}(k)$ describe the scattering process undergone by the photoelectron, the former depending only on the scattering atomic species j (N and Si), the latter on both the absorbing (Si) and the scattering ones.

$G_{ij}(r)$ in the formula exibits the radial structure function. Theoretical values of $|f_j(k)|$ and $\phi_{ij}(k)$ are available[2]. The radial structure functions are caluculated and the results are shown in Fig.5. There are slight difference in the atomic distance of the second shell between the thin films formed by LP-CVD and ECR-CVD. The atomic distance of second shell of the ECR-CVD is slightly longer than that of LP-CVD.

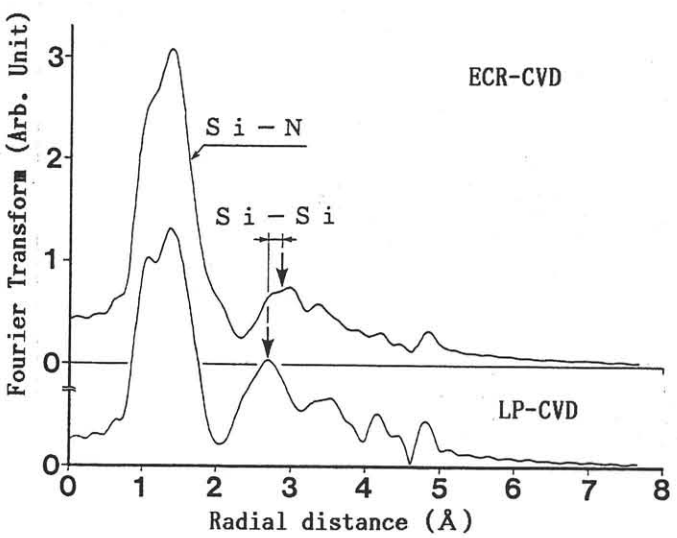

Fig.5 Radial Distribution of Silicon Nitride

4. SUMMARY

The difference of the $\partial\mu(E)/\partial E$, because the existence of the lower energy of absorption edge near Si-Si bond (1.84keV). The profile of ECR-CVD is almost same as those of the stoicheometric standard samples of α- and β-Si_3N_4 crystalline. But it is well known that thin films formed by ECR-CVD involves hydrogen[3] and Si- bonds are terminated H or N.

The difference between the atomic distance of the second shell indicates the difference of the short range structure. The second nearest neighbour of crystalline phase is Si-Si. The average length of the Si-Si is 2.92Å for α-Si_3N_4 and 3.00Å for β-Si_3N_4. Short range structures of the amorphous silicon nitride filmes formed by LP-CVD and ECR-CVD resemble to α- and β-Si_3N_4 crystalline phases, respectively.

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