Derivation of pair distribution functions for interface interdiffusion analysis for multilayered thin films using high-energy electron diffraction

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Abstract
High-energy electron diffraction has been used to obtain reduced density functions from multilayered thin films. Due to the very nature of the experiment, only interatomic correlations perpendicular to the incoming electron beam are responsible for the scattered intensity. This allows an investigation of the interface interdiffusion of inner surfaces. Since no specimen preparation is needed, the technique is uninfluenced by preparation artefacts. We describe the theory and the experimental requirements for the application of this method and present results obtained for a terbium/iron multilayer film.

1. Introduction

In modern technology multilayered thin films are of great interest, because they can be designed to have new or improved physical properties compared to bulk materials. These properties can be strongly influenced by the quality of the interfaces between the individual layers. For detailed studies of this influence it is especially necessary to determine the degree of intermixing of atoms from adjacent layers. In the case of multilayer films with very thin amorphous-to-polycrystalline single layers this is rather difficult to achieve.

The calculation of **p**air **d**istribution **f**unctions (PDFs)—also called reduced density functions—from diffraction intensities is a well established method of structure investigation for amorphous and polycrystalline materials [1]. Usually this method is applied to specimens which are assumed to be spatially isotropic. However, multilayer films are not three-dimensionally isotropic because of the layer structure. In this paper we describe the basic idea, the theory and the requirements for the application of the PDF method to detect interface interdiffusion in thin multilayered films. The potential of the technique is demonstrated in the comparison of a terbium/iron multilayer film consisting of very thin individual layers with an alloy of the same overall composition.

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2. Principle

If one considers a polycrystalline or amorphous multilayer film with alternate layers of atoms A and B, then in the case of sharp interfaces between the layers, i.e. no intermixing of A and B, there are no A–B pairs parallel to the film plane (figure 1(a)); thus no pairs of type A–B can be detected along the interface (it should be noted, however, that perpendicular to the interface there will be such pairs). If atoms A and atoms B are intermixed in the region between the single layers as shown in figure 1(b), there are a certain multitude of A–B pairs parallel to the interface plane and accordingly peaks appear in the PDF at corresponding specific distances.
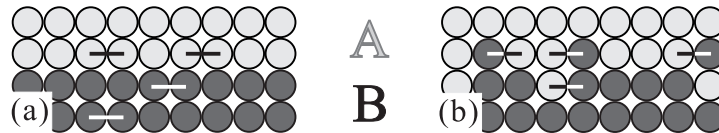
Figure 1. Schematic representations of the atomic pairs parallel to the interface in the case of an ideal interface (a) and in the case of interdiffusion (b).

3. Theoretical approach

3.1. Spatially isotropic specimen

The scattering theory that is commonly used to deduce pair distribution functions from electron diffraction patterns of spatially isotropic specimens has been extensively developed by Cockayne and co-workers [1].

Following Warren [2], the scattered intensity for the scattering vector $\vec{k}$, with modulus $k = 4\pi \sin(\Theta)/\lambda$, for a sample with atoms at positions $\vec{r}_i$ and scattering factor f_i is

$$I(\vec{k}) = \sum_m \sum_n f_m f_n e^{i\vec{k}\cdot\vec{r}_{mn}} \tag{1}$$

where $\vec{r}_{mn} = \vec{r}_m - \vec{r}_n$.

Generally the pair distribution function is the Fourier transform of the so-called reduced interference function $i(k)$ defined as

$$i(k) = \frac{I(k) - N\langle f^2 \rangle}{N\langle f \rangle^2} \tag{2}$$

where N is the total number of atoms in the selected volume of the sample. The abbreviations used in equation (2) are

$$\langle f \rangle^2 = \frac{1}{N^2}\left(\sum_i N_i f_i\right)^2 \qquad \text{and} \qquad \langle f^2 \rangle = \frac{1}{N}\sum_i N_i f_i^2$$

where $N = \sum_i N_i$ and N_i is the number of atoms of type i with scattering factor f_i.

Following Cockayne and McKenzie [1], the measured scattering intensity is given by

$$I(k) = N\langle f^2 \rangle + N\langle f \rangle^2 \int_0^\infty 4\pi r[\varrho(r) - \varrho_0]\frac{\sin(kr)}{k}\,\mathrm{d}r \tag{3}$$

where ϱ_0 is the average atom density in the sample and $\varrho(r)$ is the atomic distribution function which represents the number of atoms at a distance r from any given atom.

Hence

$$i(k) = \int_0^\infty 4\pi r [\varrho(r) - \varrho_0] \frac{\sin(kr)}{k}\, \mathrm{d}r. \tag{4}$$

Fourier inversion then yields the pair distribution function (PDF)—also called the reduced density function (RDF)—$g(r)$:

$$g(r) := 4\pi r \left[\varrho(r) - \varrho_0\right] = \frac{2}{\pi} \int_0^\infty k i(k) \sin(kr)\, \mathrm{d}k. \tag{5}$$

The PDF $g(r)$ describes the deviation of the local atomic density $\varrho(r)$ from the mean atomic density ϱ_0. The amplitude of the PDF for a specific distance r corresponds to the frequency of these interatomic distances r in the sample.

3.2. Multilayered films

Equation (4) is based on the assumption that there is no preferred orientation in the sample, so the general expression $\varrho(\vec{r})$ can be written as $\varrho(r)$ and the following averaging over the solid angle can be carried out [2]:

$$\int \left[\varrho(\vec{r}) - \varrho_0\right] \exp(\mathrm{i}\vec{k} \cdot \vec{r})\, \mathrm{d}\vec{r} = \int 4\pi r \left[\varrho(r) - \varrho_0\right] \frac{\sin(kr)}{k}\, \mathrm{d}r. \tag{6}$$

In the case of multilayered films there is a direction in which modulation takes place—in the following this direction is referred to as the z-direction—so the averaging of equation (6) is not allowed and

$$i(\vec{k}) = \int_{-\infty}^\infty \left[\varrho(\vec{r}) - \varrho_0\right] \exp(\mathrm{i}\vec{k} \cdot \vec{r})\, \mathrm{d}\vec{r}. \tag{7}$$

To get the desired information on the inner boundaries as described above, it is necessary to detect the atomic distribution parallel to the specimen's x–y plane. The $k_z = 0$ plane in reciprocal space contains exactly this information. This is the well known condition which is used when working with a Buergers precession camera in x-ray crystallography. Using high-energy electron diffraction in a 300 kV TEM allows—because of the large wave vector—a selective detection of the $(k_x, k_y, [k_z = 0])$ plane in reciprocal space if the multilayer film plane is orientated perpendicular to the electron beam. Then, in cartesian coordinates

$$i(k_x, k_y, 0) = \int_{-\infty}^\infty \int_{-\infty}^\infty \left[\mathcal{P}(x, y) - \varrho_0\right] \exp(\mathrm{i}k_x x)\, \mathrm{d}x\ \exp(\mathrm{i}k_y y)\, \mathrm{d}y \tag{8}$$

where we find—averaged along the z-direction—$\mathcal{P}(x, y)$ as the (local) particle density in the direction of $\vec{r} = (x, y)$ in the distance $|\vec{r}| = \sqrt{(x^2 + y^2)}$ relative to an arbitrary atom of the sample.

The inversion of the Fourier transform then gives the two-dimensional PDF:

$$\mathcal{P}(x, y) - \varrho_0 = \frac{1}{2\pi} \int_{-\infty}^\infty \int_{-\infty}^\infty i(k_x, k_y) \exp(-\mathrm{i}k_x x)\, \mathrm{d}k_x\ \exp(-\mathrm{i}k_y y)\, \mathrm{d}k_y =: g^{(2)}(x, y). \tag{9}$$

The PDFs obtained from the reduced diffraction intensities $i(k_x, k_y)$ contain the information on the atomic short-range order parallel to the film plane and therefore parallel to the inner boundaries of the multilayers. This allows the proposed detection of interface interdiffusion.

4. Experimental requirements and procedure

As stated above, the scattering intensity of the $k_z = 0$ plane has to be detected. Therefore the specimen has to be orientated precisely perpendicular to the electron beam. In general, this is only possible for single-crystalline material. The method presented here is, however, for non-epitaxially grown multilayer films consisting of very thin single layers with amorphous-to-polycrystalline structure. Diffraction images from these samples show a more or less diffuse ring pattern which does not allow the necessary orientation.

4.1. Substrates

A very good way to solve this problem is by the use of silicon nitride membranes as substrates. These substrates are produced using a silicon wafer, coated with a thin Si_3N_4 film on both sides. From the back the silicon is chemically etched after photolithographically structuring the silicon nitride film. The etching stops at the Si_3N_4 film at the front, where in the case of the substrates used, 100 μm × 100 μm wide and 25 nm thick Si_3N_4 membranes remain (figure 2). Along the sides of these membranes the adjacent single-crystalline silicon is thin enough to get a spot diffraction pattern which enables an exact orientation of the substrate—and therefore also of the multilayer film on these substrates—perpendicular to the electron beam. Beyond that, the spot diffraction pattern from the silicon (figure 3) enables a precise calibration of the axes in reciprocal space which is very important, because the calibration of the real-space axes of the PDFs depends on them. A further valuable advantage in the use of these substrates is the fact that no preparation has to be done; in particular, the specimen is not removed from the substrate. Therefore no damage or alteration of the samples can take place.
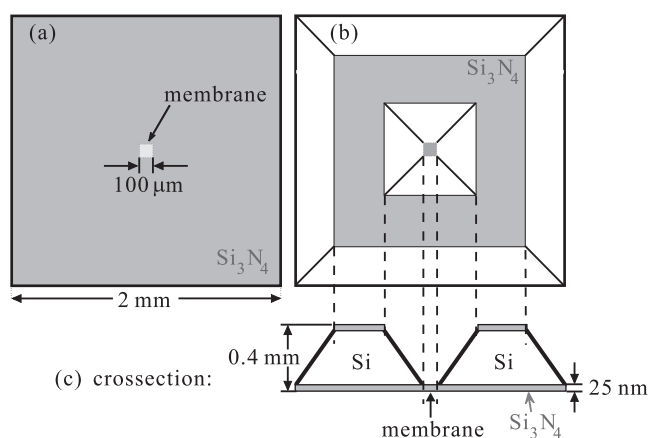

Figure 2. With the use of these silicon nitride membrane substrates, no further preparation has to be done.

4.2. Reciprocal lattice

To be able to distinguish between the different atomic distances it is necessary to achieve a sufficient radial resolution of the PDFs. Due to the Fourier transform, the radial resolution Δr is inversely proportional to the length of the scattering vector k_{max} up to which the scattered intensity is measured. In the case of a multilayered specimen one has to take care of how far the scattered intensity can or should be measured maximally—until the Ewald sphere and thus
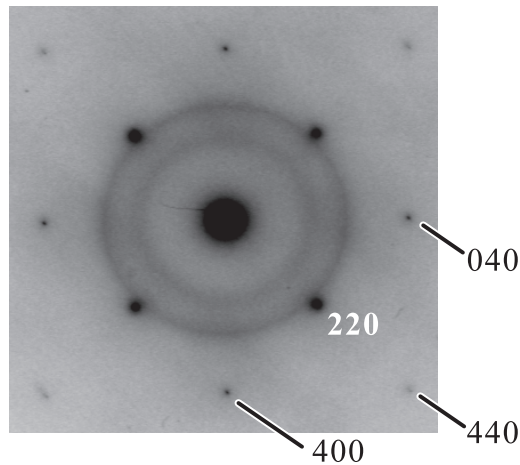
Figure 3. The diffraction pattern of the silicon from the edge of the membrane allows both exact orientation of the specimen and calibration of the axes in reciprocal space.

the scattering vector deviates significantly from the condition $k_z = 0$. Therefore it is necessary to consider the reciprocal lattice of such films [3]: since the structure of the single layers is in the range from amorphous to polycrystalline, the reciprocal structure basically consists of more or less blurred or broadened concentric spheres. A two-dimensional section through the centre of such a Debye–Scherrer ring structure is shown in figure 5(a), later.

Simplified, i.e. ignoring the different lattice constants or atomic diameters, the modulation caused by the alternating deposition of two different materials corresponds as regards the amplitude of scattering to the multiplication of the scattering potential of a homogeneous specimen with a periodic rectangle function like the one shown in figure 4(a). In reciprocal space this corresponds to the convolution of the concentric sphere structure described above
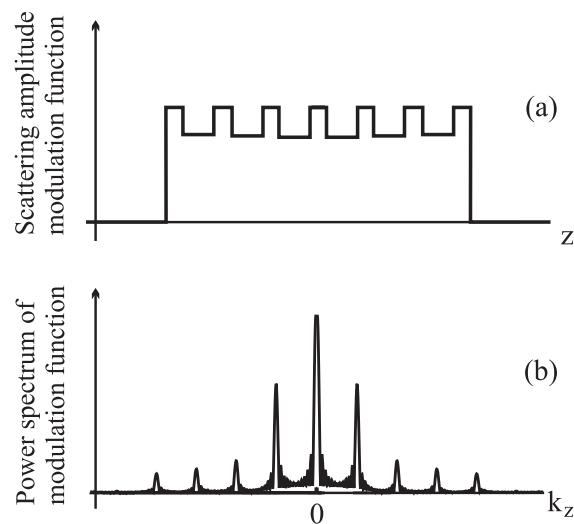

Figure 4. The periodic modulation function (a) and its power spectrum (b).

(figure 5(a)) with the Fourier transform of the rectangle function (figures 4(b), 5(b)). Figure 5(c) shows schematically a calculated cross section from the result of this convolution, containing the k_z-axis. Rotated around the k_z-axis this gives the reciprocal 'lattice' of a multilayered film consisting of polycrystalline layers. Clear to see are the so-called satellite peaks of the central spot along the k_z-axis. Each of these satellites is surrounded by a complete sphere structure.
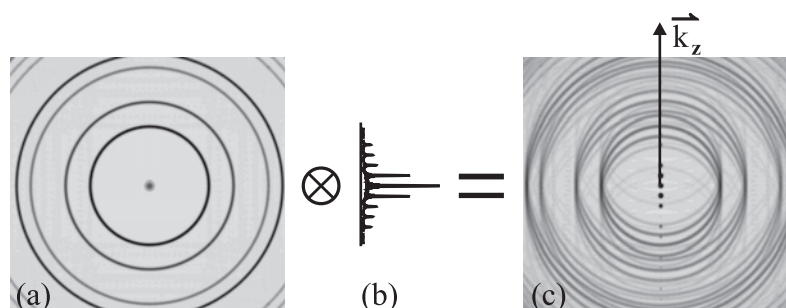

Figure 5. The convolution ($\otimes$) of a Debye–Scherrer-like ring pattern (a) with the power spectrum (b) of the modulation function gives a schematic image of the reciprocal lattice of a multilayer structure (c).

As the diffraction pattern corresponds to the section of the Ewald sphere with the reciprocal lattice, figure 6 again shows how important it is to have the specimen orientated precisely perpendicular to the electron beam. Otherwise the diffraction pattern is disturbed by the multilayer modulation and the PDF calculated from it is of no use at all. Too great a deviation of the Ewald sphere from the $k_z = 0$ plane leads to the same problem. As can be seen from figure 6, a small deviation of the Ewald sphere from the $k_z = 0$ plane is tolerable, as long as
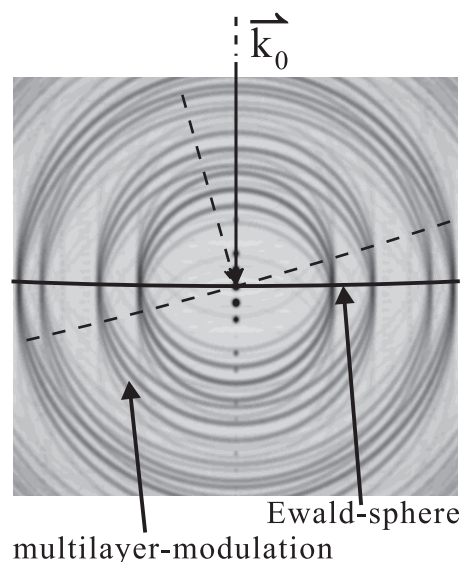

Figure 6. Precise specimen orientation is necessary to avoid modulation contributions to the diffraction pattern. Solid line: the Ewald sphere orientated to cut through unmodulated reciprocal lattice. Dashed line: the Ewald sphere in the case of misorientation.

it does not intersect the modulation. This is necessary because the maximum length k_{max} of the scattering vector $\vec{k}$ up to which the scattered intensity can be measured gives the radial resolution Δr of the PDFs. A maximum scattering vector length k_{max} of about a tenth of the length of the electron wave vector $\vec{k}_0$ is reasonable. In the case of 300 keV electrons, $k_0 = 3192$ nm^{-1}, so $k_{max} \approx 320$ nm^{-1}.

With respect to the two-dimensional Fourier transform for the PDF calculation, the radial resolution Δr of the PDFs—determined by the Airy distribution—is

$$\Delta r = 1.22 \times 2\pi/k_{max} = 0.024 \text{ nm}.$$

4.3. Experimental application

The experiments were carried out in a conventional transmission electron microscope (Philips CM30) at the maximum electron energy of 300 keV. The diffraction patterns were recorded with a Gatan model 679 slow-scan CCD camera.

4.3.1. Data collection.
In order to get intensity data with a sufficient signal-to-noise ratio, a series of images at increasing distance from the centre of the diffraction pattern have to be recorded with increasing integration time. Since no cylindrical symmetry of the distribution of the atomic pairs in the specimen is to be assumed, the scattering intensity is measured two dimensionally and evaluated two dimensionally according to equation (9). This has, compared to the usual measurement of a one-dimensional radial linescan, the additional advantage that all of the information of the diffraction pattern is used, which gives very reliable PDFs which are strongly reduced in noise. As the PDF calculation is based on the kinematical theory of scattering, the measured intensities should not contain contributions from inelastic and multiple scattering. These contributions can be reduced by using high-energy electrons (300 keV) and thin specimens (less than 50 nm). Especially for the calculation of coordination numbers, one has to take care of dynamical scattering effects [4], but this is not part of this work.

4.3.2. Data presentation.
Despite real two-dimensional PDFs having been calculated, it is reasonable to display only radial linescans of them. The reason for this is that it is very difficult to find a suitable presentation for the two-dimensional data which shows the details of the PDF as clearly as these can be seen from the contours of a linescan.

4.3.3. Results.
We shall demonstrate the results possible with the method presented for a terbium/iron multilayer film. Rare-earth/transition-metal films are used as magneto-optical storage media, at present mainly in the form of alloy films. If the same materials are arranged in a multilayer stack, it is expected that on the one hand the magnetic properties of such a film could be intentionally modified and on the other hand the origins of these properties could be better understood [5]. Thereto, especial attention has to be paid to the interface quality. The utility of pair distribution functions for this purpose can be demonstrated by the comparison of a multilayer film with an alloy.

The PDF of an alloy film consisting of 68 atomic per cent (at.%) iron and 32 at.% terbium ($Fe_{68}Tb_{32}$) has been determined in an earlier work by Tewes *et al* [6]. The multilayer film consists of 18 periods of alternating layers of 0.8 nm iron and 1.5 nm terbium ([Fe 0.8/Tb 1.5]$_{18}$). The structure of both films is amorphous rather than polycrystalline since there are only a few blurred rings in the diffraction patterns. Calculated from the layer thicknesses and the atomic density of the bulk materials, the overall composition of the multilayer is 65 at.% Fe and 35 at.% Tb.

Figure 7 shows the PDFs from these two specimens, which have about the same overall composition. The most obvious difference between the PDFs of the films [Fe 0.8/Tb 1.5]$_{18}$ and Fe$_{68}$Tb$_{32}$ is the missing FeTb nearest-neighbour peak in the multilayer PDF. This means that there are hardly any Fe–Tb pairs parallel to the film plane. Therefore, there is almost no intermixing at the interfaces, although the film is not grown epitaxially and the thickness of the single layers is only less than four to five times the atomic diameter of the elements. Further, there is a clear TbTb peak in the multilayer PDF due to the undisturbed Tb layers, whereas the alloy PDF shows no TbTb nearest neighbours. This is caused by the higher percentage of iron compared to terbium in the sample, which decreases the probability of forming TbTb pairs in the alloy film. In conclusion, the comparison shows that the multilayer film formed sharp inner boundaries though the single layers are rather thin. The peaks at $r > 0.4$ nm correspond to larger interatomic distances. Their amplitudes are not so easy to interpret because they are the result of a superposition of different atomic distances (like those for FeFe: 0.476 nm, 0.496 nm; and TbTb: 0.504 nm). The Fe–Fe, Fe–Tb and Tb–Tb distances indicated in figure 7 show only the nearest-neighbour distances where no such superposition of different peaks within the radial resolution ($\Delta r = 0.024$ nm) appears. This allows a direct interpretation of the PDFs without any prior knowledge of the expected results. However, it is helpful to know the nearest-neighbour distances for clear identification of the peaks or to see whether there is a peak missing—like the FeTb peak in the multilayer PDF, indicating that there is (nearly) no intermixing.
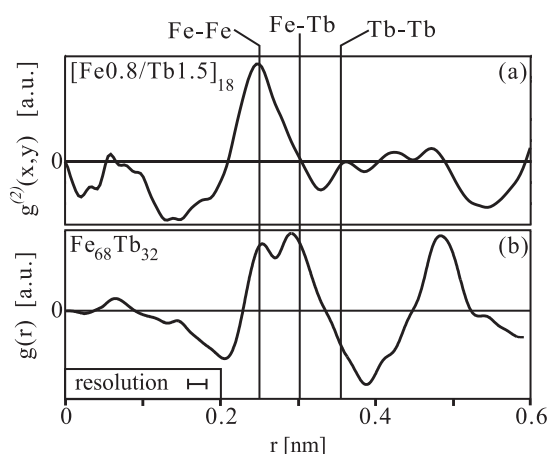

Figure 7. The comparison of the pair distribution function of a multilayer film (a) and an amorphous alloy film (b) of about the same overall composition shows that the multilayer film formed sharp inner boundaries because there is no FeTb nearest-neighbour peak in the multilayer PDF (a). Only the three different nearest-neighbour peaks are indicated.

4.3.4. Sensitivity of the method. The comparison of the multilayer and the alloy film (figure 7) shows the sensitivity of the PDF analysis. In the multilayer film the thickness of the iron layers is 0.8 nm. This is 3.2 times the FeFe nearest-neighbour distance of 0.248 nm or 2.8 times the lattice constant 0.287 nm of bcc iron. The terbium layers are 1.5 nm thick, which is 4.3 times the TbTb nearest-neighbour distance of 0.352 nm. The multilayer stack consists of 36 layers: 18 periods of alternating layers of iron and terbium, so there are 35 interfaces. The films are grown by magnetron sputtering. In view of the diffraction pattern consisting only of a few blurred rings, the structure of the film can be characterized as amorphous. Looking

at the different atomic diameters of Fe and Tb (which are the same as the nearest-neighbour distances), one could well assume that in the case of amorphous layers at least about one atomic layer at each interface can be regarded as an alloy of both elements. This would result in a large number of FeTb pairs parallel to the interface and, compared to the number of FeFe and TbTb pairs in the remaining really thin undisturbed single layers, the PDF would show a clear FeTb peak. The PDF in figure 7(a) shows only a slight broadening of the right-hand side of the FeFe peak. Having in mind the really thin single layers, this indicates that there can be almost no intermixing of Fe and Tb.

5. Summary

We have shown that the calculation of pair distribution functions from high-energy transmission electron diffraction intensities is a very interesting method for structure investigation of multi-layered thin films. The theory, the principle and the requirements have been described.

Using the suggested silicon nitride membrane substrates allows both the exact calibration of the distance axis of the PDFs and the application of the method without any preparation; thus no structural alteration of the samples can take place. The pair distribution functions are easily interpretable, at least at the nearest-neighbour distances. The example shows that the method allows a very sensitive detection of intermixing at the interfaces of multilayers and is especially suitable for multilayered films consisting of very thin layers.

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