

# Industrial Applications

## EVALUATION OF PHASE SEPARATION OF Hf-SILICATE FILMS BY IN-PLANE SAXS

High-k films (ex. HfSiO) have been investigated as next-generation gate dielectric films to serve as an alternative to SiO<sub>2</sub> for the reduction of direct leakage current. Amorphous HfSiO is needed to improve device characteristics. HfSiON containing N will be used, because HfSiON is amorphous and stable after high temperature annealing (1000 °C). However, there is a concern about the generation of small HfO<sub>2</sub> phase separation and crystallization after annealing because of the increase in the dispersion of device characteristics [1]. Thus, a high sensitive evaluation method is required to determine the state of the film accurately.

As methods for the evaluation of crystallization and phase separation of thin films, there are TEM, XRD and small angle X-ray scattering (SAXS). It is difficult to determine the boundary of the HfO<sub>2</sub>/SiO<sub>2</sub> accurately from the TEM image. Although XRD (ex. GIXD) is useful for the evaluation of crystallization of very thin films (~1 nm), the evaluation of phase separation (not crystalline) cannot be carried out by XRD. SAXS is expected to provide a quantitative analysis (ex. average diameter and distribution) of the phase separation. We have already ensured that In-Plane SAXS using conventional laboratory equipment could be used for the quantitative analysis of phase separation of thick HfSiON (more than 10 nm). However, it was difficult to analyze thin films (less than 5 nm) using conventional laboratory equipment.

To evaluate very thin HfSiON films (3 nm) by In-Plane SAXS, we used the synchrotron radiation X-ray at beamline **BL13XU**.

Several HfSiO films (3 nm, Hf/(Hf+Si) = 50%) were deposited by MOCVD on Si (100) surface treated with dilute HF. After nitridation, some samples were annealed at 1000 °C in N<sub>2</sub>. The measurement was performed using XRD goniometer (ATX-GSOR). The energy of the X-ray was 11.919 keV (1.04 Å). The sample was set in a He atmosphere to reduce the air scattering. Incident X-ray grazed the sample at a critical angle, and the detector was scanned in-plane parallel to the sample surface (Fig. 1).

Figure 2 shows In-Plane SAXS results and estimated HfO<sub>2</sub> particle diameter. The peak at 1 degree of HfSiO (w/o N) is considered scattering from the uniformly crystallized HfO<sub>2</sub>. The average diameter of the HfO<sub>2</sub> particle is approximately 3.5 nm (at Hf/(Hf+Si) = 50%). The intensity of the scattering of the HfSiON (w/ N) decreases clearly with the increase in the N concentration, and correspondingly, the average diameter decreases to less than 1 nm. However, the distribution of the HfO<sub>2</sub> particle is disarranged and a small part of the HfO<sub>2</sub> particle grew until several nm. The distribution of as-depo. (w/o N) is the widest and the average diameter is about 1.7 nm. By including N, the HfO<sub>2</sub> particle is destroyed and this suppresses the regrowth of the HfO<sub>2</sub> particle. This is why the Hf-N bond, as shown in the XPS data, is formed.

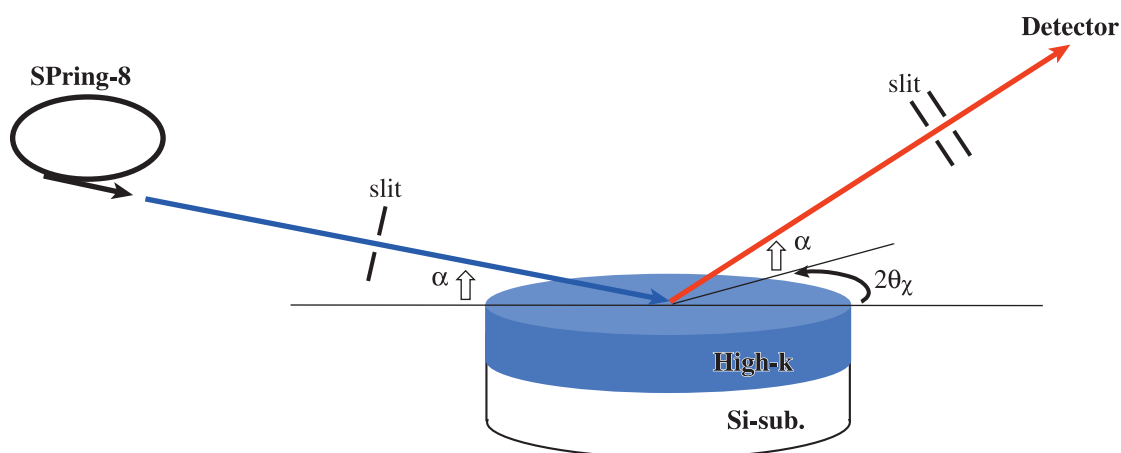


Fig. 1. Schematic of the experimental arrangement setup of In-Plane SAXS (BL13XU).

These samples were evaluated by TEM to observe the HfO<sub>2</sub> phase separation and the crystallization directly, TEM is widely used to determine the diameter of particles (Fig. 3). However, the boundary between the HfO<sub>2</sub>/SiO<sub>2</sub> in as-depo. and samples with high N content is not clear and it is impossible to determine the average diameter of the HfO<sub>2</sub> particles accurately from the TEM image. Moreover, using conventional

laboratory equipment, it is difficult to detect this very small change, even with thick films (more than 10 nm). Only by using synchrotron radiation will it be possible to evaluate small changes of even less than 1 nm.

These new information about HfSiON films will help in the detailed understanding of electric characteristics and these experimental data can be used for process refinement.

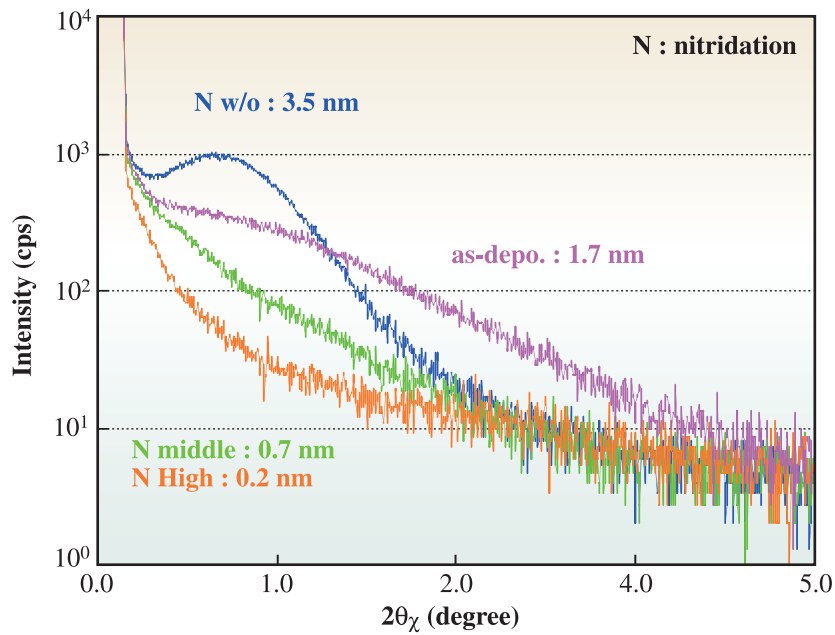


Fig. 2. In-Plane SAXS result and HfO<sub>2</sub> particle diameter (Hf/(Hf+Si) = 50%).

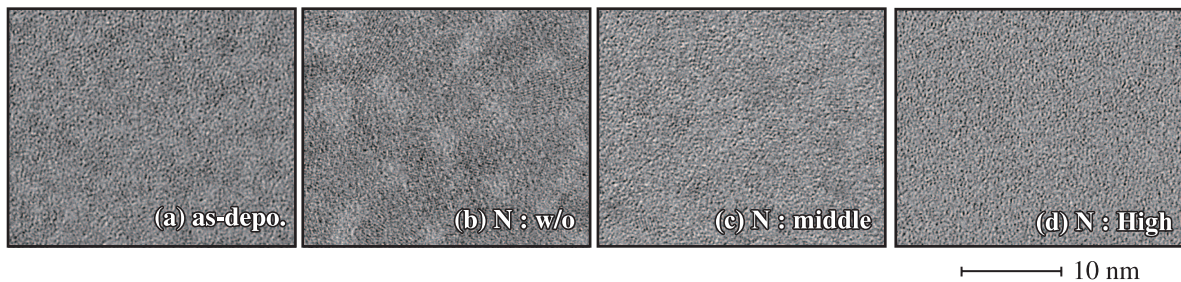


Fig. 3. TEM image (N: nitridation). (a) as-depo, (b) N:w/o, (c) N:middle, (d) N:High.

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**Reference**  
[1] M. Koyama *et al.*: IEDM2002, p. 849

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