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Small-angle neutron scattering study of anisotropic growth morphology and irreversible photodensification in a-$GeSe_3$ films

T. Rayment and S. R. Elliott
Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, England
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The anisotropic growth morphology of obliquely evaporated amorphous $GeSe_3$ thin films has been studied by small-angle neutron scattering. Films deposited at 80° to the normal contain ellipsoidal voids 240 Å in length and 120 Å in diameter inclined at 70° to the normal, and which account for 47% of the volume. Absorption of band-gap light reduces the level and anisotropy of the scattering. The ellipsoidal voids collapse to form smaller spherical voids distributed isotropically.

I. INTRODUCTION

Vapor-deposited amorphous chalcogenide thin films exhibit remarkable changes in their physical, chemical, and mechanical properties on irradiation by band-gap light.[1,2] In the case of germanium selenide films, photoinduced densification changes of up to 15% have been observed in obliquely deposited evaporated films.[3] The presence of columnar voids in such as-deposited films has been suggested, and their role in causing the photodensification has been invoked. Evidence for a columnar growth morphology in very thin films deposited at normal incidence has been inferred from transmission electron microscopy (TEM) studies,[4] although sample charging and heating problems preclude high-resolution studies by this technique. Furthermore, while the lateral column dimensions have been estimated to be $\simeq 150$ Å by TEM,[4] the void dimensions normal to the surface could not be obtained in this way. Hence, a different technique is required in order to gain a complete knowledge of the shape and orientation of the voids, and how they are changed by optical irradiation: One such technique is small-angle scattering.

This paper presents the results of the first series of small-angle neutron scattering (SANS) experiments on thin obliquely deposited evaporated $GeSe_3$ films. The advantages of using neutrons rather than x rays are twofold: Thick, structurally homogeneous substrates may be used to support the films, and because neutrons are very penetrating they will be scattered much less by the substrates than by the structurally inhomogeneous thin films; the availability of large area neutron detectors, together with the point-source nature of the neutron beams, also greatly facilitates the study of anisotropic structural inhomogeneities by small-angle neutron scattering.

II. EXPERIMENTAL

The measurements reported in this paper were performed on the D17 SANS diffractometer at the Institut Laue-Langevin, Grenoble, using neutrons of 10-Å wavelength and with the area detector positioned 1.4 m from the sample. This configuration maximizes the neutron flux at the detector and gives a Q range from 2×10^{-3} Å^{-1} to 2.5×10^{-2} Å^{-1}.

Thin films of amorphous $GeSe_3$ were produced by evaporation of powdered bulk $GeSe_3$ (Ref. 5) using the method described in Ref. 3. The films were deposited at a rate of $\simeq 20$ Å s^{-1} on the silica substrates held at 20 °C, using a configuration which ensured that the rate of deposition was approximately constant for all angles of deposition ($\alpha = 0$–$80°$, relative to the film normal). Two different sets of samples were used, having thicknesses of $\simeq 2$ μm and $\simeq 20$ μm. Counting times of about 6 and 2 h were required for thin and thick films, respectively, in order to give sufficiently good statistics in the SANS intensity data.

III. RESULTS

Small-angle scattering was observed from all the films studied, but the scattering intensity was greatest for those films (both thin and thick) which had been deposited at the largest angles of incidence, i.e., $\alpha = 80°$. A contour plot showing the scattering intensity resulting from the normal incidence of neutrons on a thin, $\alpha = 80°$ film is shown in Fig. 1(a). It is immediately apparent that the small-angle scattering from such films is markedly anisotropic, giving direct evidence for the presence of structural inhomogeneities which are anisotropic in shape relative to the film normal. The inhomogeneities in this case are elongated, rodlike voids or low-density regions, which delineate the columnar morphology of the high-density regions, but which do not necessarily lie parallel to the direction of the original evaporant beam.

Many materials when deposited as thin films by evaporation at oblique angles of incidence exhibit a columnar growth morphology, for which invariably the columnar direction (inclined at β to the film normal) does not lie parallel to the original evaporant beam direction (at α to the film normal). The empirical relationship between α and β,

$$\tan\alpha = 2\tan\beta \quad , \qquad (1)$$

has been found to be obeyed for a wide variety of materials.[6] In the present case, for films deposited such that $\alpha = 80°$, the "tangent rule" predicts that $\beta = 70°$. The columnar orientation within the films can be ascertained straightforwardly using small-angle scattering. Rotation of the sample with respect to the incident neutron beam direction will change the degree of anisotropy in the scattering intensity; when the neutron beam is aligned with the columnar direction, the SANS will be isotropic (assuming that the column cross section prependicular to the long axis is

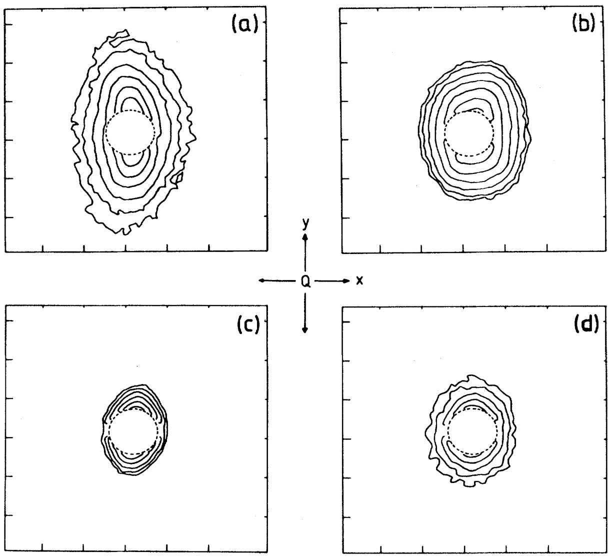

FIG. 1. Contour plots of SANS from evaporated a-GeSe$_3$ films, obtained with the neutron beam normal to the film surface unless stated to the contrary: (a) As-deposited film evaporated at $\alpha = 80°$ to normal; (b) same as (a) but with neutron beam inclined at 70° to film normal; (c) after illumination with band-gap light for 22 h; (d) after annealing irradiated film for 10 min at 250 °C. In all cases, contours correspond to a factor of 2 in intensity and are plotted on a logarithmic scale. The scattering geometry is as shown in the inset to Fig. 2.

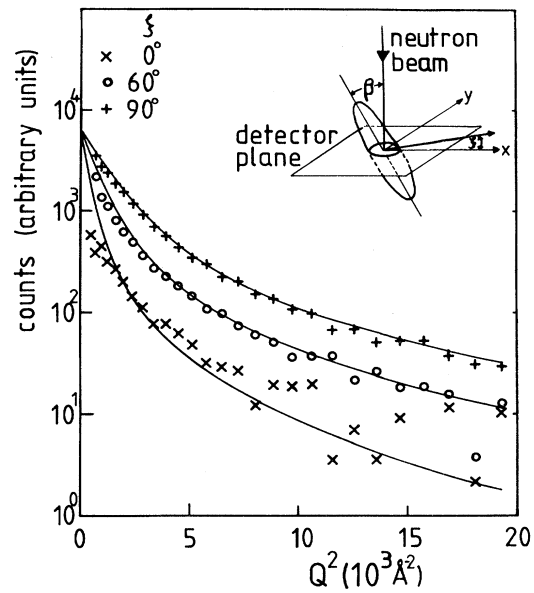

FIG. 2. Sector-averaged SANS data (points) for an as-deposited $\alpha = 80°$ a-GeSe$_3$ film. Each point in $|Q|$ is the mean of all detector cells within a sector 15° wide whose average angular value is ζ. The continuous lines are fits to the data using the model of independently scattering ellipsoids [Eq. (3)] discussed in the text. The scattering geometry employed in the experiments is shown in the inset, where β is the angle the ellipsoidal voids make with respect to the film normal (which has been taken to lie in the xz plane).

equiaxed). The small-angle scattering from the thin, $\alpha = 80°$ film [whose normal incidence SANS pattern is shown in Fig. 1(a)], rotated through 70° with respect to the neutron beam, is shown in Fig. 1(b). The contour plot clearly indicates that the scattering is more nearly isotropic [cf. Fig. 1(a)] although the contours are not perfectly circular. This could result for one of two reasons: Either the neutron beam was not aligned perfectly parallel to the column direction in the experiment, i.e., the columns are inclined relative to the normal at an angle of more than 70° (the maximum value attainable using the sample holder on D17), and/or the columns are elliptical, not circular, in cross section. On the basis of the present experimental evidence we are unable to distinguish between these two alternatives.

In principle, measurement of the SANS intensity allows the spatial dimensions (i.e., shape) of each void, and the total void volume, to be determined. Unfortunately, the voids present in these as-evaporated films do not satisfy the constraints of the absence of both polydispersity in void sizes and interparticle (void) interference which makes quantitative analysis straightforward (using, e.g., the Guinier approximation). Nevertheless, application of simple models gives valuable insight into the macroscopic structure of these films.

A (Guinier) plot of the logarithm of $S(Q)$ is not linear with respect to Q^2 in any region of Q measured, i.e., $2\times10^{-3} < Q < 2.5\times10^{-2}$ Å^{-1} (see Fig. 2), and so a single radius of gyration cannot be assigned to the voids. The small-angle x-ray scattering from voids in another material, evaporated amorphous Ge, has previously been interpreted by Cargill[7] using a model representing the voids as a set of identical ellipsoids each scattering independently. The scattering intensity produced by an ellipse is oscillatory in Q, but such oscillations were not observed experimentally. This unphysical feature of the model can be removed by considering the ellipsoids to be randomly orientated about the long axis, whereby the oscillations are averaged out if the two minor axes have unequal lengths, $A_1 \neq A_2$. This model is only suitable when the incident radiation is parallel, and the scattering vector therefore approximately perpendicular, to the long axis of the voids. The oscillations in the scattering intensity are not averaged out if there is a projection of the long ellipse axis (A_3) onto the plane of scattering [as in the case for the data shown in Fig. 1(a)].

In order to overcome this difficulty, we have modified and extended the simple model proposed by Cargill[7] by making the plausible assumption that there is a distribution of void sizes. More specifically, we take the voids to be represented by a collection of independently scattering ellipsoids with semiaxis lengths $A_1 = A_2 < A_3$ (such that A_1/A_3 is a constant), the distribution of each length about an average A_i^0 being described by $g(x)$. We take the distribution function to be a Gaussian, $g(x) = e^{-x^2}/\sqrt{\pi}$, where for the ith semiaxis

$$x = \frac{A_i^0 - A_i(x)}{A_i^0 \delta} \tag{2}$$

and where δ is the fractional polydispersity parameter, taken to be the same for all semiaxes. The scattering cross section for an individual ellipsoid (of semiaxes A_1^0, A_2^0, A_3^0) can, by changing variables to convert it to a sphere, be shown to be

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given by

$$\frac{d\sigma}{d\Omega}=\hat{b}^2\left|\int\int\int e^{i\vec{Q}\cdot\vec{r}}\,d\vec{r}\right|^2$$
$$=\left\{\frac{4\pi\hat{b}A_1^0A_2^0A_3^0}{(QR)^3}[\sin(QR)-QR\cos(QR)]\right\}^2 ,$$

where $\hat{b}$ is the neutron scattering length per unit volume, and

$$QR=[(Q_xA_1)^2+(Q_yA_2)^2+(Q_zA_3)^2]^{1/2} .$$

Thus for an assembly of independently scattering ellipsoids (voids) in a sample, each having a distribution of semiaxes governed by $g(x)$, the total scattering cross section is

$$\frac{d\sigma}{d\Omega}=N\frac{(4\pi\hat{b}A_1^0A_2^0A_3^0)^2}{\sqrt{\pi}}\times\int_{-\infty}^{\infty}e^{-x^2}(1-\delta x)^3\left[\frac{\sin(QR)-QR\cos(QR)}{(QR)^3}\right]^2dx , \tag{3}$$

where N is the total number of voids in the sample. We have assumed that the difference in scattering lengths between bulk and ellipsoid is simply $\bar{b}$, the composition weighted average for the bulk; i.e., we assume the low-density regions are devoid of material, i.e., they are empty voids.

A fit to the data for the thin, $\alpha=80°$ film using a Gaussian distribution is shown in Fig. 2, where it can be seen that the model accounts for the anisotropic scattering reasonably well. The uppermost set of data points, on this model, give information only about the size distribution of the minor axis, and as such are the simplest to fit. Having obtained the best fit to these points by varying A_1 and δ, the long semiaxis length A_3 was varied in order to obtain the best agreement with the data for the other sectors which contain scattering contributions from the projection of the long axis onto the scattering plane. The overall fit shown in Fig. 2 was obtained with a cross-sectional semiaxis length of the rodlike voids of $\simeq 60$ Å and a (longitudinal semiaxis) length estimated to be $\simeq 120$ Å, with a fractional polydispersity of 0.4. The estimate for the length of the voids is less reliable than that for the cross-section diameter because the quality of the fits to the data which involve the length are less good. Almost certainly this is because most of the scattering from the long axis was inaccessible in the range of Q values employed in these experiments ($Q_{min}=2\times10^{-3}$ Å^{-1}), and thus we are observing in effect only the tail of the distribution of A_3 values.

It has been observed in the past, and confirmed in this study, that the density of obliquely deposited films decreases with increasing angle (α) of the evaporant beam to the film normal. This behavior is strikingly manifested in the small-angle scattering, where the sector-averaged scattering intensity increases as α is increased from 0° to 80° (Fig. 3), indicating that the more void the volume is introduced the more oblique is the angle of incidence of evaporation. The anisotropy in the scattering (for the case of neutrons incident normal to the film) also increases as α increases, as is to be expected. Adopting the model of independently scattering ellipsoids and employing the parameter values obtained thereby from a fit to the data using Eq. (3) for the thin, $\alpha=80°$ film (Fig. 2), we have estimated the percentage void volume fraction for this film to be

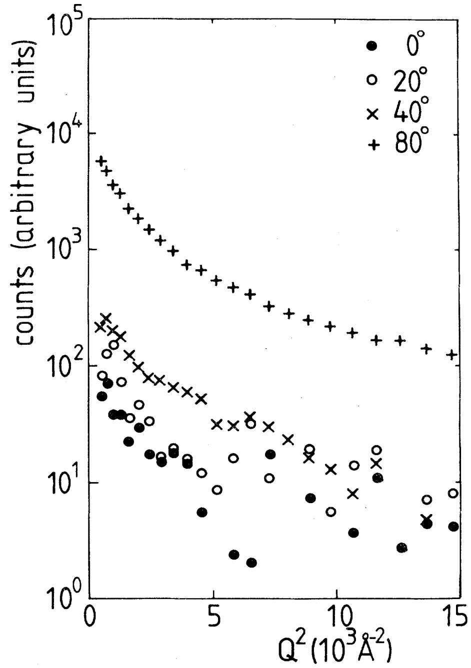

FIG. 3. Sector-averaged ($\zeta=0°$) SANS data for as-deposited a-$GeSe_3$ films evaporated at the angles indicated, taken with the neutron beam normal to the film surface.

47 ± 5. For comparison, the measured percentage density deficit of this film, with respect to one evaporated at normal incidence ($\alpha=0°$) at the same time, is 34 ± 10. We regard the correspondence between these two figures to be a confirmation of the validity of the model of independently scattering ellipsoids used in this study. The discrepancy between the two values could be due to a variety of factors. The estimate for the long semiaxis length of the ellipsoids obtained from fits to the SANS data may be in error as indicated earlier, because the region in which the scattering is governed predominantly by this length was not explored in this study. In addition, the film deposited at normal incidence ($\alpha=0°$) also contains void volume, albeit a lower proportion, and so its density, although higher than that of the $\alpha=80°$ film, is not truly representative of the bulk.

IV. DISCUSSION OF THE PHOTO-DENSIFICATION EFFECT

We have also investigated by SANS the irreversible photodensification effect which occurs in obliquely deposited thin films of amorphous Ge-Se alloys.[1,2,5] The effect on the SANS of illumination of a thin, $\alpha=80°$ film for 22 h with light from a 1-kW xenon arc lamp passed through an infrared-cut filter is shown in Fig. 1(c). A dramatic decrease in the anisotropy of the structural inhomogeneities is clearly apparent; annealing the irradiated film at 250 °C for 10 min reduced somewhat further the degree of anisotropy [Fig. 1(d)].

Figure 1(c) indicates that the absorption of band-gap light changes the SANS in two ways: The overall level of the scattering is reduced and the anisotropy is removed. The latter result is incontrovertible evidence that optical irradiation causes the elongated, rodlike voids to disappear while the former result can be interpreted as being due to a decrease in the overall void volume on irradiation. These two conclusions are reconciled by assuming that the action of the absorbed light is to cause the columnar morphology of the as-deposited, obliquely evaporated material to disappear due to the collapse of the intercolumnar volids. We suppose this occurs because of a photoinduced reconstruction of the structure across the voids (or low-density tissue regions), presumably by rearrangements involving the chalcogen (Se) atoms, whose lone-pair π orbitals form the top of the valence band and are therefore preferentially optically excited. The voids which remain after photodensification scatter more isotropically [Fig. 1(c)], indicating that the only remnants of the elongated rodlike low-density regions delineating the columns in the as-deposited material are small, isolated, approximately spherical, voids.

In conclusion, SANS experiments have been shown to give information on the microscopic changes which are responsible for the large, irreversible photocontraction effects in obliquely deposited amorphous chalcogenide films, as well as being readily able to give structural information on the growth morphology of the as-deposited films.

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