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Shallow Angle X-Ray Diffraction from *In-Situ* Silica: Titania Sol-Gel Thin Films

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Abstract

X-ray diffraction at shallow angles of incidence has been used to examine three silica:titania sol-gel thin films. Comparison with transmission x-ray diffraction measurements of similar materials in the bulk shows a distinct increase in disorder in the silica network. An increase in porosity of the network in thin films is also likely, suggested by an increase in Si-O-H bonds. No differences in structure between samples with differing titania contents were observed using this technique.

Introduction

Many experimental methods are available which enable structural information to be gleaned from amorphous or crystalline materials in their bulk form. However, there is an increasing number of applications of a wide variety of materials in which the active substance is in the form of a thin film; it is important, then, to consider whether the material shows the same structure when in thin films of ~1μm thick, as it does when produced in the bulk. Many experimental techniques are unsuitable for studying thin films due to the difficulty in separating properties of the film from those of the substrate. Shallow angle x-ray diffraction, where sample penetration depths are lessened by reducing the incident angle of radiation into the film, is a relatively new technique which can enable scattering, and therefore structural information, from the thin film to be isolated.

The shallow angle technique was first developed by Lim and Ortiz [1] in 1987, who studied crystalline iron oxide layers on glass substrates, i.e. sharp Bragg peaks on a diffuse Debye Scherrer background. The method and analysis has recently been developed further [2,3] and used to study a variety of both amorphous and crystalline thin films. The technique is used here to examine several mixed silica:titania thin-films, produced by the sol-gel method.

Mixed silica:titania materials are of significant technological importance. Silica glasses with a few mol% TiO_2 are used as ultra low thermal expansion (ULE) glasses [4] and mixed titanium:silicon oxides are important as catalysts and catalytic support materials [5]. In the optical industry they can be produced as anti-reflective thin film coatings, or with tailored or graduated refractive indices [4]. The properties of these useful materials are highly dependent on their chemical composition, homogeneity and texture, which in turn depend on synthesis conditions. Sol-gel synthesis, based on the hydrolysis and subsequent condensation of metal alkoxide precursors, is a relatively new method that combines this atomic homogeneity with a high degree of porosity [4].

The Samples

Three bulk sol-gel samples were prepared by hydrolysis of alkoxides with water and ethanol mixtures in the approximate ratios 1:2:7.5, with varying titania contents [6]. Sample 1, labelled 'pure silica', contained no titania, Samples 2 and 3 contained small amounts of titania, the 'low titania' sample was approximately silica $_{0.89}$:titania $_{0.11}$ whilst the 'high titania' sample was silica $_{0.77}$:titania $_{0.23}$.

All samples contained ~ 4 atomic% silicon in the bulk, with substantial residual amounts of volatiles such as ethanol.

The bulk sol-gels were converted to thin films by the *spin coating* method [4]. An excess of liquid is dispensed onto the surface of the substrate, and then the sample is rotated at low speed so that the liquid flows radially outwards, driven by centripetal force. Any surplus liquid flows to the edge of the substrate and drips off. As the film thins, the rate of removal of liquid slows down as the viscosity increases; in the final stages most of the thinning occurs by evaporation of volatiles [7]. The method produces a very uniformly thin coating, and the process may be repeated several times to build up a thicker film or, for example, to produces layers of slightly differing qualities. In the samples used herein, six layers of film were deposited to produce a film ~1μm thick on a silicon wafer.

Although the underlying physics and chemistry that govern polymer growth and gelation are the same for films and bulk sol-gels, several factors in the evolution of thin films mean that structurally the two forms can be quite different [8]. In bulk systems evaporation usually occurs after gelation, whereas in thin films the deposition and evaporation processes happen simultaneously, and this results in a competition between compaction of the structure caused by evaporation and the stiffening (and therefore resistance to compaction) of the material caused by the condensation process. The short duration of deposition and evaporation/drying in thin films means that considerably less cross-linking occurs than in bulk gels, which generally results in more compact, dried structures [4]. Also, thin films are constrained by their geometry, and the continued shrinking causes stresses; this is particularly true for films made by spinning methods. It is likely, therefore, that there is a marked difference between the structure of sol-gels in thin films and in the bulk; it is expected that the rapid gelation of thin films will result in a more porous, and more disordered material than in the bulk with a lower concentration of volatiles.

The Shallow Angle Technique

The refractive index of materials at x-ray wavelengths is less than unity, consequently, at incident angles below a critical value, α_c, total external reflection occurs. Below α_c limited penetration is achieved via the evanescent mode, and is exponentially damped: in principle sampling depths of ~10Å to ~1000Å may be achieved. Above α_c the penetration depth increases rapidly with incident angle, inversely with the wavelength of the radiation, and is limited by photoelectric absorption; it is this region where shallow angle diffraction can be used to isolate scattering from a thin film mounted on a substrate.

Shallow angle x-ray diffraction data was collected on Station 9.1 at the Synchrotron Radiation Source at Daresbury Laboratory, UK. The intrinsically highly parallel nature of the beam provided by a synchrotron source is of advantage over conventional focused laboratory x-ray sources for the shallow angle technique, in that the associated serious geometric aberration effects are avoided. Further, the high intensity beam provided by a synchrotron source is necessary for the relatively weak scattering from the small volume of material sampled in the shallow angle geometry; the availability of relatively hard x-rays allows a wide dynamic range (up to ~18Å^{-1}). The conventional (transmission) x-ray diffraction arrangement is modified to produce the shallow angle configuration, as shown schematically in Fig. 1. The white beam from the synchrotron source is monochromated by a channel cut crystal and proceeds through a pair of slits which define the incident beam profile; a narrow slit profile of 100μm by 10mm is used in shallow angle work to limit contamination from the straight through beam at the lowest incident angles. The sample is set at a fixed, small angle α_i to the

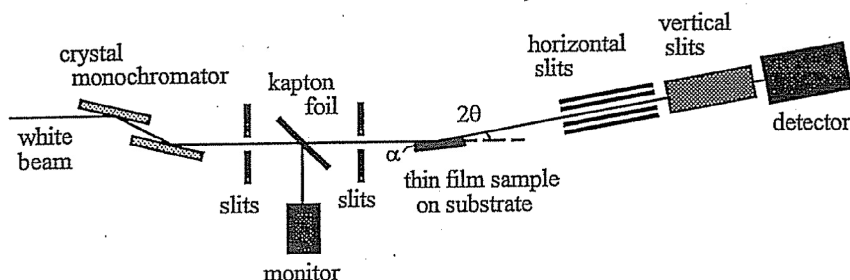

Figure 1: Schematic diagram of the shallow-angle arrangement

ncident x-rays. An iterative procedure of height and angle adjustment is used to define the zero-ngle for the sample [2,3]; this procedure is very important given the small angles used in data ollection. It is also essential that the sample is smooth and flat: any significant irregularity in the ilm thickness will produce a high uncertainty in α_i and hence in the collected scattering profile. The cattered radiation passes through an arrangement of horizontal and vertical slits to the detector. A ong slit package reduces the angular spread of scattered radiation incident on the detector and esults in a resolution of ~ 0.07°. Data is collected sequentially at angles 2θ = 2° to 130°; this is ater converted to scattering vector $Q = 4\pi/\lambda \sin\theta$.

ata Analysis

Basic data reduction for shallow angle x-ray diffraction accounts for detector dead-time, hanges in incident beam current and beam polarisation effects. A further correction is needed to ccount for the fact that the collected x-ray beam is actually scattered from the refracted beam within he sample; this produces a small shift in the measured scattering angle 2θ [3]. More sample-specific orrections such as sample absorption are not included in the reduction procedure for the shallow ngle technique; the correction is complicated by unknown factors in the sample geometry which nake it difficult to measure the actual penetration depth into the sample and/or substrate and the ontributions from each. This situation could be clarified if the incident x-rays did not penetrate the ubstrate; this can be achieved by either using thicker films, reducing the incident angle, or increasing he incident x-ray wavelength, however, increasing λ decreases the Q-range and therefore the real-pace resolution.

Subtraction of the background scattering in the shallow angle geometry is also problematic, as here is no direct method of removing the sample and measuring the 'background' scatter. It must herefore be assumed that the background scattering would be a smooth curve showing no structure, nd can therefore be removed, along with the atomic form factor, by fitting a Chebyshev polynomial hrough the data. While this method produces an 'interference function' which shows the same peak ositions as would be derived by following standard procedures for transmission geometry data [9], here is no method of converting the data to electron units, and therefore it is not possible to produce oordination numbers from the real-space information.

Results

Fig. 2 shows the corrected data for the three sol-gel samples, before and after fitting and ubtracting a polynomial from the data. In both cases the scattering from the samples containing itania look very similar, but the 'pure silica' sample shows a much stronger scattering across the

whole Q-range. Small Bragg peaks due to the silicon substrate are visible at approximately 6.0, 9.5 and 13.5$Å^{-1}$ in the 'pure silica' and 'low titania' samples, although only the peak at ~ 6$Å^{-1}$ appears to be present in the 'high titania' sample; this is likely to be due to the fact that the higher titania film is more dense and therefore the incident beam is attenuated more quickly. This observation, coupled with the fact that the silicon peaks are very small, suggests that the penetration depth covered by the incident x-rays is only just greater than the thickness of the films and so penetration into the silicon wafer is very small.

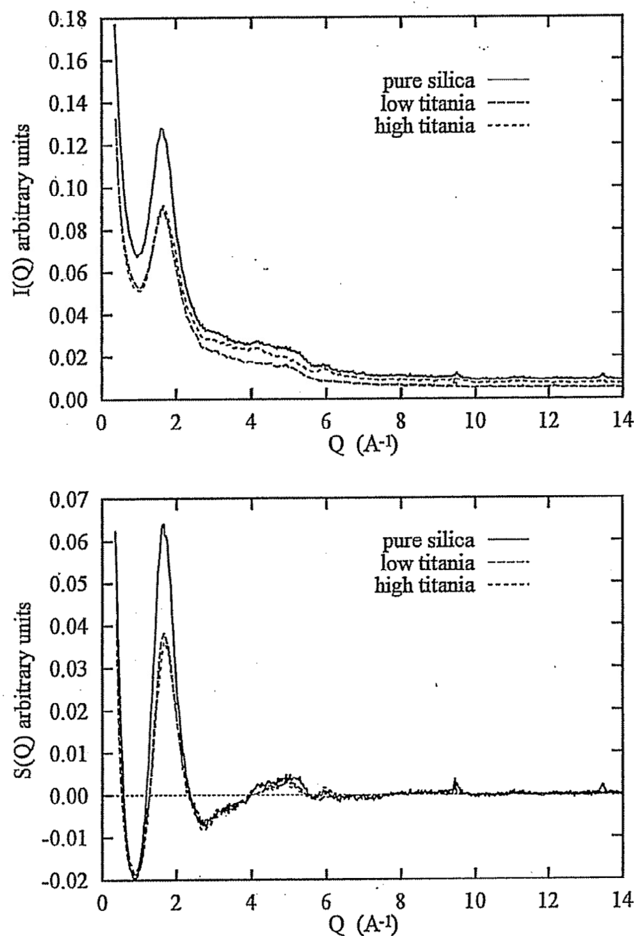

Figure 2: Corrected sol-gel data before (top) and after (bottom) polynomial subtraction

The interference functions reveal the similarities between the scattering from all three samples after the first major peak. The sharpness of this first peak in the 'pure silica' data may indicate contamination from an underlying residual silicon Bragg reflection. It is clear that the visible Bragg peaks, particularly the one at ~ 6$Å^{-1}$, represent a significant problem if analysis were to continue by way of Fourier transform to a pair distribution function; their presence could lead to strong silicon correlations in the $g(r)$. The rapid decay of the data to the asymptotic value, after the first sharp peak at ~1.8$Å^{-1}$ and a small second peak at ~ 4.5$Å^{-1}$, indicates that all three samples show a high

degree of disorder. This is demonstrated in Fig. 3 where scattering from the 'high titania' sample in thin film form (shallow angle geometry) is compared to scattering from the bulk (transmission geometry); both data sets are at a similar stage of data reduction.

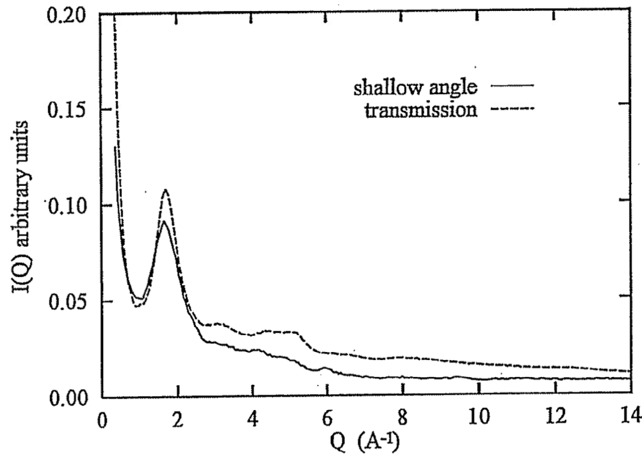

Figure 3: Comparison of shallow-angle and transmission diffraction results

Both curves are dominated by a first sharp peak, but the bulk sample also shows definite second and third peaks; for the thin film sample it is very difficult to determine any distinct correlations, although some evidence of structure in that region is visible. Due to the contamination by silicon Bragg reflections, and the large amount of statistical noise in the data produced by scattering from very small volumes, the information available from a Fourier transformation into real-space is limited; Fig. 4 shows the Fourier transform of the *S(Q)* function for the 'high titania' sample as an example of the *r*-space information obtainable. The *S(Q)* data is initially weighted by a sharpening function, and then a heavy windowing function is used in the Fourier transform to reduce ripples resulting from statistical noise or termination effects.

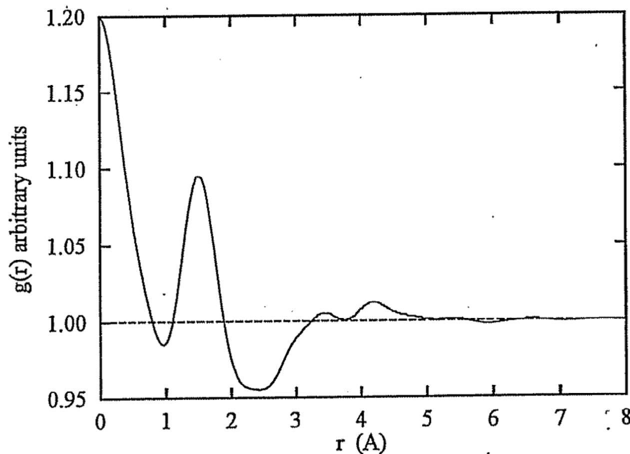

Figure 4: Fourier transform of *S(Q)* gives the pair distribution function *g(r)*

The strong correlation visible at ~ 1.5Å is expected to result from a Si-O distance; in bulk silica the Si-O first neighbour distance is 1.61Å, however, the silicon-oxygen distance is reduced to 1.50Å when taken out of the confines of the silica network, for example when part of an $Si(OH)_4$ unit. This may be further evidence that the silica network has become more disordered when in a thin film, and, contrary to the case for the bulk material, there are few long silicon-oxygen chains and more hydrogen atoms terminating the network. There is little order apparent in the *g(r)* after the first main peak, in particular, interatomic distances resulting from O-Si-O (2.6Å) and Si-O-Si (3.0Å) bonds which would be prominent in *g(r)* data from bulk silica:titania sol-gels [10] are not visible.

Discussion

Shallow-angle x-ray diffraction has been used to examine three silica:titania sol-gel thin films. Whilst difficulties arising from contamination from the substrate can reduce the quantitative nature of the collected data, it is still possible to make clear qualitative statements about the structure of the films in comparison with their bulk counterparts. There is evidence for a high degree of disorder in the silica network of the thin films, with many Si-O bonds but a reduction in the number of rigid Si-O-Si chains compared to when in the bulk. An apparent shortening of the Si-O first neighbour distance may indicate that there is a tendency for Si-O-H bonds to form, which would suggest that the silica network is more porous in thin films than in the bulk; this is consistent with observations of the properties of sol-gel thin films discussed earlier [8].

It was not possible to determine small differences in structure between the 'pure silica' sample and those containing titania; this might be expected considering the very small titania content and the fact that it bonds substitutionally into the silicon network at these low titanium levels. It is unlikely that differences could be observed with the shallow-angle technique until a method is devised of allowing an exact background subtraction process, and this remains a severe limitation to the usefulness of the technique. The penetration depth of the x-rays into the sample would also have to be reduced, using either thicker samples (in which case the films might be structurally different from those used in applications), or higher wavelengths (limiting the resolution of the real-space information available). The method also collects data from a *range* of scattering volumes, dependent on the penetration and film thickness; this results in a range of absorption effects and therefore a blurring of the data. These problems would have to be solved before quantitative structural information could be gleaned from sol-gel thin films using the shallow-angle technique.

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