J. Phys.: Condens. Matter **2** (1990) 4111–4118. Printed in the UK

Finite size effects in crystalline/amorphous multilayers

D Neerinck†, H Vanderstraeten†, L Stockman†, J-P Locquet†§, Y Bruynseraede† and Ivan K Schuller‡

† Laboratorium voor Vaste Stof—Fysika en Magnetisme, Katholieke Universiteit Leuven, B-3030 Leuven, Belgium

‡ Physics Department-B019, University of California at San Diego, La Jolla, California 92093, USA

Received 1 November 1989, in final form 22 January 1990

Abstract. Extended x-ray diffraction experiments have been used to investigate the structure of Pb/Ge multilayers with a small (<15) number of bilayers. The detailed finite size structure in the x-ray diffraction profiles indicates that the multilayers are of very high quality. We present a one-dimensional kinematical calculation for these diffraction profiles, including continuous and discrete random fluctuations in layer thickness. The introduction of both continuous and discrete fluctuations causes a decrease in the number of secondary single-layer 'finite size' maxima in the high angle region, in agreement with the experimental results. No quantitative agreement is reached for the low angle region, which shows more finite size structure than predicted by the fluctuations deduced from the high angle region.

1. Introduction

In recent years, the structural analysis of multilayers has received considerable attention [1]. The details of the structure of the individual components and the interface are often crucial for the understanding of the superconducting [2] and magnetic [3] properties of the multilayers. It has also been shown that the structure of the interface plays a dominant role in the melting [4] or crystallisation [5] behaviour of one of the components. Among various methods of characterising these composite materials, x-ray diffraction techniques are most often used. Since x-ray intensity profiles cannot be directly inverted to provide structural information, models have to be developed to calculate the diffracted intensity which is then compared to the experimental result.

Here, we present θ–2θ x-ray diffraction profiles of Pb/Ge multilayers with a small number of bilayers, typically less than 15, in order to ascertain the effect of the finite size. All profiles reveal a very detailed finite size structure in the low angle region originating from both the crystalline component and the superlattice, whereas in the high angle region only the finite size effect of the crystalline component can be observed. These finite size effects seem to be very sensitive to the presence of interfacial disorder, and are expected to serve as a very accurate check for the correctness of models. A new model allowing continuous thickness fluctuations in the non-scattering amorphous layer and discrete thickness fluctuations in steps of one interlayer spacing in the scattering

§ Present address: IBM Research Division, Säumerstrasse 4, CH 8803 Rüschlikon, Switzerland.

0953-8984/90/184111 + 08 $03.50

crystalline layer, is introduced. This way, the nature of the distribution of thickness fluctuations of the layers is inherent to their state of crystallinity. This model reproduces the number of secondary finite size maxima in the high angle region, and causes a disappearance of the finite size effects in the low angle region, in qualitative agreement with experiments. However, none of the models available to date is able to explain quantitatively both the high angle and low angle regions of the diffraction profiles.

2. Experimental procedure

Pb/Ge multilayers were prepared in a load-locked molecular beam epitaxy apparatus equipped with two electron beam guns, with evaporation rates (7 Å s^{-1} for Pb, 5 Å s^{-1} for Ge) controlled using a quadrupole mass spectrometer in feedback mode. The liquid nitrogen cooled sapphire substrate was exposed to the evaporant at a pressure smaller than 1×10^{-8} Torr during evaporation [6]. The final sample was covered with an extra Ge layer to prevent Pb oxidation.

θ–2θ x-ray diffractometer scans were performed on a computer controlled 12 kW DII Max Rigaku rotating anode diffractometer using Cu Kα radiation, filtered with a flat pyrolytic monochromator. As is well known, the position of the sample with respect to the circumference of the focal circle is very critical in the low angle region (typically below 5° to 6°, 2θ) [7], since slight misalignments may cause serious shifts and deformation of the low angle peaks. To avoid this, a goniometer head with two extra degrees of freedom was used to microposition the surface of the sample with respect to the focal circle, and to adjust the inclination of the sample with respect to the scattering plane.

3. Experimental results

The periodicity of the multilayered structure, Λ, was determined from the positions of the low angle peaks using Bragg's law

$$\Lambda = \frac{(m-n)\lambda}{2(\sin\theta_m - \sin\theta_n)} \tag{1}$$

where m and n are the orders of the peaks, and λ is the wavelength of the x-rays for Cu Kα. Figure 1 shows the low angle x-ray diffraction profile of a [Pb (45.4 Å)/Ge (29.5 Å)]$_5$ sample. The subscript indicates the number of bilayers. The profile shows up to the twelfth-order Bragg peaks, with three binary fringes between superstructure peaks, reproduced up to the ninth-order peak. This implies that the layered crystalline/amorphous structure is very well developed. The minima indicated by the arrows in figure 1 arise from the finite size minima of the crystalline component and imply a Pb thickness of 45.4 Å [8].

The high angle diffraction pattern of the multilayer discussed above shows a finite size structure around the Pb(111) direction (figure 2), with a coherence length approximately equal to the thickness of one Pb layer:

$$\xi_\perp = \frac{0.9\lambda}{\Delta(2\theta)\cos\theta_0} = 46.7\ \text{Å} \tag{2}$$

where θ_0 is the position of the diffraction maximum and $\Delta(2\theta)$ is the full width at half maximum.

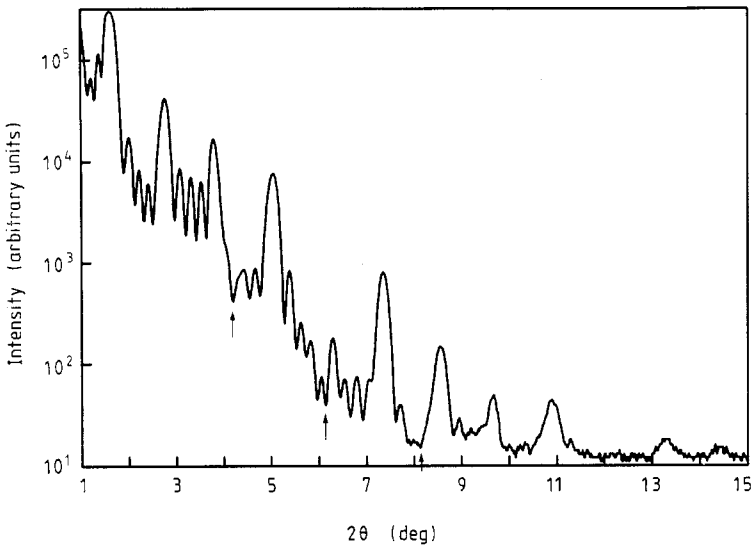

Figure 1. The small angle x-ray diffraction profile of a [Pb (45.4 Å)/Ge (29.5 Å)]$_5$ multilayer. The subscript indicates the number of bilayers. The intensity profile is taken with a $\frac{1}{8}°$ divergence slit and a 0.15 receiving slit.

4. Discussion

Because in x-ray diffraction the phase information is lost, real space models have to be developed and their calculated intensities compared with experiment. The simplest model is the step model, assuming a perfect multilayer consisting of M bilayers, each bilayer being composed of a perfectly amorphous part of width a and scattering power zero, and a perfectly crystalline part, with N layers of atoms, separated by a distance d. For this configuration, the diffracted intensity becomes

$$I(q) = |F(q)|^2 = f(q)^2 \frac{\sin^2(Nqd/2)\sin^2(Mq\Lambda/2)}{\sin^2(qd/2)\sin^2(q\Lambda/2)} = f(q)^2 I_1(q) I_2(q) \tag{3}$$

where $\Lambda = a + Nd$ is the modulation wavelength and $q = (4\pi/\lambda)\sin\theta$ is the scattering vector.

The low angle experimental curve of figure 1 exhibits all the qualitative features of the step model. It shows a large number (twelve) of multilayer diffraction peaks, with three secondary maxima caused by the limited number (five) of bilayers, as predicted by the factor $I_2(q)$. The minima indicated by arrows in figure 1 originate from the minima of the single-Pb-layer envelope function $I_1(q)$. Since the position of these minima is determined by Nd, the individual Pb layer thickness ($=Nd$) can be deduced very accurately from the low angle diffraction profile. This is the first time that the layer thickness of one of the components has been determined from the low angle region. The low angle profile is found to correspond very well to the simple step model, provided the multilayer is of high quality and has a limited number of bilayers. The high angle diffraction profile in figure 2, however, is in strong disagreement with the step model. There is no trace of any superstructure, only one Pb layer scatters coherently and therefore the step model gives incorrect results at high angles. The lack of superstructure in the high angle region

gave rise to the development of several models, all based on the presence of roughness, located at the interface. Sevenhans *et al* [9], introduced a continuous Gaussian variation of the thickness of the non-scattering amorphous layer. A continuous fluctuation larger than 2 Å was found to wash out all high angle superlattice structure. On the other hand, Clemens and Gay [10] showed that a discrete Gaussian variation of the non-scattering amorphous layer only slightly reduces the intensity of the superlattice peaks in the high angle region and washes out the multilayer secondary maxima. The application of only a continuous type of disorder (equation 5 of [9]) does not sufficiently reduce the number of finite size maxima in the high angle diffraction profile.

We present for the first time a one-dimensional kinematical structure factor calculation for crystalline/amorphous multilayers including *both* discrete fluctuations on the crystalline layer and continuous fluctuations on the amorphous layer as an attempt to explain the experimental high angle diffraction profile. The structure factor for a multilayer consisting of M bilayers where each bilayer is formed by N_j crystalline planes with atomic scattering power f and interplanar spacing d, and an amorphous layer of thickness a_j, is given by

$$F(q) = f\Big(\sum_{n=0}^{N_1-1} \exp(\mathrm{i}qnd) + \exp(\mathrm{i}q(N_1 d + a_1)) \sum_{n=0}^{N_2-1} \exp(\mathrm{i}qnd) + \cdots + \exp(\mathrm{i}q(N_1 d + \cdots + N_{M-1} d + a_1 + \cdots + a_{M-1})) \sum_{n=0}^{N_M-1} \exp(\mathrm{i}qnd)\Big). \quad (4)$$

The scattering intensity $I(q)$ is given by

$$I(q) = F(q)F^*(q) = f^2 \sum_{k=1}^{M} \frac{\sin^2(N_k qd/2)}{\sin^2(qd/2)} + 2f^2 \sum_{k=1}^{M-1} \sum_{l=k+1}^{M} \frac{\sin(N_k qd/2)}{\sin(qd/2)} \frac{\sin(N_l qd/2)}{\sin(qd/2)} \times \mathrm{Re}\Big[-\mathrm{i}q\Big(\sum_{j=k+1}^{l-1} N_j d + \sum_{j=k}^{l-1} a_j + (N_k + N_l)d/2\Big)\Big]. \quad (5)$$

The amorphous layer thicknesses a_j are assumed to have a continuous Gaussian distribution around $\bar{a}$ of width c_c^{-1} and the N_j are distributed on a discrete Gaussian around $\bar{N}$ with width c_d^{-1}:

$$a_j \simeq (c_c/\sqrt{\pi}) \exp(-c_c^2(a_j - \bar{a})^2) \qquad N_j \simeq (c_d/\sqrt{\pi}) \exp(-c_d^2(N_j - \bar{N})^2).$$

Averaging $I(q)$ over all real a_j values and all integer N_j values gives the average diffracted intensity

$$\langle I(q)\rangle = f^2 \frac{M}{\sin^2(qd/2)} [S_{\bar{N}}^2(1 - 2S_{\bar{N}}^2) + S_{\bar{N}}^2] + f^2 2 \sum_{i=1}^{M} \frac{M-i}{\sin^2(qd/2)} [(C_{\bar{N}}^2)^2 S_{\bar{N}}^2 \cos(\mathrm{i}q\Lambda) - (S_{\bar{N}}^2)^2 C_{\bar{N}}^2 \cos(\mathrm{i}q\Lambda) - 2S_{\bar{N}}^2 C_{\bar{N}}^2 C_{\bar{N}} S_{\bar{N}} \sin(\mathrm{i}q\Lambda)] \Delta_{\bar{N}}^{i-1} \exp(-\mathrm{i}q^2 c_c^{-2}/4) \quad (6)$$

with

$$1/K = \sum_{N=-\infty}^{+\infty} \exp(-N^2 c_d^2)$$

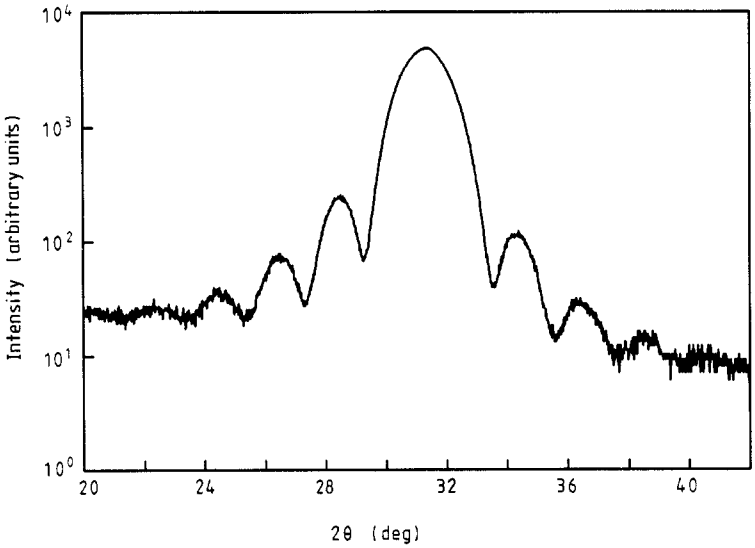

Figure 2. The high angle x-ray diffraction profile of a [Pb (45.4 Å)/Ge (29.5 Å)]$_5$ multilayer. The subscript indicates the number of bilayers. The intensity profile is taken with a $\frac{1}{8}°$ divergence slit and a 0.15 receiving slit.

$$S_N^2 = \sum_{N=-\infty}^{+\infty} K \exp(-N^2 c_d^2) \sin^2(qNd/2)$$

$$C_N^2 = \sum_{N=-\infty}^{+\infty} K \exp(-N^2 c_d^2) \cos^2(qNd/2)$$

$$S_{\bar{N}} = \sin(q\bar{N}d/2)$$

$$C_{\bar{N}} = \cos(q\bar{N}d/2)$$

$$\Delta_N = \sum_{N=-\infty}^{+\infty} K \exp(-N^2 c_d^2) \cos(qNd)$$

$$\Lambda = \bar{N}d + \bar{a}.$$

We have only included a random type of disorder, excluding systematic changes such as non-integer layers, drift in the preparation process or interdiffusion. Cumulative disorder in the growth direction has been included and surface roughness (in the x–y plane) has only been averaged in an incoherent way.

With c_c^{-1} and c_d^{-1} equal to zero, equation (6) reduces to the step model, whereas for c_c^{-1} and c_d^{-1} tending to infinity, it gives the incoherent scattering intensity from M crystalline layers each consisting of $\bar{N}$ planes. With $c_d^{-1} = 0$, equation (6) reduces to equation (5) of [9].

A discrete distribution on the number of crystalline planes alone does not broaden the high angle multilayer peaks, but leads to a slight reduction in intensity and a disappearance of the secondary multilayer fringes.

A small continuous fluctuation on the amorphous layer thickness, however, broadens the high angle multilayer peaks until the finite size limited, high angle diffraction profile

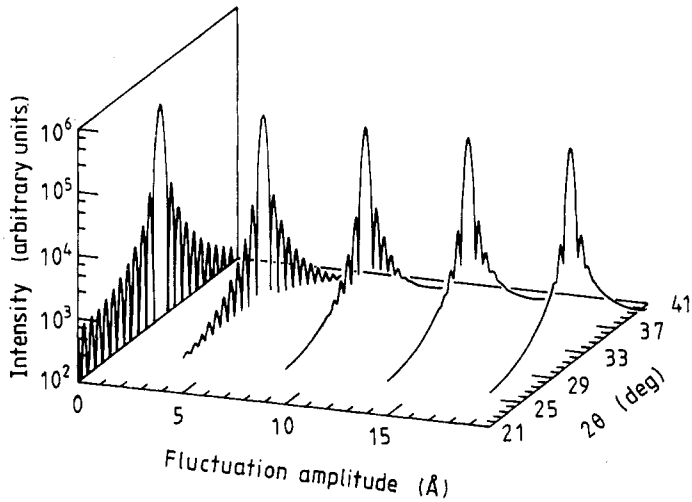

Figure 3. The evolution of the x-ray diffraction profile of a Pb (100 Å)/Ge (60 Å) multilayer as a function of c_d^{-1} using equation (6) when c_c^{-1} = 2.5 Å, M = 15 and d = 2.87 Å.

of a single crystalline layer is reached [9]. Because of this, the high angle region only allows the determination of a lower limit of the amorphous layer thickness fluctuation. For Pb/Ge multilayers, this lower limit for c_c^{-1} is 1.7 Å. This value is independent of the layer thickness, but depends strongly on the crystalline interplanar spacing d. The larger d, the more interfacial disorder needed to destroy all superstructure [11].

Figure 3 shows the effect of discrete disorder on the x-ray diffraction profile of a Pb (100 Å)/Ge (60 Å) multilayer, with a fixed continuous fluctuation of 2.5 Å. Clearly, the introduction of discrete fluctuations in the crystalline layer thickness causes a decrease in the number of finite size maxima. The evolution of the intensity profile can be understood using an intuitive argument. Applying a discrete fluctuation to the Pb layer thicknesses implies that crystalline layers with different thicknesses contribute differently to the total intensity. Since the positions of the 'finite size' secondary peaks depend strongly on the layer thickness, the superposition of the scattering intensities from layers with different thicknesses will tend to smear out these peaks. The width and intensity of the main peak, however, will be much less affected by this type of disorder. It is important to note that only through the simultaneous introduction of both types of fluctuation can the decrease in the single-layer finite size effects at high angles be explained. This is a qualitatively different result from the model of Clemens and Gay [10], who explain the decrease of multilayer finite size effects in terms of discrete fluctuations on a non-scattering layer. Their model is more suitable for crystalline/crystalline multilayers where one of the components is a low scatterer.

Figure 4 shows the best fit to the high angle data of figure 2 using equation (6) with c_d^{-1} = 5.5 Å. This high angle profile is insensitive to the continuous fluctuations above the lower limit. The value of the continuous fluctuations could then be approximated by fitting the low angle region. However, all values of the continuous fluctuations severely suppress the low angle 'finite size' multilayer peaks in disagreement with the experimental data. Clearly this type of model cannot reconcile in detail high and low angle data; however, it is able to explain qualitative features of the data. Because of this, further modifications of the model are necessary, such as including the effect of coherent

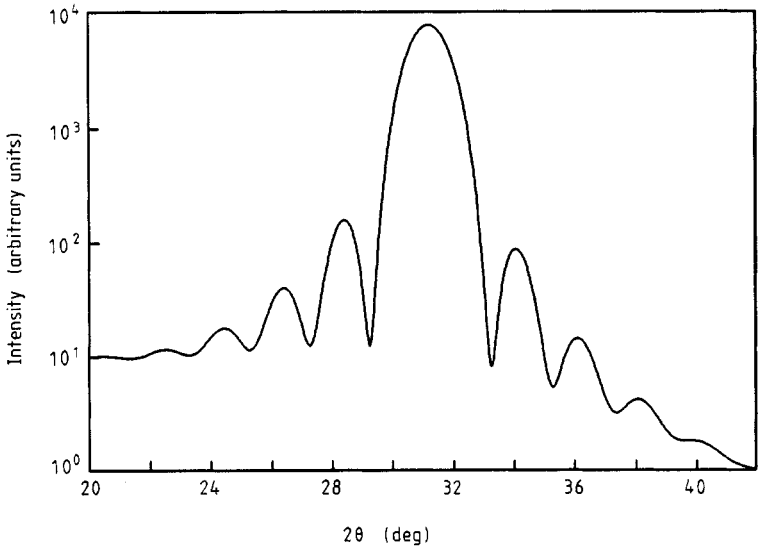

Figure 4. The simulation of x-ray high angle diffraction profile for a [Pb (45.4 Å)/Ge (29.5 Å)]$_5$ multilayer, with $c_c^- = 3$ Å and $c_d^{-1} = 5.5$ Å, as calculated from equation (6), corrected with Debye–Waller and Lorentz polarisation factors.

lateral roughness and a non-integral number of layers, and perhaps the development of new approaches that combine dynamic and kinematic approaches. This type of work is currently under way.

5. Conclusions

We have presented detailed x-ray diffraction profiles of crystalline/amorphous multilayers (Pb/Ge) with a small number of bilayers. The low angle region shows structure, which originates from the finite size of the superstructure and the crystalline component. The high angle region shows a decreased number of single-crystalline-layer finite size maxima. Via a comparison with kinematical model calculations, introducing both continuous and discrete fluctuations in layer thickness, the discrete interfacial roughness can be deduced from the high angle region, and a qualitative agreement for the full diffraction profile may be reached. Quantitative comparison requires further development of the models.

Acknowledgments

We would like to thank H Reynaers for useful discussions and practical advice on x-ray diffraction measurements. This work was supported by the Belgian Inter-University Institute for Nuclear Sciences (IIKW), the Inter-University Attraction Poles (IUAP), the Concerted Action (GOA) Programmes (at KUL) and the US Department of Energy under contract number DE-FG03-87ER45332 (at UCSD). International travel was provided by NATO and the Belgian National Fund for Scientific Research (NFWO). D Neerinck is a research assistant of the NFWO and H Vanderstraeten and J-P Locquet are research fellows of the IIKW.

References

[1] For a recent review see
Dhez P and Weisbuch C (ed) 1988 *Physics, Fabrication and Applications of Multilayered Structures 1988* (New York: Plenum)
[2] Locquet J-P, Neerinck D, Vanderstraeten H, Sevenhans W, Van Haesendonck C, Bruynseraede Y, Homma H and Schuller I K 1987 *Japan. J. Appl. Phys.* **26** 1431
[3] Majkrzak C F, Axe J D and Boni P 1985 *J. Appl. Phys.* **57** 3657
[4] Sevenhans W, Vanderstraeten H, Locquet J-P, Bruynseraede Y, Homma H and Schuller I K 1988 *Multilayers: Synthesis, Properties and Non-Electronic Applications, Materials Research Society Symp. Proc.* vol D103, ed T W Barbee Jr, F Spaepen and L Greer (Pittsburgh, PA: Materials Research Society) p 217
[5] Sevenhans W, Locquet J-P, Bruynseraede Y, Homma H and Schuller I K 1988 *Phys. Scr.* **38** 426
[6] Sevenhans W, Locquet J-P and Bruynseraede Y 1986 *Rev. Sci. Instrum.* **57** 937
[7] *International Tables for X-ray Crystallography* 1967 vol II, ed J S Kasper and K Lonsdale (Birmingham: Kynoch) pp 220–5
[8] McWhan D B 1988 *Synthetic Modulated Structures* ed L L Chang and B C Giessen (New York: Academic) ch 2, p 45
[9] Sevenhans W, Gijs M, Bruynseraede Y, Homma H and Schuller I K 1986 *Phys. Rev.* B **34** 5955
[10] Clemens B M and Gay J G 1987 *Phys. Rev.* B **35** 9337
[11] Locquet J-P, Neerinck D, Sevenhans W, Bruynseraede Y, Homma H and Schuller I K 1988 *Multilayers: Synthesis, Properties and Non-Electronic Applications, Materials Research Society Symp. Proc.* vol D103, ed T W Barbee Jr, F Spaepen and L Greer (Pittsburgh, PA: Materials Research Society) p 211