A NEW SMALL ANGLE X-RAY SCATTERING TECHNIQUE FOR DETERMINING NANO-SCALE PORE/PARTICLE SIZE DISTRIBUTIONS IN THIN FILM

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ABSTRACT

We have developed a new Small Angle X-ray Scattering (SAXS) technique by use of reflection geometry for determining particle / pore size distribution in thin film. In order to avoid strong specular reflection, we used offset scan ($2\theta / \theta+\delta\theta$) for measuring scattering data. To deal with reflection and refraction at surface and interfaces, we calculated X-ray wave field in the film based on Distorted Wave Born Approximation (DWBA) [1]. We assume the particle / pore size distribution follows Γ-distribution function, and optimized the parameters of distribution by non-liner least square method comparing simulated and experimental data. We applied the present X-ray scattering technique to pore size analysis in porous low dielectric films on Si substrates. The results of X-ray technique agreed fairly well with those of gas adsorption and TEM techniques.

INTRODUCTION

Evaluation of nano-scale particle or pore size distribution in thin films deposited on substrates is important. So far, Small Angle X-ray Scattering (SAXS) technique has been one of the popular techniques to measure particle or pore size, and most of SAXS experiments are done by transmission geometry. Conventional transmission SAXS, however, has disadvantages for measuring thin films or thick substrate. Scattered X-ray cannot penetrate through the substrates and scattering volume is very small when film thickness is very thin. Therefore, we have developed reflection geometry SAXS technique in order to overcome such problems. However, strong specular reflection is observed if X-ray incident angle is equal to the exit angle. To avoid the specular reflection, we used offset scan ($2\theta / \theta+\delta\theta$) technique. In reflection geometry SAXS, X-ray wave field in thin films varies by changing X-ray incident angle and film density, thickness, and roughness. We calculated X-ray wave field by Fresnell's formula, and we calculated scattering cross section based on DWBA as an eigenstate in this X-ray wave field[2], [3]. We have assumed the particle or pore is sphere, and the diameter follows Γ-distribution function, which has two parameters, average diameter D_0, and shape parameter M. For estimating particle or pore size distribution, we optimized two parameters of Γ-distribution by non-linear least square method comparing experimental and calculated SAXS curves. We applied the present technique for analyzing pore size distribution in porous low dielectric films, which are extensively studied as an interlayer insulator of micro electric devices.

THEORY

We calculated X-ray wave field in thin films based on Distorted Wave Born Approximation (DWBA) to deal with reflection and refraction at interfaces. First, we calculated the eigenstate of

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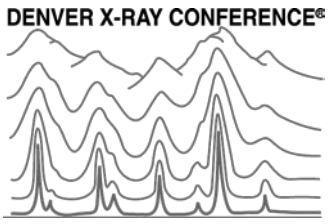

X-ray wave field of incident X-ray by use of Fresnel's formula. Scattered X-ray wave field also must be another eigenstate. This eigenstate is given as conjugation of time reversal solution of incoming wave [1]. Transition amplitude with scattering potential is calculated by the transition from eigenstate of incident X-ray to that of scattered X-ray. Scattering cross section is given by square of an absolute value of transition amplitude.

If there are fluctuations of electron density in the material, X-ray diffuse scattering is observed. Scattering patterns depend on shape and size. If scattering materials is spherical in shape with diameter D_0, its form factor F and scattering intensity I can be calculated as follows:

$$F(q,D_0)=\frac{4\pi D_0^3}{(qD_0)^3}\left(\sin\frac{qD_0}{2}-\frac{qD_0}{2}\cos\frac{qD_0}{2}\right),\quad I(q,D_0)=|F(q,D_0)|^2 \qquad (1)$$
$$q=\frac{4\pi}{\lambda}\sin\frac{2\theta}{2}$$

Here, q is scattering vector, λ is X-ray wavelength and 2θ is scattering angle. In addition, we have introduced the distribution of the diameter as Γ-distribution function as follows:

$$P_{D_0}^{M}(D)=\frac{1}{\Gamma(M)}\left(\frac{M}{D_0}\right)^{M} D^{-1+M}\exp\left(-\frac{MD}{D_0}\right) \qquad (2)$$

Γ-distribution function has two parameters, average particle / pore diameter D_0, and shape parameter M. M has a relationship to normalized variance σ as follows:

$$\sigma[\%]=\frac{1}{\sqrt{M}}\times 100=\frac{\sqrt{\langle \delta D^2\rangle}}{D_0}\times 100 \qquad (3)$$

Scattering intensity is calculated by the following convolution integral:

$$I(q;D_0,M)=|F(q;D_0,M)|^2=\frac{1}{\Gamma(M)}\left(\frac{M}{D_0}\right)^{M}\int_0^{\infty}|F(q;D)|^2 D^{-1+M}\exp\left(-\frac{MD}{D_0}\right)\frac{D_0^3}{D^3}dD \qquad (4)$$

EXPERIMENTALS

We have characterized three porous low dielectric films deposited on Si substrate. Low dielectric materials are expected to play as an interlayer insulator in the next generation ULSI technology. For characterization of porous low dielectric films, we carried out both X-ray reflectivity and X-ray diffuse scattering analysis. From X-ray reflectivity analysis, we characterized density, thickness, and roughness of the films, and these parameters are applied for calculation for eigenstate of X-ray electric wave field. From X-ray diffuse scattering analysis, we characterized pore size distribution in the films.

The following measurements were performed using the RIGAKU ATX-G diffractometer with Cu rotating anode X-ray generator operated at 50kV and 300mA. First, we measured X-ray reflectivity with Ge(220) 4-bounce crystals as an incident optics. Fig. 1 shows X-ray reflectivity

patterns of three porous low dielectric films. The optimized parameters are listed in table 1.

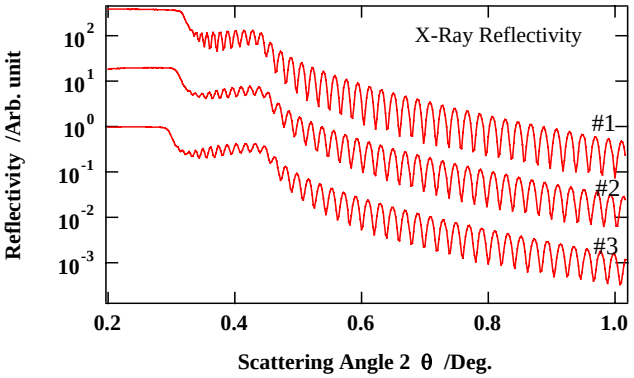

Fig. 1. X-ray reflectivity patterns of three porous low dielectric films

	Density [g/cm3]	Thickness [nm]	Roughness [nm]
#1	1.17	405.23	1.64
#2	1.10	402.83	1.63
#3	1.00	398.38	1.60

Table 1. Parameters optimized by X-ray reflectivity analysis.

The dielectric constants of samples #1, #2, and #3 are 2.54, 2.43, and 2.28 respectively. These results indicate that dielectric constant and film density decrease by introducing pores. As a result, measuring X-ray reflectivity is an effective way to evaluate porosity.

Second, we measured reflection geometry SAXS for these three samples to characterize average pore diameter and size distribution. For measuring scattering patterns, we used offset scan (2θ / θ+δθ) technique to avoid strong specular reflection. An appropriate value of offset angle can be judged from rocking scan patterns of specular reflection. The measured offset scan patterns are shown in Fig. 2. For estimating pore size distribution, we calculated scattering patterns based on film construction by X-ray reflectivity analysis listed in Table 1. The calculated scattering patterns are also shown in Fig. 2.

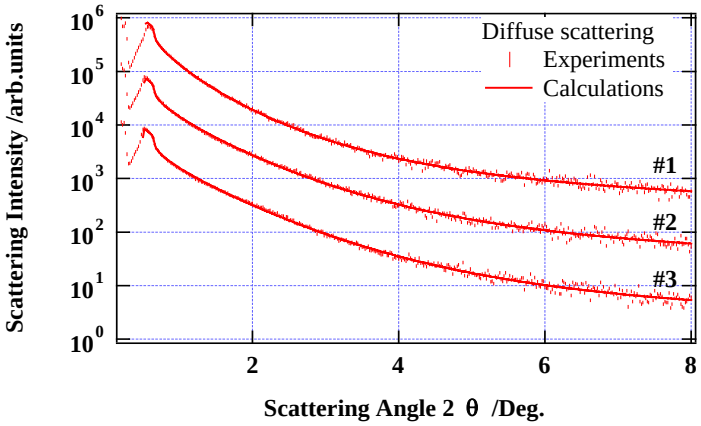

Fig. 2. Experimental and simulated data of diffuse scattering.

	D_0 [Å]	σ [%]
#1	18	85.1
#2	16	71.8
#3	17	64.4

Table 2. Optimized parameters

We can see that the simulated patterns agree very well to that of the experimentals. The optimized two parameters D_0 and σ obtained by least square fitting are listed in Table 2. The resultant pore size distributions obtained by the optimized parameters are given in fig. 3(a). In

fig. 3, we also show the pore size distribution analyzed from N_2 gas adsorption technique, which is commonly used for porosity analysis of porous materials.

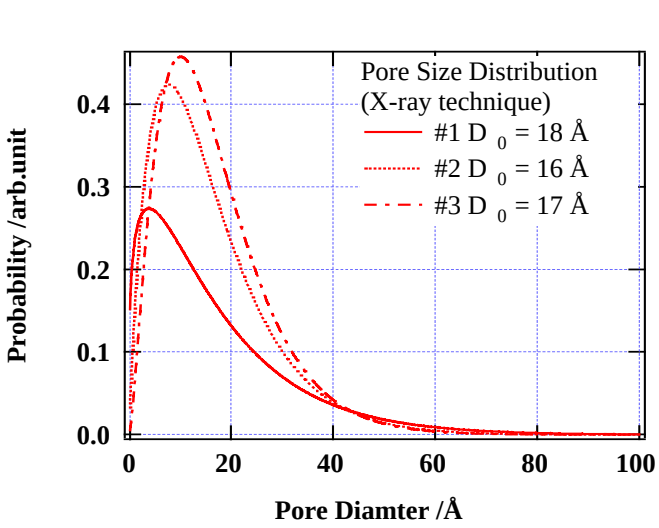

Fig. 3 (a)

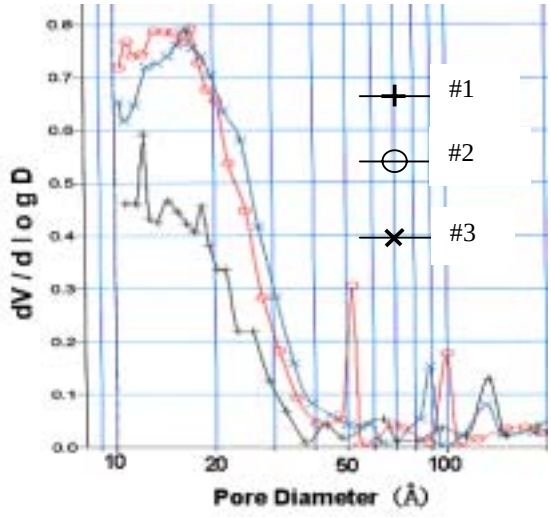

Fig. 3 (b)

Fig. 3. Pore size distribution of the three porous low dielectric films. (a) Present X-ray scattering technique. (b) N_2 gas adsorption technique.

The present X-ray scattering technique gives almost the same results with gas adsorption technique, even though principles of these two techniques are completely different.

Gas adsorption technique gives the information of size distributions of open type pores only. On the other hand, X-ray technique gives the size distributions of both open and closed type pores. So, we can suppose that these porous films contain only open type pores or both open and closed type pores have the same size distribution. As seen in fig. 3 (b), there are no data in gas adsorption technique for the size distribution in the range of pore diameter less than 10 Å. Nitrogen molecular cannot migrate into the pore less than its own size. Another attention point is measuring time. Our new X-ray technique needs about ten minutes to measure. On the other hand, gas adsorption technique needs about half a day.
Next, we compared results of X-ray technique and TEM. TEM gives real images of pores by comparing contrast of density between matrix and pore. By pre-experiment, because density contrast was small, we were not able to confirm pores clearly. Therefore we made tungsten particles adsorb pores by atomic layer deposition method. This experiment means that we measured particle size distribution of tungsten. Fig. 4 shows comparison between results of X-ray and TEM technique.

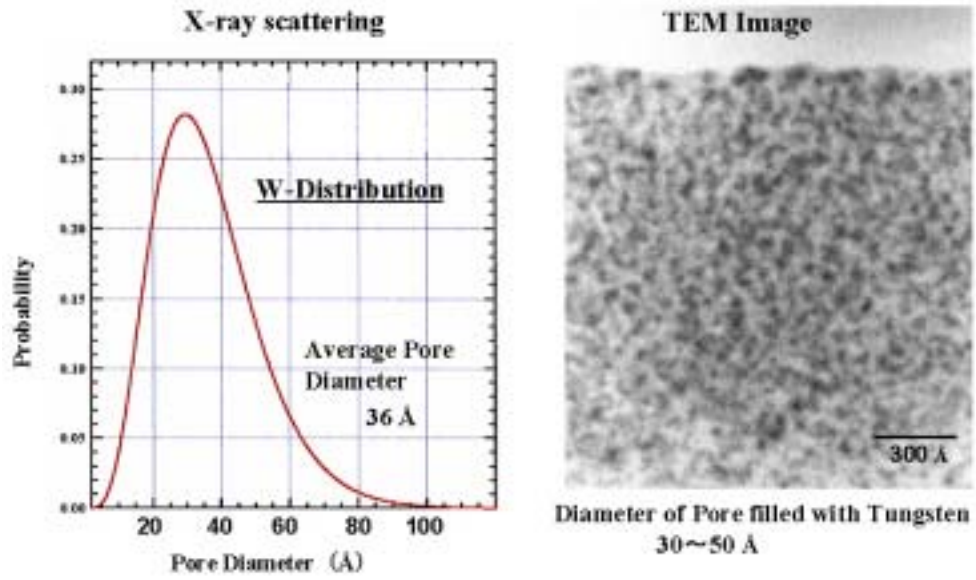

Fig. 4. Tungsten particles size distribution. (a) Present X-ray scattering technique. (b) TEM Image.

Black spots in TEM image indicate tungsten particles. From fig. 4, we confirmed that X-ray technique gives almost the same result as TEM without destroying wafer samples.

CONCLUSION

We have developed a method for particle / pore size analysis with reflection geometry SAXS. In this analysis, we calculated initial and final state of X-ray wave field in thin films and scattering cross section based on DWBA by using film structure (density, thickness, roughness) obtained by X-ray reflectivity. We assumed size distribution follows Γ-distribution function with two parameters D_0 and M, and these parameters are optimized by non-linear least square method for comparing simulated and experimental data. Results of our technique agreed with the results from gas adsorption and TEM techniques very well.

Our new X-ray technique is relatively quick to evaluate particle or pore size in a non-destructive way. We believe that the present technique is widely applicable to various materials in the field of nano-scale technology.

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