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Determination of Grain-Boundary Film Thickness by the Fresnel Fringe Imaging Technique

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Abstract

The defocus Fresnel fringe imaging (FFI) technique is applied to the determination of nanoscale amorphous grain-boundary film thickness in a silicon nitride ceramic. By using only the transmitted beam and imaging out of focus, an amorphous grain-boundary film can be detected. The thickness of the amorphous film is determined by extrapolating the fringe spacing data obtained from a series of defocus images to zero defocus. High-resolution electron microscopy (HREM) has been suggested as the method capable of providing the most accurate measurements of film thickness (±0·1 nm). Thus, the thickness of a grain-boundary film obtained by FFI is compared with that measured by HREM. It is found that FFI can provide a reliable value for grain-boundary film thickness, with an accuracy of ±0·15 nm. Additionally, FFI is easier to use, and is applicable to any grain boundary of interest whereas the HREM method has some limitations. This make it more amenable to gathering statistical information on grain boundary thickness. It is suggested that FFI is a valid and useful method for determining the thin intergranular film thickness.

1 Introduction

Densification of many ceramics (e.g. Si_3N_4) requires the addition of sintering aids, which form a liquid phase at high temperatures. The resulting microstructure usually contains a thin amorphous film at two-grain boundaries, which can have dramatic effects on the properties of polycrystalline materials. To improve the properties of these materials it is necessary to understand the role of such films and control their formation during fabrication. Quantitative information on the thickness and composition of these thin films can be obtained by using transmission electron microscopy (TEM).

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A number of TEM techniques have been used to detect grain-boundary amorphous films. The width of these films can be determined by high-resolution electron microscopy (HREM) as an area of discontinuity in the lattice fringes of the grains;[1–3] by diffuse dark-field imaging (DDF) as an area of bright contrast relative to the bounding grains,[3–5] or by defocus Fresnel fringe imaging (FFI), based on the extrapolation of defocus fringe-spacing data.[2,3,5] Although both HREM and DDF techniques enable direct measurements of grain-boundary film thickness to be made, they suffer from some disadvantages which make the accurate determination of the film width difficult. For example, a poorly defined interface and a low intensity are usually associated with the DDF method.[2,3] Thickness determination by HREM can be limited by uncertainty in the degree of lattice fringe overlap into the amorphous region as a function of boundary tilt and objective defocus.[4] The FFI technique has been applied to the detection of the boundary film for some time. However, it has been suggested[2,3] that this technique is best suited for detecting the presence of thin films rather than for accurately measuring their widths. Thus the question arises as to which method can best be used to quantitatively measure the widths of intergranular films. The advantages and disadvantages of these techniques in terms of experimental ease and accuracy of thickness determination have been discussed previously.[2,3] Cinibulk *et al.*[3] concluded that HREM is the most accurate method for quantitative measurements of film thickness (±0·1 nm) whereas DDF is the most inaccurate technique. In this paper, the FFI technique is used to measure intergranular film widths, and the results are compared with those obtained from HREM. Thus one aim of this work is to assess the accuracy to which the boundary film thickness can be determined by the FFI technique. The advantages of FFI over HREM in quantitative measurements of statistical variability in intergranular film thickness are also discussed.

2 Experimental Methods

Amorphous grain boundary films were examined in a high purity silicon nitride. Specimens for electron microscopy were prepared from 3 mm discs, cut using an ultrasonic drill and mechanically polished to 100 μm thickness prior to thinning to perforation using standard ion-beam milling techniques. The specimens were coated with a thin layer of carbon to prevent charging under the electron beam. The TEM examination was performed on a 200 kV microscope (JEOL 2010 FEG-STEM) with a point-to-point resolution of 0·2 nm.

Two techniques were used to determine the boundary film thickness: Fresnel fringe imaging and lattice fringe imaging. The measurement of intergranular film thickness by lattice imaging has been described elsewhere by Clarke[2] and Cinibulk *et al.*[3] It is essential that the grain boundary be viewed edge-on while obtaining good diffraction conditions from both grains on either side of the grain boundary. At least one set of lattice planes are imaged in both grains and the discontinuity in the lattice fringes is identified as an intergranular film. The thickness of the film corresponds directly to the area of the discontinuity. In the Fresnel fringe imaging mode, only the transmitted beam is allowed to pass through the objective aperture. By imaging out of focus, the presence of an intergranular film is revealed by the occurrence of fringes associated with the difference in mean inner potential of the amorphous film and the two crystalline grains. The thickness of the film, however, is not determined as straightforwardly as in the HREM mode; this will be discussed in detail in Section 3.1. To compare directly the two techniques for the measurement of intergranular film thickness, grain boundaries must be chosen to which both methods could be applied. Obviously, such a boundary must be parallel to the electron beam and also satisfy the necessary conditions for lattice fringe imaging. Since the Fresnel fringes produced on defocusing are only symmetric on both sides of the boundary when the interface is exactly parallel to the electron beam,[2,6] the FFI method is used to align a grain boundary edge-on.

3 Results and Discussion

3.1 Determination of grain-boundary film thickness

The use of the Fresnel fringe imaging technique for detecting thin intergranular films was first reported by Clarke.[2] The formation of the Fresnel fringes along a grain boundary is caused by the difference in the mean inner potential between the grains (V_g) and the intergranular phase (V_i), as shown schematically in Fig. 1. The behaviour of Fresnel fringes at a straight edge in a thin foil has been analyzed in detail.[7,8] The position of the first fringe from the edge has been found to be proportional to $\Delta f^{1/2}$, where Δf is the defocus distance of the objective lens.[8] Applying this analysis to an intergranular amorphous film which has a smaller inner potential than that in the adjacent grains (as in Fig. 1), the relationship between fringe spacing W and the boundary film thickness W_0 is obtained

$$W = W_0 + c\Delta f^{1/2} \tag{1}$$

where c is a microscope dependent constant approximately equal to $(3\lambda)^{1/2}$,[8] and λ is the wave length of the electron beam. For the TEM used in this study $c = 0{\cdot}086\ \text{nm}^{1/2}$ with $\lambda = 0{\cdot}0025$ nm.

To determine an intergranular film thickness, the images of the boundary film in the through-focus series are recorded. Figure 2 shows an intergranular film at four different defocus values. When the mean inner potential of the intergranular amorphous film is lower than that of the grains, as in Si_3N_4 ceramics, the underfocused images contain a bright line at the film and alternating dark and bright Fresnel fringes on either side [(a) and (b)]. The overfocused images display the reverse contrast [(c) and (d)]. The spacing of the fringes decreases with decreasing defocus, consistent with the expectation of eqn (1). To obtain the thickness of the boundary amorphous film, the data of fringe

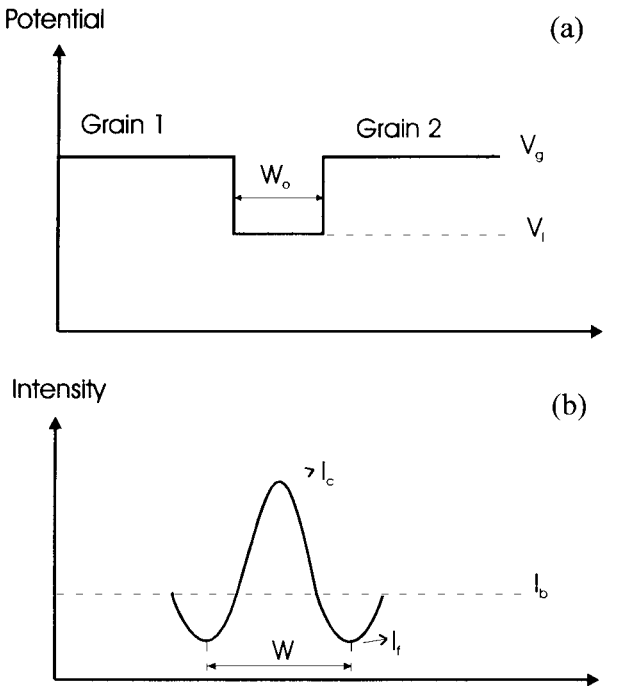

Fig. 1. Schematic diagrams representing (a) the boundary potential model and (b) the corresponding schematic profile of intensity for underfocus.

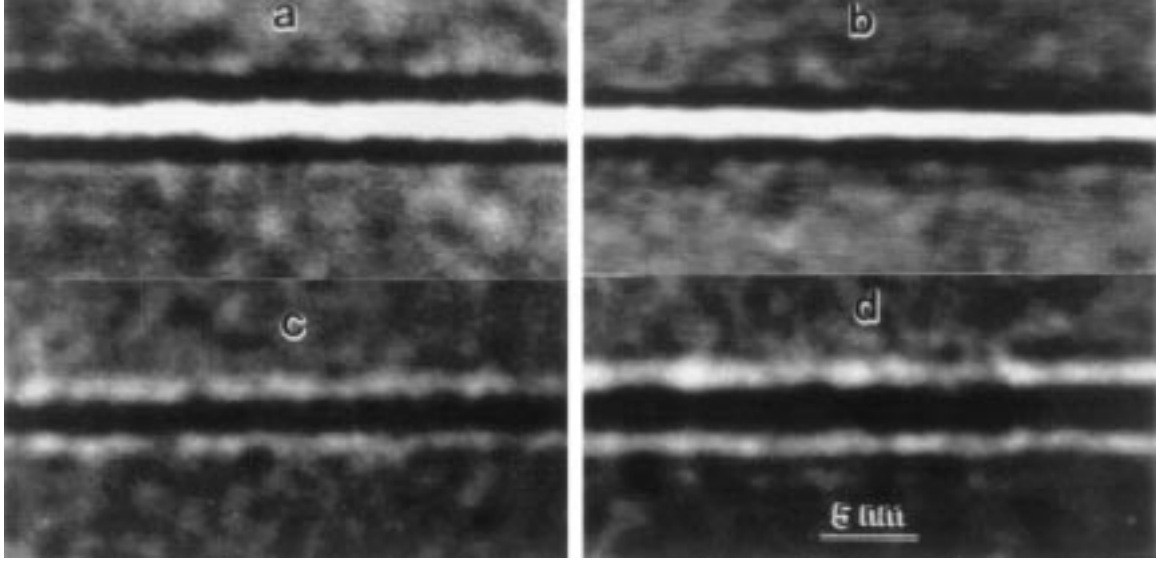

Fig. 2. Through focal series of images of a gain boundary in silicon nitride: (a) underfocus of 1400 nm, (b) underfocus of 700 nm, (c) overfocus of 700 nm, and (d) overfocus of 1400 nm. The fringe spacing decreases with decreasing defocus.

spacing obtained from a series of defocus images are fitted to a function defined by eqn (1). The thickness of the amorphous film corresponds to the spacing found at zero defocus.

Figure 3 contains curves obtained by fitting the spacing data of the Fresnel fringes for a number of defocus values. The curve obtained from the underfocus series results in a boundary film thickness of 0·91 nm. The curve from the overfocus series gives a value of 1·0 nm, slightly greater than that determined from the underfocus series. This result is consistent with that obtained by Cinibulk *et al.*[3] in determining the grain-boundary film thickness by FFI.

3.2 Accuracy and validity of measurement

To assess the accuracy of the FFI method, the same grain boundary was also characterized by HREM. To do this, an objective aperture was chosen that allowed a maximum number of diffracted beams to form the image while maintaining adequate image contrast. The high-resolution image of the grain boundary is shown in Fig. 4. The thickness of the boundary film is found to be 1·05 nm, in good agreement with the results of FFI.

A key factor in applying the defocus Fresnel fringe technique involves how one fits the experimental data. Since the value of film thickness is obtained by extrapolation of a curve to $\Delta f = 0$, it is apparent that the data from the low-defocus images is more important for film thickness determination. In general, however, fringes become

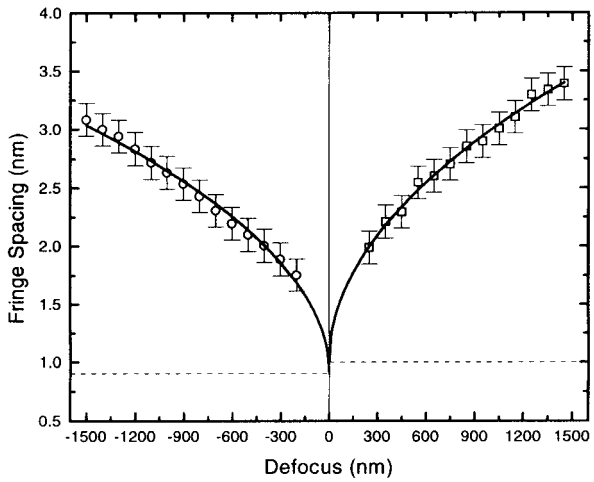

Fig. 3. Measured fringe spacing data as a function of defocus for the boundary shown in Fig. 2(a)–(d). The fitting function $W = W_0 + c\Delta f^{1/2}$ is used to obtain the boundary film thickness.

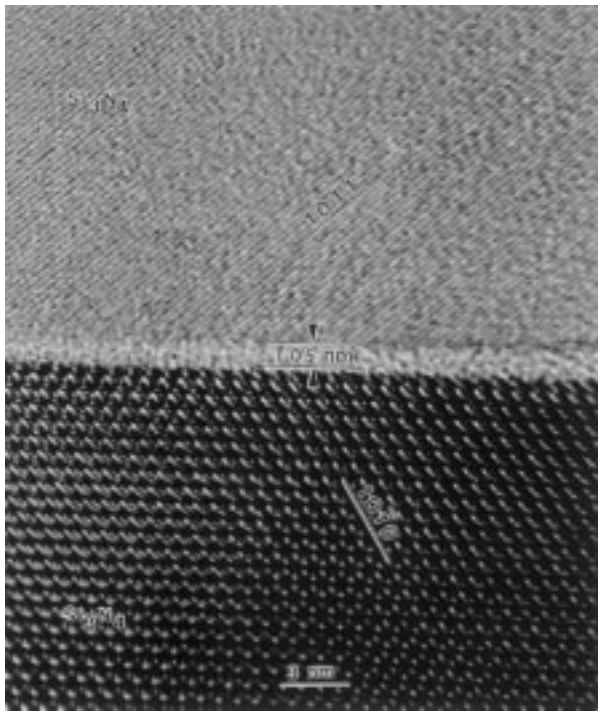

Fig. 4. High resolution lattice fringe image of the grain boundary shown in Fig. 2.

visible only when $\Delta f > 200$ nm. Therefore, higher defocus values have to be used to obtain sufficient data for extrapolation. This approach has also been suggested by Cinibulk *et al.*[3] In this case, selection of a fitting function is critical since different functions could result in significant difference sin the value of film thickness. When the number of data are limited, it is difficult to identify what relationship the experimental data actually obeys. In this study, the relationship defined by eqn (1) has been observed between the fringe spacing and the defocus.

Using the relation $W = W_0 + c\Delta f^{1/2}$ as a fitting function, the value of c can be obtained from the experimental data. For the boundary shown in Fig. 2, c is $0{\cdot}055\,\mathrm{nm}^{1/2}$ for the underfocus series and $0{\cdot}063\,\mathrm{nm}^{1/2}$ for the overfocus series. These data are close to the value of $c = 0{\cdot}086\,\mathrm{nm}^{1/2}$ expected from eqn (1) with $\lambda = 0{\cdot}0025$ nm. To examine whether the value of c is constant for any grain boundary, 20 grain boundaries were selected randomly and the film thickness was measured by FFI at three different locations for each grain boundary. The values of c display a Gaussian distribution with a mean value of $0{\cdot}053\,\mathrm{nm}^{1/2}$ and a standard deviation of $0{\cdot}011\,\mathrm{nm}^{1/2}$, as shown in Fig. 5. This result suggests that the fitting function defined by eqn (1) really does reflect the relation between the fringe spacing and defocus value. Jepps *et al.*[6] also found this relationship in their investigation of intergranular film widths in SiC materials.

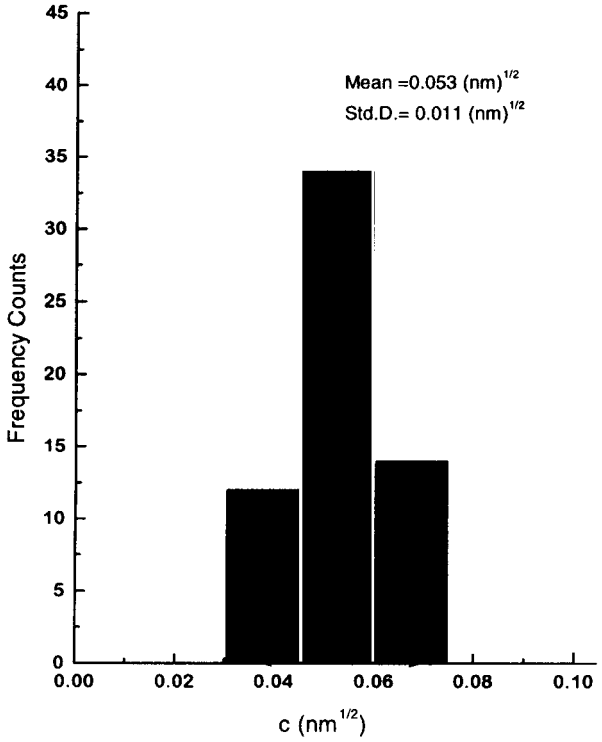

Fig. 5. Histogram of the distribution of parameter c in the fitting function $W = W_0 + c\Delta f^{1/2}$ obtained from different grain boundaries.

Provided that the fitting function is correct, the main source of error in measuring the film thickness by the FFI method comes from the experimental uncertainty in defining the position of the first fringe maxima due to poor contrast at low defocus. The determination of the defocus value could also introduce an error to the value of film thickness. However, by carefully locating the position of the fringe maxima and by accurately calibrating the defocus, the film thickness can be determined to an accuracy of $\pm 0{\cdot}15$ nm. The accuracy has also been demonstrated by statistical analysis of intergranular film widths in two as-sintered silicon nitride ceramics.[9] In that study [9] it was found that the widths of grain-boundary films display a Gaussian distribution with standard deviations $\leq 0{\cdot}15$ nm. As indicated by Kleebe *et al.*,[10] two factors may contribute to the standard deviation. One is a real variation in film thickness at different grain boundaries. The other is the measurement error introduced by the measurement method. Clarke[11] proposed that in a given Si_3N_4 ceramic, a stable equilibrium intergranular film thickness exists. TEM studies[12] of different Si_3N_4 materials supported his theory and have generally found that the film thickness has a characteristic value for a given chemical composition and is independent of grain boundary orientation. Based on this, it is reasonable to suggest that the value of the standard deviation found in this study (0·15 nm) primarily reflects the accuracy of measurement of this technique.

3.3 Advantages of FFI and limitations of HREM

HREM is capable of providing detailed information on a grain boundary at the atomic level. Moreover, an accuracy of $\pm 0{\cdot}1$ nm can be achieved in determining the boundary film thickness.[3,12] However, the measurement of the intergranular film width by this method requires that strict geometrical conditions be met. The grain boundary must be viewed edge-on while maintaining good diffracting conditions for both adjacent grains. These requirements limit its application to a small number of grain boundaries in a typical TEM sample. For most grain boundaries, only one of the conditions can be satisfied. When a grain boundary is oriented edge-on by tilting to obtain symmetric Fresnel fringes, one or both of the adjacent grains are usually not at good diffracting conditions for HREM.

Interpretation of high-resolution images also complicates its application. Both a defocus change and specimen tilting cause the lattice fringes in the crystalline grains to extend into the amorphous phase and lead to a significant error in film thickness determination. The influence of boundary tilt

on the lattice imaging method has been discussed by Lou *et al.*[13] As the lattice-fringe images are recorded in a defocus condition, relative shifts could occur between the two sets of fringes originating from the adjacent grains. According to Krivanek *et al.*,[4] the displacement of the Bragg beam **r** is expressed as

$$\mathbf{r} = C_s\lambda^3|g|^3 + f\lambda|g| \qquad (2)$$

where C_s is the spherical aberration coefficient of the objective lens, λ is the wavelength of the electron beam, $|g|$ is the magnitude of the reciprocal lattice vector and Δf is the defocus. From this equation, it is obvious that only one defocus value ($-C_s\lambda^2|g|^2$) places the lattice fringe terminations exactly at the crystal edge, i.e. no shift of the fringes occurs. At the Scherzer defocus (−60 nm) for the TEM used in this study ($C_s = 1{\cdot}5$ nm, $\lambda = 0{\cdot}0025$ nm), the lattice fringes of the β-Si_3N_4 $\{10\bar{1}0\}$ reflection will shift 0·12 nm from the edge of the crystal. For higher defocus values, the shift becomes more significant. A good example of the effect of a defocus change on the lattice-fringe images can be found in Ref. 4. The amorphous phase at two-grain boundaries could disappear when the defocus does not coincide with the optimum value. Thus determination of the widths of thin intergranular films by lattice imaging may lead to false conclusions if the defocus value is not chosen carefully. Another factor to be taken into consideration in lattice imaging is the effect of the foil thickness. The sensitivity of lattice-fringe visibility to the foil thickness has been discussed by Clarke[2] for silicon nitride. To measure the intergranular film thickness accurately by HREM, both adjacent grains must be of a thickness at which the lattice fringes display a high contrast. In general only grain boundaries in the very thinnest regions of a specimen satisfy this requirement.

From these considerations, it is clear that detecting very thin films (about 1 nm) by this method can be problematic. In order to ensure that the high-resolution images are a reliable reflection of the projection of both the adjacent grains and the intergranular film, the interface must be carefully oriented parallel to the electron beam, and the image must be taken from the thinnest regions of a specimen and recorded at the optimum value of defocus. This was the procedures followed to obtain the HREM image shown in Fig. 4. Due to these limitations, the HREM technique cannot be applied to an arbitrary grain boundary.

The major advantage of the FFI technique is that it can be applied to any grain boundary of interest. The symmetry of Fresnel fringes indicates clearly whether the boundary is parallel to the electron beam. This advantage enables a statistical analysis of a large number of grain-boundary films to be undertaken, e.g. to study the redistribution of a grain-boundary glass phase during high temperature creep of ceramic materials. For glass-containing ceramics such as silicon nitride, viscous flow is an important process contributing to creep deformation of the material. Although several models have been developed to describe this process,[14–16] the analysis is mainly based on indirect evidence such as the creep response or strain recovery phenomenon. By using the FFI method to measure the grain-boundary film widths before and after creep, direct evidence of the microstructural evolution due to viscous flow has been obtained.[9] The film thickness change on the boundaries perpendicular to the stress axis can be obtained from the difference in standard deviations before and after creep. This value enables a direct comparison between the creep response predicted by viscous flow models and the experimental observations. To undertake such a statistical analysis many grain boundaries have to be selected in a TEM specimen, a difficult procedure for HREM but straightforward for FFI studies.

4 Summary

The defocus Fresnel fringe technique has been addressed as a method for determining the widths of intergranular films in materials such as silicon nitride. It has been shown that this method is capable of relatively precise determination of the boundary film thickness (±0·15 nm), and is much easier to operate experimentally than the high-resolution lattice imaging technique. Therefore, it is suggested that the FFI method is a useful technique for quantitatively determining intergranular film thickness. To ensure a reliable value of film thickness the fitting function for the experimental data is very critical, in that the thickness of the boundary film is determined by the extrapolation to zero defocus. The determination of intergranular film thickness by the high-resolution lattice imaging technique is confined to some specific grain boundaries due to the set of very strict geometrical and electron-optical conditions that must be satisfied. If the defocus value is not appropriate the lattice imaging technique could lead to a large error in the value of the boundary film thickness. In contrast, the defocus Fresnel imaging technique can be applied to any grain boundary of interest. This method exhibits significant advantages when a statistical analysis of the intergranular film widths is required.

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