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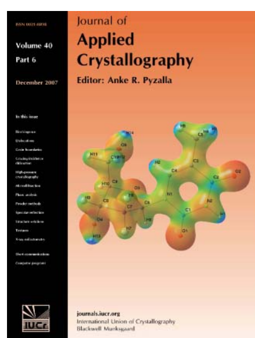

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An approach to high-throughput X-ray diffraction analysis of combinatorial polycrystalline thin film libraries

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With the demand for higher rates of discovery in the materials field, characterization techniques that are capable of rapidly and reliably surveying the characteristics of large numbers of samples are essential. A chemical combinatorial approach using thin films can provide detailed phase diagrams without the need to produce multiple, individual samples. This is achieved with compositional gradients forming high-density libraries. Conventional raster scanning of chemical or structural probes is subsequently used to interrogate the libraries. A new, alternative approach to raster scanning is introduced to provide a method of high-throughput data collection and analysis using an X-ray diffraction probe. Libraries are interrogated with an extended X-ray source and the scattering data collected using an area detector. A simple technique of 'partitioning' this scattering distribution enables determination of information comparable to conventional raster scanned results but in a dramatically reduced collection time. The technique has been tested using synthetic X-ray scattering distributions and those obtained from contrived samples. In all cases, the partitioning algorithm is shown to be robust and to provide reliable data; discrimination along the library principal axis is shown to be ~500 μm and the lattice parameter resolution to be $\sim 10^{-3}$ Å mm^{-1}. The limitations of the technique are discussed and future potential applications described.

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1. Introduction

Production and characterization of new functional materials is an important component of materials science advancement. However, the identification of new material compositions with desirable and optimized properties (*e.g.* through the preparation of phase diagrams) is traditionally time consuming and costly; less than 5% of ternary and 1% of quaternary alloys have been fully characterized (Zhao, 2006). A technology area that is currently seeking to rapidly survey a wide range of materials with substantial compositional variation is photovoltaics. The future successful development of solar cells requires the identification of new materials with properties optimized for features such as energy generation, long-term sustainability and low cost. Material optimization required for solar cell improvements includes, for example, optimization of the conductivity and optical properties of transparent conducting oxides such as In_2O_3 by the addition of elemental dopants (van Hest *et al.*, 2006). The multitude of possible combinations of these additions means that a full systematic study of their effects by conventional methods is not economically feasible.

In recent years the use of combinatorial techniques has translated from organic (*e.g.* pharmaceutical) to inorganic materials. The exploitation of thin inorganic films fabricated into high-density chemical libraries has shown great potential for rapid surveying of wide compositional ranges (Takeuchi *et al.*, 2006). Libraries with homogeneous compositional areas and continuous compositional spreads (CCSs) can now be produced routinely in a single deposition step (Thelakkat *et al.*, 2004). High-throughput or combinatorial X-ray diffraction studies of polycrystalline thin films have so far relied on conventional raster scanning of either CCS samples (*e.g.* Gorrie *et al.*, 2008) or arrays of individual samples (*e.g.* Yanase *et al.*, 2002), with the high-throughput aims being achieved by the automation of this data collection method.

Previous work by Ohtani *et al.* (2001) links structural determination to spatial mapping for epitaxial samples, by the use of simultaneous data collection with a wide X-ray beam. However, this method has not previously been adopted for polycrystalline materials owing to difficulties arising from the interpretation of the overlapped diffraction data.

In this paper, a new approach is demonstrated which uses both an extended X-ray beam profile and analytical interpretation of subsequent scattering data from polycrystalline thin films. In this initial assessment, the new approach is shown to significantly increase the interrogation speed of X-ray diffraction data compared with conventional methods (such as pencil beam probes).

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The study investigates the potential use of a ‘line’ probe that illuminates a narrow rectangular area along a principal axis (y) of the library. The two-dimensional scattering distribution is subsequently measured in a single exposure using an area detector. This scatter distribution is thus the superposition of diffraction patterns from all loci along the illuminated area. A significant challenge, as a result of the complexity of polycrystalline materials, is to derive the structural information corresponding to each locus from this scatter distribution, a process termed ‘partitioning’. The whole library can subsequently be interrogated by scanning the sample in one direction through the X-ray line beam.

2. Method

2.1. Partitioning

The method used here was developed following consideration of several alternative approaches. These included deconvolution and wavelet synthesis which, although successful elsewhere, were undermined by the poor signal-to-noise ratio that is characteristic of these scattering distributions. Thus we have adopted a pragmatic, empirical approach that transforms the intensity scattering distribution data directly into a normalized intensity map [In(d, y)] on a d spacing *versus* locus (y) grid. From such maps, phase and lattice parameters at any point along the library can be determined. The transformation process is simply achieved through

$$\mathrm{In}(d, y) = \int_{\chi_1}^{\chi_2} I_{2\theta,y}(\chi)\,\mathrm{d}\chi/(\chi_2 - \chi_1), \quad (1)$$

where χ_1 and χ_2 are the azimuthal limits of the detector and are dependent on scattering angle for our system, and $I_{2\theta,y}(\chi)$ is the measured intensity at particular values of 2θ and y.

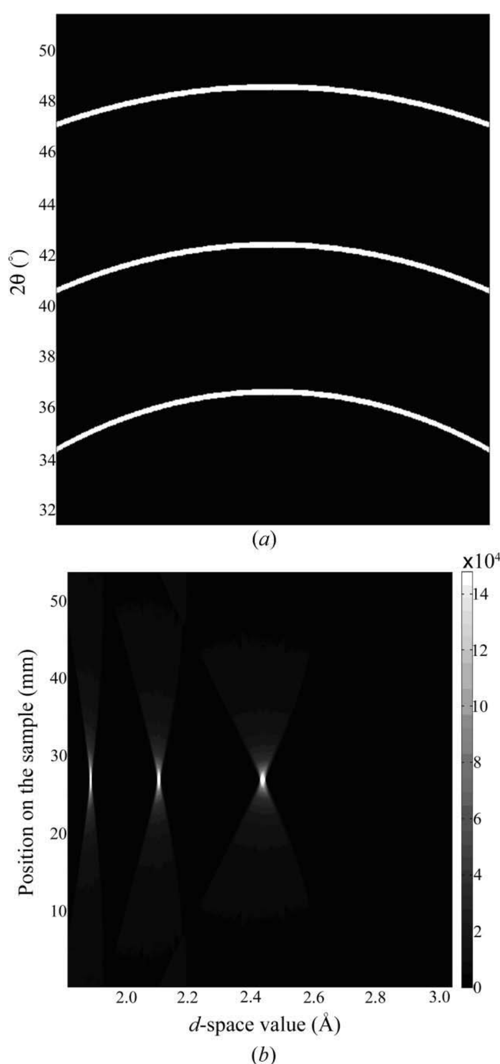

Figure 1
Simulated diffraction intensity distribution of an ideal single compositional area (a) and the associated transformed distribution (b).

2.2. Experimental

To illustrate this partitioning method and test its limitations, we have produced (i) a series of simulated scattering patterns and (ii) experimental scattering data from well controlled, ‘phantom’ samples. In all cases we have applied the partitioning algorithm to produce the corresponding In(d, y) maps and directly compared these with the simulation models and phantoms.

All the experimental scattering data were measured using a Bruker D8 diffractometer fitted with a GADDS detector. The incident X-ray beam (Cu $K\alpha$) was conditioned to produce a beam of $\sim$30 $\times$ 1 mm at the sample using a single Geöbel mirror. Scattering data were corrected for detector distortions (geometric and response) prior to analysis.

The transformation algorithms were embodied within a new code, *Bandit*, that was developed in *Matlab* (The MathWorks Inc., Natick, MA, USA). This code reads the detector output and applies a calibration based upon an external standard to ensure accurate d-spacing determinations from each intensity maximum. It subsequently applies the transformation (1) and produces In(d, y) contour plots. *Bandit* was also used to produce the simulated scattering distributions based upon structural models that were varied along the length of the X-ray beam.

The phantom samples examined were produced from bulk powders and polycrystalline, metallic thin films, fabricated by sputter coating. These included the following:

(a) A glass slide containing a linear array of wells ($\sim$5 $\times$ 5 mm) that could be loaded with silicon powder (NBS 640c) to produce a user-defined distribution of scattering material along the length of the illuminated area. This was used to illustrate and test features of the partitioning algorithms along the illuminated area.

(b) A glass step wedge where the height of each step was 0.34 mm and where each step could be loaded with silicon powder. The area of each step was $\sim$2 $\times$ 3 mm. This provided an extended sample where each component step was displaced by a fixed amount from the centre of the diffractometer. This deliberate displacement error resulted in diffraction maximum shifts as

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$$\Delta 2\theta = -2S\cos\theta/D, \qquad (2)$$

where $\Delta 2\theta$ is the variation of scattering angle, D is the sample-to-detector distance and S is the sample displacement relative to the instrument centre.

Thus this phantom represented a first approximation to a material with discrete changes in lattice parameter along the illuminated area.

(*c*) Homogeneous metallic thin films deposited upon glass slides. These were mounted within the diffractometer, initially with their surfaces parallel to the long axis of the incident beam (conventional setting). Subsequent data collections were undertaken with the samples rotated such that each end of the sample was displaced by the same amount (but one end a positive displacement and the other a negative displacement) from the instrument centre. The midpoint of the library sample remained on the instrument centre. Thus, as a result of the displacement gradient, the diffraction data would appear to derive from a continuously graded composition along the illuminated area. This gave diffraction maximum positional shifts analogous to the changes in lattice parameters expected of samples with a changing compositional gradient obeying Vegard's law.

3. Results and discussion

In this section the data are presented in pairs in order that the scattering distributions can be easily compared with the corresponding transformed data.

3.1. Simulations

Bandit was employed to produce a number of simulated scattering distributions. These have the same number of pixels as the measured images (1024 × 1024). A simple example is shown in Fig. 1(*a*), which illustrates the intersection of Debye cones (*d* spacings of 2.4334, 2.1075 and 1.8859 Å) from a 'point', polycrystalline sample with a flat plate detector. This simulated distribution replicates diffraction from a cubic system with a lattice parameter of 4.216 (1) Å. The corresponding transformed data are presented in Fig. 1(*b*), where the intensity distribution indicates, as expected, three discrete maxima at constant '*y*' loci. As the simulated sample is a point source of scatter, there is no component of scattering along the

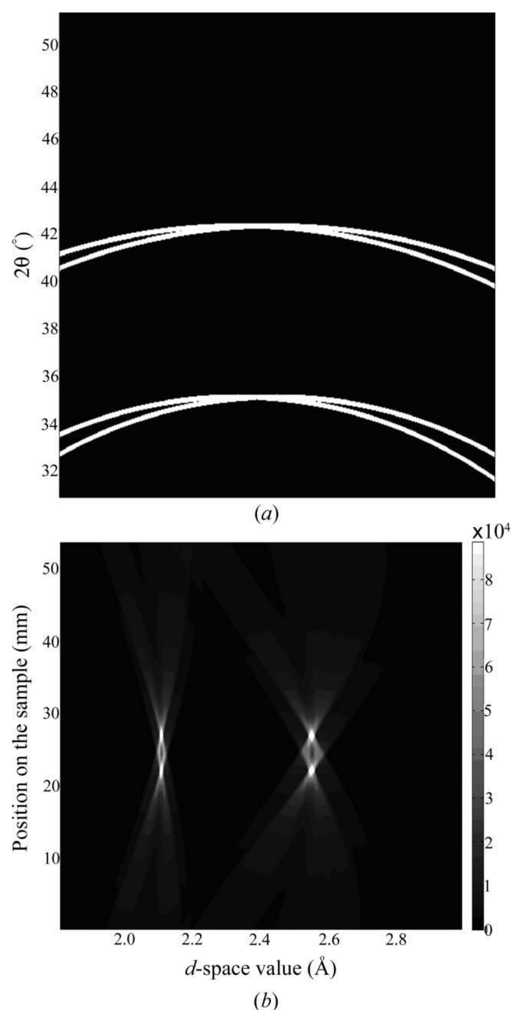

Figure 2
Simulated diffraction intensity distribution of two ideal compositional areas (*a*) and the corresponding transformed distribution (*b*).

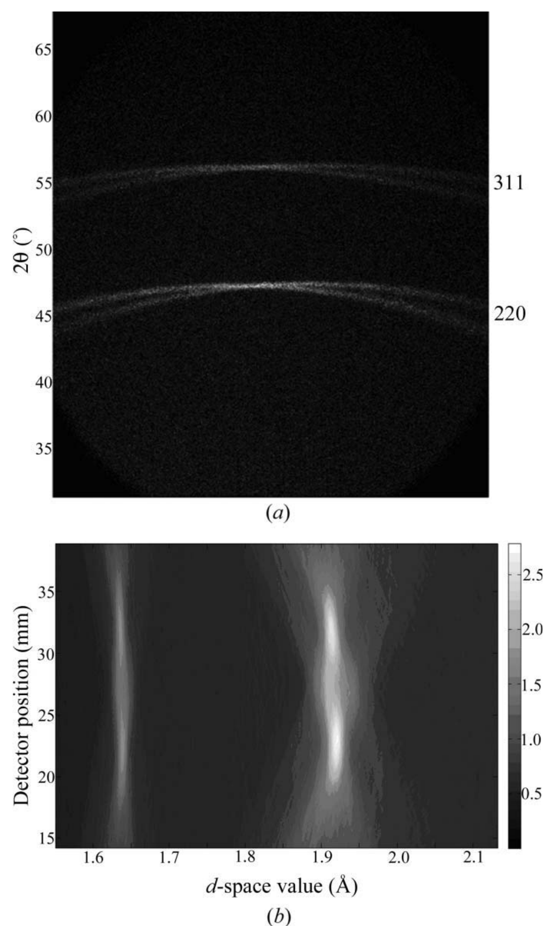

Figure 3
Experimentally produced diffraction intensity distribution from a two-component Si library (*a*) and the corresponding transformed distribution (*b*).

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principal library axis, 'y'. The d spacings determined from the transformed data are 2.433, 2.108 and 1.886 Å [a = 4.216 (2) Å], indicating the reliability of the transformation algorithm. Using repeated measurements, under these ideal conditions the minimum change detectable at a d spacing of 2.5 Å was determined to be 0.003 Å.

Fig. 2(a) is the simulated scattering distribution as would be measured from an ideal cubic material with diffraction maxima corresponding to d spacings of 2.43 and 2.10 Å [a = 4.204 (6) Å]. In this case the model consists of two 'point' samples separated along the illuminated area by a distance of 4.8 mm. The transformation algorithm produces four intensity maxima and clearly spatially separates the individual scattering centres (Fig. 2b). The d spacings determined from the transformed data are 2.545 and 2.109 Å [a = 4.31 (10) Å], and the sample separation is measured to be 4.8 mm. With these ideal conditions, the minimum step discernible in the y axis was determined to be 2060 μm.

The linear array of wells was loaded with silicon powder (NBS 640c) by filling two of the wells separated by an unfilled well, *i.e.* two sources of diffraction with the same diffraction patterns but with the respective sample centres separated by ~10.0 (1) mm along the library principal axis. This was the experimental equivalent of the previously simulated case. The resulting diffraction pattern and transformed data are shown in Figs. 3(a) and 3(b), respectively. Compared with the equivalent simulation, the transformed maxima are extended in the 'y' direction. This is to be expected because of the finite well size (5 × 5 mm) in contrast to the idealized simulation model possessing a minimal 'y' component. The sample separation was determined to be 9.89 (13) mm. The d spacings were determined to be 1.931 Å for the 220 and 1.642 Å for the 311 maxima [a = 5.45 (1) Å]. The NIST certified values for the corresponding maxima are 1.920 Å for 220 and 1.640 Å for 311 [a = 5.435 (6) Å from these maxima only] measured by conventional powder diffraction techniques.

An example of the scattering distribution from the glass step wedge phantom is shown in Fig. 4(a) where, for clarity, only two of the steps were loaded with silicon powder. The steps were separated by 4 mm along the illuminated area and were displaced in height by 0.34 mm. The resulting transformed data are shown in Fig. 4(b), and from this intensity distribution, the distance between the steps was determined to be 3.9 (1) mm. The transformed data were used to calculate

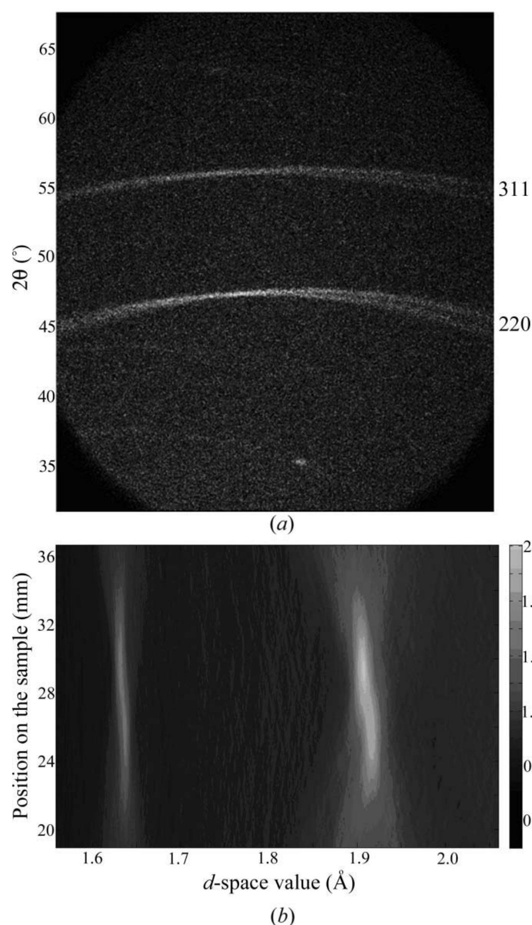

Figure 4
Experimentally produced diffraction intensity distribution of a two-component Si library with relative sample displacement between the areas (a) and the corresponding transformed distribution (b).

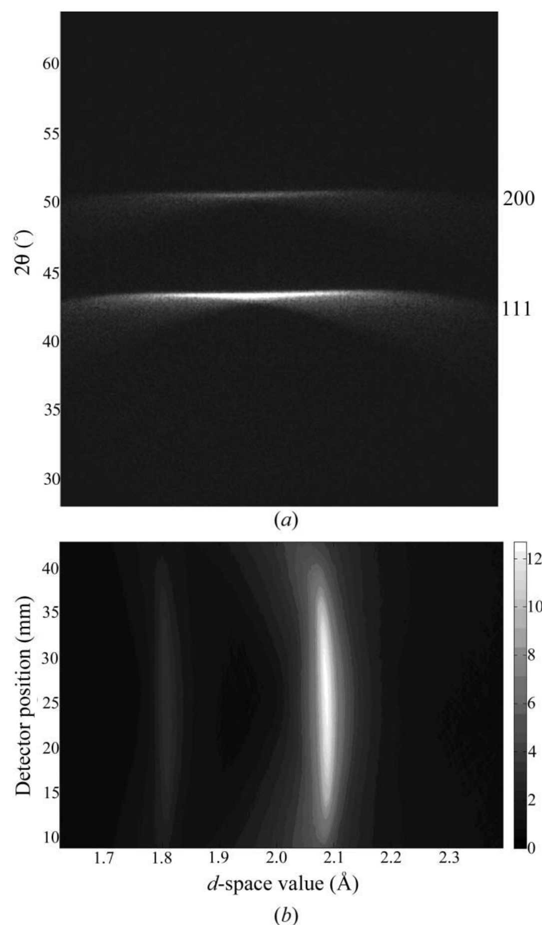

Figure 5
Experimentally produced diffraction intensity distribution of a homogenous copper thin film illuminated with an extended X-ray source (a) and the corresponding transformed distribution (b).

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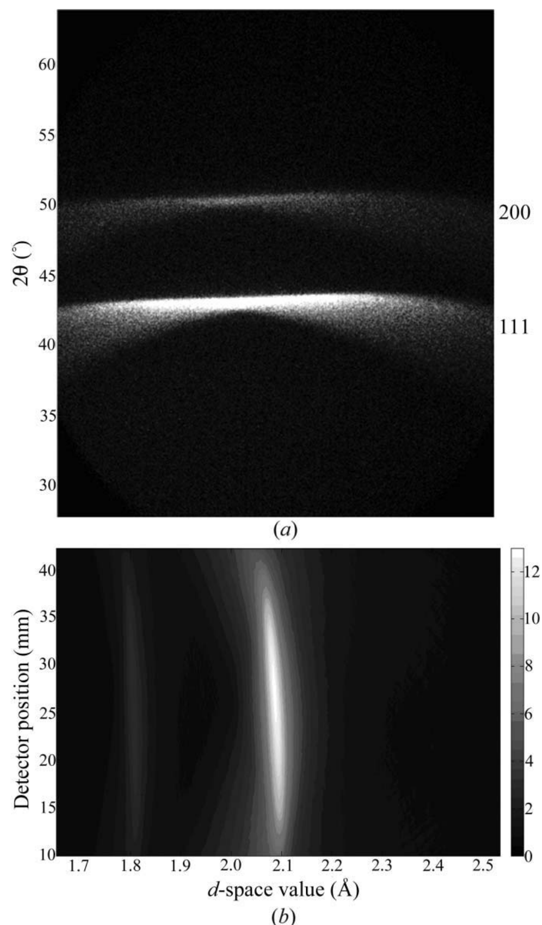

Figure 6
Experimental diffraction intensity distribution of a homogenous copper thin film tilted to simulate a compositionally graded material (*a*) and the corresponding transformed distribution (*b*).

differences in *d* spacings from each of the steps of 0.008 Å for 220 and 0.005 Å for 311. These are in good agreement with those calculated from equation (1).

The scattering data from a homogeneous Cu thin film deposited upon a glass slide and illuminated with the elongated source is shown in Fig. 5(*a*). The detector was positioned to receive scattering from the 111 and 200 crystal planes. The data transformed by *Bandit* are illustrated in Fig. 5(*b*), which indicates, as expected, two intensity maxima extended in the '*y*' direction but each with a constant *d* spacing corresponding to the 111 and 200 maxima of Cu. Assuming a homogeneous film, any intensity variation at constant *d* spacing would indicate variations in intensity along the interrogating X-ray beam, and this could be used subsequently as a correction factor.

To experimentally simulate scattering from a library possessing a continuous lattice parameter gradient, data from the copper thin film were collected following a rotation of the sample by 1°, thus creating a displacement error gradient. This was calculated to produce a change in *d* spacing of 0.015 and 0.011 Å across 24 mm for the 111 and 200 maxima, respectively. The consequent scattering data are presented in Fig. 6(*a*) and the corresponding transformed data in Fig. 6(*b*). The *d*-spacing changes measured from the transformed data were 0.015 and 0.010 Å for 111 and 200, respectively. Thus we have been able to measure an apparent lattice parameter gradient of 9.911×10^{-11} (equivalent to 9.911×10^{-4} Å mm^{-1}), which is probably better than that required for most materials.

4. Conclusion

In conclusion, we have been able to demonstrate how the use of an extended X-ray beam to illuminate compositional libraries has the potential to significantly reduce library interrogation times.

We have estimated the integrated volume separation for polycrystalline thin films to be approximately double that for the ideal case, *i.e.* ~500 µm. Therefore it would be possible to extract measurements every 500 µm along a library principal axis. Given our library length of 24 mm, this approach would therefore reduce data collection times by a factor of almost 50 compared with an equivalent raster scan. Changes in lattice parameter along the library principal axis could be detected at a resolution (~10^{-3} Å mm^{-1}) that is suitable for most of the semiconductor materials that we are investigating.

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