INVESTIGATION OF NANOCRYSTALS USING TEM MICROGRAPHS AND ELECTRON DIFFRACTION TECHNIQUE*

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Received September 26, 2006

The aim of this work is to determine mean diameter of polycrystalline samples using Scherrer equation. These represent direct connection between mean diameter and crystal structure and morphology by including the Bragg angle and shape factor. Two samples are investigated, first a nano-sized particles of MgO and second a CVD (Chemical Vacuum Deposition) obtained polycrystalline aluminum film. First, shape factor and mean diameter are evaluates using direct measurement of particle morphology from BF-TEM (Bright Field – Transmission Electron Microscopy) images. The value of mean diameter is determined by assuming a lognormal distribution. Than, mean diameter values are evaluated using Scherrer equation applied to SAED (Selected Area Electron Diffraction) images. We obtain for MgO nano-sized a mean diameter about 48 nm from direct measurement, and 70 nm respectively using Scherrer equation, and for Al film 77 nm, and 70 nm respectively.

Key words: CVD, BF-TEM, SAED, Scherrer, polycrystalline, nano-sized, lognormal.

INTRODUCTION

Bragg's law states the condition for a sharp diffraction peak from an infinite crystal with perfect 3-d order. Typically the diffraction peak has a finite width which is associated with imperfection in some of the Bragg parameters. These imperfections can be associated with beam divergence, a somewhat polychromatic source, or imperfections in the 3-d order of the crystals. The latter can be a basis for quantitative measurement of the deviation from the Bragg requirement for perfect 3-d order which is infinite in all spatial directions. Deviations from the latter requirement have been explained in terms of 3 features: finite crystallite size (Scherrer equation [1–3]), distortions of the first kind, which are random motion of atoms in a crystalline lattice (Debye thermal broadening) or other local randomization of lattice sites which do not disturb the 3-d repetition or crystalline motif, and distortions of the second kind, which involve

* Paper presented at the National Conference on Applied Physics, June 9–10, 2006, Galați, Romania

destructive of long range order in the crystal, *i.e.* at long distances the lattice does not repeat perfectly. These usually lead to preferential broadening of high order peaks. The Scherrer equation can be writing as:

$$\bar{D} = \frac{57.3 \cdot k \cdot \lambda}{\beta \cos \theta} \tag{1}$$

where $\bar{D}$ = mean diameter, k = shape factor, λ = wavelength, β = the full-width at half maximum, and θ = Bragg angle for studied ring. The factor 57.3 is used for conversion of β from degree to radians.

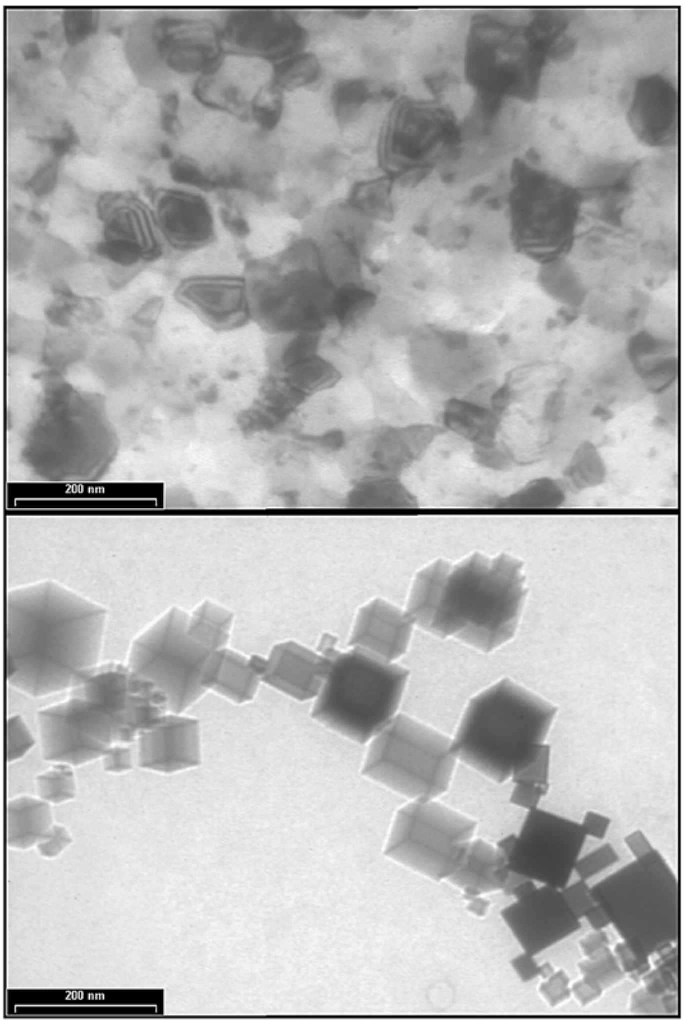


Fig. 1 – BF-TEM image of aluminum film and MgO nano-sized crystal.

The Scherrer equation, (1) above, predicts crystallite thickness if crystals are smaller than 1000 Å. Since small angular differences in angle are associated with large spatial distances (inverse space), broadening of a diffraction peak is expected to reflect some large scale feature in the crystal. The simplest way to obtain the Scherrer equation is to take the derivative of Bragg's law holding the wavelength constant and allowing the diffraction angle and the Bragg spacing to vary, $2d\sin\theta = \lambda$. Take derivative in d and θ yields $2\Delta d\cos\theta\Delta\theta = \lambda$ since $\Delta\theta$ can be positive or negative the absolute value must be taken and it reflects the half-width of the peak (really half-width at half-height) so $2\Delta\theta$ is the peak full-width at half-height, β. Δd reflects the crystallite thickness,

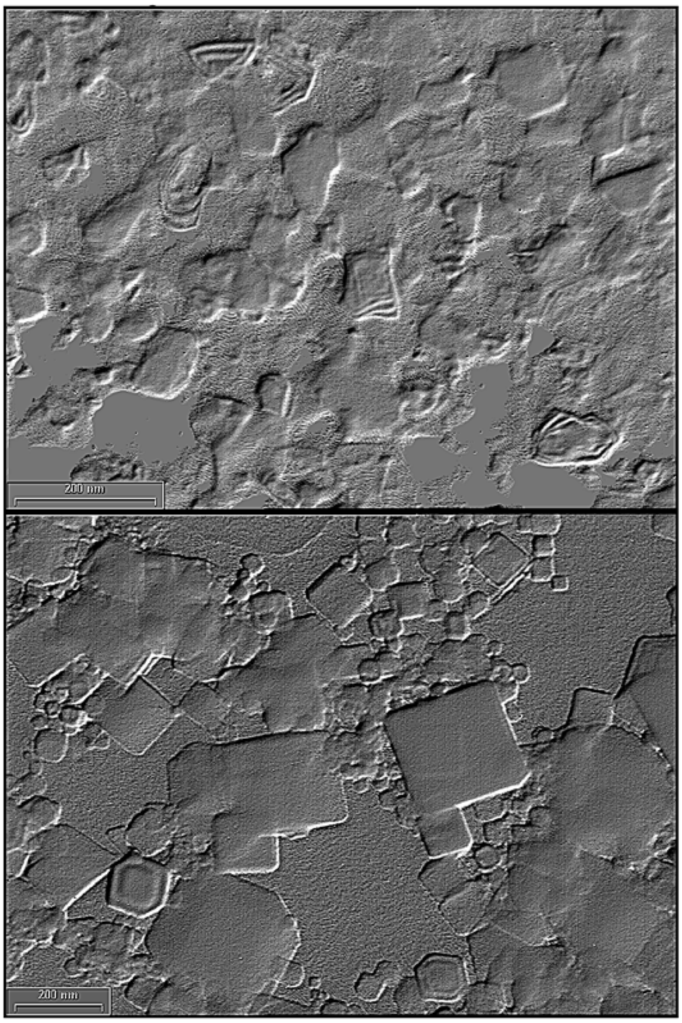


Fig. 2 – Processed BF-TEM image of aluminum film and MgO nano-sized crystal using shadow filter to improve contrast of particle.

$$Thickness = t = \Delta d = \frac{\lambda}{\beta \cos \theta_\beta} \quad (2)$$

If a Gaussian function (rather than a triangle function) is used to describe the peak a prefactor of 0.9 occurs so the Scherrer equation is given as $t = 0.9\lambda / \beta \cos \theta_\beta$.

The shape factor provides information about the "roundness" of the particle. For a spherical particle the shape factor is 1, for all other particles it is smaller than 1. The formula for this calculation is:

$$shape\ factor = 4 \cdot \pi \cdot \frac{area}{perimeter^2} \quad (3)$$

Mean diameter represents the arithmetic mean of all diameters of a particle (for α = 15°, 30°, 45°, 180°). The value of mean diameter is estimated using assumption that mean diameter verify lognormal distribution [4–7]. Experimental data are fitted using lognormal function, given by:

$$y = Ae^{-\frac{\ln^2(x/xc)}{2w^2}} \quad (4)$$

where A is an arbitrary constant related to particle number, xc represents the distribution maximum and w is dispersion of particle diameters. In Figs. 1 and 2 we can observe a good correlation between experimental data and theoretical curve (4).

EXPERIMENTAL METHODS

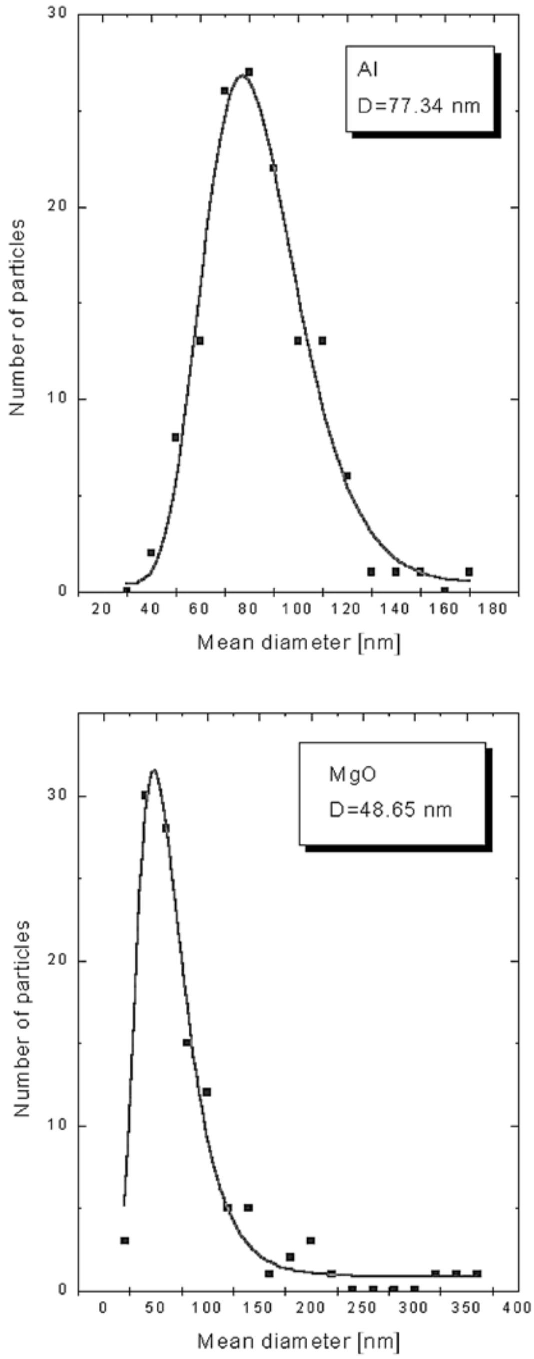
Samples are prepared using chemical vaporization. MgO is obtained by burning Mg ribbon in air [8]. Special cooper grid with amorphous carbon thin film is used to capture the smoke. Aluminum film is obtained using CVD. The substrate for film is formvar coated cooper grid mounted on glass slide. These samples not require special treatment for feature used. Only aluminum prepared grid can be wash using chloroform and ethylic alcohol to remove formvar substrate.

BF-TEM images (Fig. 1 and 2) are obtained from samples using a Philips CM120 electron microscope with 100 kV acceleration voltages. SAED images (Fig. 5. a, b) are taken using 420 mm camera length.

RESULTS

In Fig. 1 we present Al and MgO samples. These are BF-TEM image acquired at low magnification, around 29000×. In Fig. 2 are processed images for

Fig. 3 – Mean diameter distribution of aluminum film and MgO nano-sized crystal fitted with lognormal function.



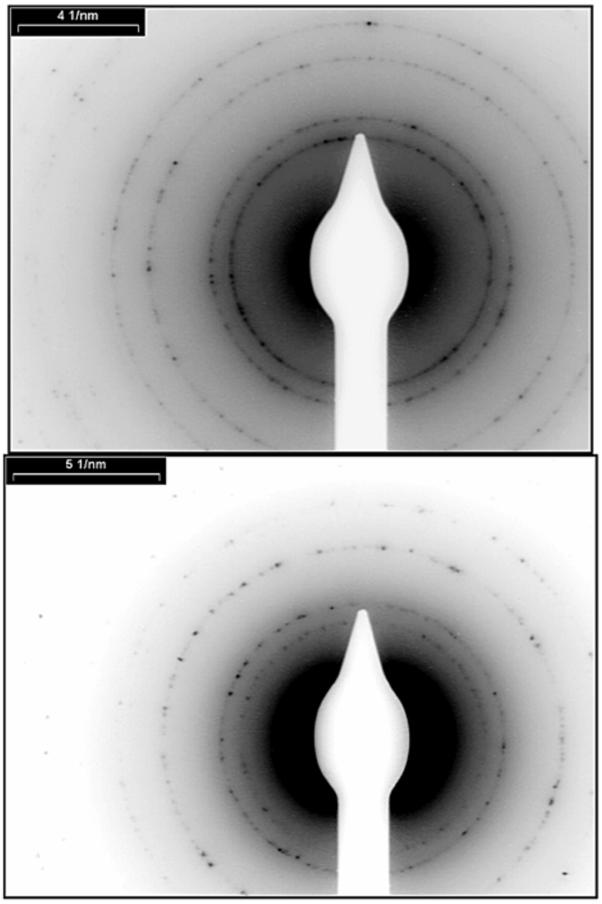


Fig. 4 – SAED image used for evaluate mean diameter. First interior ring in both images represent (111) reflection used in Scherrer equation to evaluate mean diameter.

both samples to increase contrast of particle. The resulted image is obtained after applying a pseudo filter on original image. This filter emphasizes the transitions between bright and dark image points. The transitions from bright to dark are valued positive, those from dark to bright negative. The image will be normalized in such a way that the zero level becomes gray value 128. This means, that a gray shade area within the limits –127 and +128 is available. The filter produces the impression of a one-sided lighting effect and a seemingly topographic contrast (pseudo 3d). Employed 3 × 3 matrix are:

$$\begin{matrix} 0 & -1 & 0 \\ -1 & 2 & 0 \\ 0 & 0 & 0 \end{matrix}$$

In Fig. 3 are given the experimental data for mean diameter statistics. Experimental curves are fitted with lognormal function.

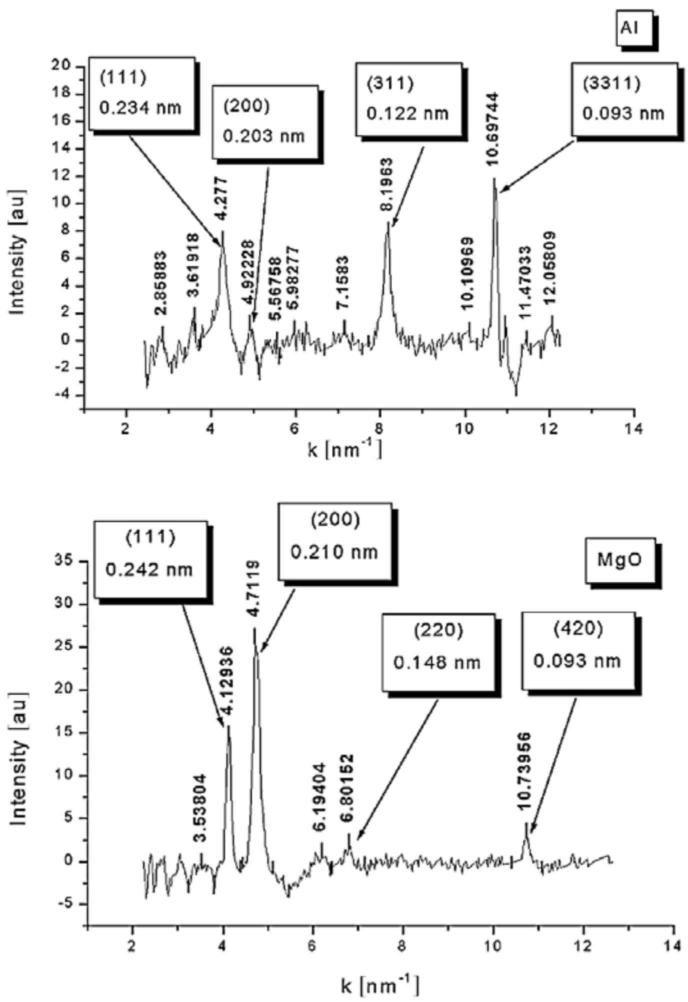


Fig. 5 – Profiles of diffraction pattern.

In Fig. 4 represents SAED images used to evaluate mean diameter from Scherrer equation. The SAED condition was in both cases 420 mm camera length. In Fig. 5 are drawing profiles of radial axis from SAED images. Initial data are processed in order to remove background. Results are fitted using 3-multipeaks Gaussian curves.

In Table 1, we present mean diameter results using methods, direct measurement and Scherrer equation.

The value determined for MgO using Scherrer equation is greater than value determined using direct measurements. These differences can be explained using Debye thermal broadening, which appear in case of thermal vibration of lattice site in crystalline structure.

Table 1

Samples	Direct [nm]	Scherrer [nm]
Al	77.34	70.97
MgO	48.45	69.98

CONCLUSIONS

This papers show that Scherrer equation is an easy way to evaluate the mean diameter in nano-sized particle cases. In some particular cases, *e.g.* MgO, this relation must be completed with other theory that take in account lattice site of crystalline structure. Otherwise, this equation can be the first evaluation of mean diameter distribution. We can conclude directly from electron diffraction, and XRD pattern, if large rings appear than samples in study has a low values for mean diameter than in case if thick rings appear.

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