Characterization of a particle size distribution in a Ni-C granular thin film by grazing incidence small-angle X-ray scattering

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Abstract. A grazing incidence small-angle X-ray scattering (GISAXS) technique has been applied for characterizing a particle size distribution of nickel nano-particles in a nickel-carbon granular (Ni-C granular) film fabricated by a cosputtering method on a silicon substrate. The particles were modelled as a spherical shape in order to calculate scattering intensity, and a Γ-distribution was employed for determining the size distribution. In addition, a grazing incidence X-ray diffraction (GIXRD) was also measured in order to determine crystallite size of the particles. The crystallite size was analyzed by the Sherrer equation. The average particle size and the crystallite size are 5.7 and 5.2 nm respectively. These results suggest most of nickel particles are single crystal.

1. Introduction
Metal magnetic granular composites, such as iron, cobalt, nickel, or these alloys, are expected as one of the functional materials for high density magnetic recording media.1,2) Nanometer-sized metal magnetic particles separated by non-magnetic matrices, such as graphite carbon, are sufficiently small to possess a single-domain structure. These nano-particles are expected to exhibit high coercivities due to surface magnetic anisotropy. The magnetic property and the storage density depend on the particle size. Therefore, uniformity of the particle size is one of the key factors for the granular films.

Small-angle X-ray scattering (SAXS) is well known as one of the powerful techniques for characterizing electron density fluctuations in the scales of sub-nanometer to sub-100 nm. SAXS studies so far carried out were based on transmission geometry. On the other hand, in recent years, SAXS with grazing incidence geometry (GISAXS) instead of transmission geometry has been developed due to some advantages: (1) Scattered X-rays from thin films can be detected without being affected by the absorption of a thick substrate. (2) Large scattering volume due to grazing incidence geometry.3) However, in the case of grazing incidence geometry, effects of reflection and refraction at the film surface and the substrate should be taken into account. In order to consider these effects, we have calculated scattering intensities based on the distorted wave born approximation (DWBA) method.

2. Theory
Scattering intensities of SAXS are proportional to a square of an absolute value of a form factor of scatters, if the scatters are distributed randomly in matrices. The form factor can be calculated by a
Fourier transfer of electron density fluctuations of the scatters. If scatters are particles of a spherical shape with diameter $D$, the form factor $F(Q,D)$ for these particles can be written as follows

$$F(Q,D) = \frac{4\pi}{Q} \left( \sin \frac{QD}{2} - \frac{QD}{2} \cos \frac{QD}{2} \right).$$

(1)

Here, $Q$ is magnitude of scattering vector. We assume that the distribution of the particle diameter $D$ can be expressed with $\Gamma$-distribution $P(D;D_0,s)$, as follow

$$P(D;D_0,s) = \frac{1}{1/\sqrt{s^2}} \left( \frac{1}{s^2D_0} \right)^{1/2} D^{1+s^2/2} \exp \left( -\frac{D}{s^2D_0} \right).$$

(2)

Here, $D_0$ is the average particle size and $s$ is the variance normalized by the average particle size. In this case, scattering intensity $S(Q;D_0,s)$ is obtained by the following integration

$$S(Q;D_0,s) = \int_0^\infty |F(Q,D)|^2 P(D;D_0,s) \frac{1}{D^2} dD.$$

(3)

In grazing incidence geometry, scattering intensities can be corrected by effects of reflection and refraction at the film surface and the substrate based on the DWBA method. Details are shown in elsewhere. 4-6) A particle size distribution can be obtained by Eq. (2) and two parameters $D_0$ and $s$, which are optimized by comparing experimental and calculated curves of GISAXS by least-squares analysis.

3. Experiment

3.1. Sample preparation
A nickel-carbon granular (Ni-C granular) film was fabricated by an rf-cosputtering method on a silicon substrate. Graphite chips were placed on a Ni target and they were cosputtered in Ar gas using a magnetron sputtering apparatus. 7) The thickness of the granular films was about 60 nm from X-ray reflectivity analysis (data not shown).

3.2. GISAXS measurement
A GISAXS measurement was performed using RIGAKU SuperLab diffractometer. As an incident X-ray source, the combination of a microfocus X-ray generator (MicroMax007HF, RIGAKU Co.) and multilayer confocal mirror optics have been applied. 8) X-ray radiation from Cu target was used ($\lambda = 0.154178$ nm). The X-ray beam size for the vertical direction (parallel to the surface normal direction) is 0.3 mm. A small vertical beam size is convenient for grazing incidence geometry. A schematic diagram of the GISAXS measurement system is shown in Fig. 1.

A GISAXS curve along the in-plane direction for the Ni-C granular film was measured with X-ray incidence and exit angles of 0.33° to a sample surface. The observed GISAXS curve is shown in Fig. 1. A GISAXS curve for a bare silicon wafer is also shown for the comparison. The intensity of the GISAXS curve for the granular film is still much higher than that from a bare silicon wafer. This shows that the scattering from the granular film is clearly detected.

The particle size distribution in the granular films was analyzed by comparing experimental and calculated GISAXS curves, and by optimizing $D_0$ and $s$ in Eq. (2) by least-squares analysis. The calculated GISAXS curve is also shown in Fig. 1. The optimized parameters of $D_0$ and $s$ are 5.70 nm and 0.29, respectively. This result of $D_0$ equal 5.70 nm is in good agreement with a result of TEM analysis. 7) These parameters are also shown in Table 1. The resultant particle size distribution by using these parameters and Eq. (2) is shown in Fig. 2.
Fig. 1. A schematic diagram the GISAXS measurement system is shown on the left. Experimental and calculated GISAXS curves for the Ni-C granular film are shown on the right. A GISAXS curve for a bare silicon wafer is also shown on the right for the comparison.

Fig. 2. Particle size distribution of nickel nano-particles in the Ni-C granular film

3.3. GIXRD measurement

Next, crystalline property of nickel nano-particles was analyzed by a GIXRD measurement. It is well known that the XRD patterns include information about crystallite size and strains as well as crystal structures. A full width at half maximum (FWHM) of diffraction peaks broadens with decreasing crystallite size. A relation between FWHM of diffraction peaks and crystallite size is roughly calculated by following Sherrer equation which assumes that strain broadening is much smaller than crystallite size broadening.\(^9\)

\[
d_{\text{hkl}} = \frac{0.94 \lambda}{\Delta 2 \theta_b \cos \theta_b}.
\]

Here, \(d_{\text{hkl}}\) is the crystallites size for the direction of plane normal of (hkl), \(\lambda\) is the X-ray wavelength, \(\Delta 2 \theta_b\) is the FWHM of the diffraction peak, and \(\theta_b\) is the Bragg angle.

In order to determine the crystallite size and the crystal structure of nickel nano-particles, GIXRD curve along the in-plane direction for the Ni-C granular film was measured with incident and exit angles of 0.33° to a sample surface. The GIXRD curve is shown in Fig. 3. We observed five diffraction peaks from nickel nano-particles and these peaks are assigned by a face-centered cubic with a lattice parameter of 0.352 nm. The crystallite sizes of the nickel nano-particles for (111), (220),
and (311) directions are determined using (111), (220), and (311) diffraction peaks by the Sherrer equation. The obtained crystallite sizes determined from (111), (220), and (311) peaks are 5.60, 5.28, and 4.82 nm, respectively. These parameters are summarized in Table 1.

The average crystallite size obtained by GIXRD is almost equal to the average particle size obtained by GISAXS. This result reveals that most of nickel nano-particles are single crystals with an average diameter of 5.7 nm.

Table 1. Optimized parameters for the particle size distribution and the crystallite size analyses.

| Particle size distribution | Crystallite sizes |
|---------------------------|------------------|
| D₀                        | (111)            | (220)            | (311)            |
| 5.70 nm                   | 5.60 nm          | 5.28 nm          | 4.82 nm          |
| s                         | 0.29             |                  |                  |
| Average                   | 5.23 nm          |                  |                  |

4. Conclusion
GISAXS and GIXRD techniques using a laboratory X-ray source have been applied for characterizing nickel nano-particles in Ni-C granular film. From the combination of GISAXS and GIXRD analyses, it is elucidated that most of nickel nano-particles are a single crystal with an average diameter of 5.7 nm.

The present techniques are also useful for determining the size of many kinds of particles in a thin film. For example, silicon nano-particles in silica matrix film, which show characteristic luminescent spectra dependent on the size of the particles.

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