PHYSICAL REVIEW B VOLUME 34, NUMBER 8 15 OCTOBER 1986

Cumulative disorder and x-ray line broadening in multilayers

W. Sevenhans, M. Gijs, and Y. Bruynseraede
Laboratorium voor Vaste Stof Fysika en Magnetisme, Katholieke Universiteit Leuven, B-3030 Leuven, Belgium

H. Homma and Ivan K. Schuller
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 12 June 1986)

We have measured the high-angle x-ray diffraction from crystalline Pb–amorphous Ge multilayers. The experimental data in conjunction with a model calculation for the fluctuation in amorphous-layer thickness show that this fluctuation is larger than about 5%. A smaller thickness variation implies the existence of high-angle peaks which have not been observed in any amorphous-crystalline multilayers.

The study of x-ray diffraction from multilayers and superlattices has received considerable theoretical and experimental attention.[1-4] For the case of amorphous-crystalline multilayers theoretical predictions imply the existence of *many* high-angle diffraction peaks due to the interference between the crystalline layers. All experiments to date, however, only show the presence of *one* broad peak due to the finite-size-limited *incoherent* scattering by the individual crystalline component. We show here that random variations in the amorphous-layer thickness ("cumulative disorder") can explain these observations. By comparing the theoretical calculations with the experimentally measured spectra from crystalline Pb–amorphous Ge multilayers we are able to set a lower limit on the amount of disorder or thickness variation present.

The structural characterization[1,2] of multilayered superlattices is the fundamental basis for the understanding of their interesting transport and magnetic properties. A variety of models such as the step[2] and the strain model[3] have been proposed. The former assumes an abrupt compositional profile and a uniform atomic spacing for each layer; in the latter model, on the other hand, lattice-spacing variations are assumed due to in-plane coherency strains. These models have been successfully applied to metallic[2,4] as well as semiconducting superlattices.[3]

A more realistic model would require including effects of disorder such as random fluctuation of modulation periodicity (Λ) and roughness at interfaces.[2,5,6] There are two types of disorder in Λ, i.e., noncumulative and cumulative. The latter type of disorder is more common than the former unless the error in Λ is compensated for during sample preparation.[5] We consider here the x-ray scattering from a crystalline-amorphous one-dimensional superlattice; the extension to the crystalline-crystalline case is straightforward.

The scattering amplitude for a multilayer formed by N crystalline layers with scattering power f and interplanar spacing d followed by an amorphous layer (of low scattering power which is set to zero) of thickness a_j is given by

$$A(Q)=\sum_{n=0}^{N-1}\exp(iQnd)f(Q)\left\{1+\exp[iQ(a_1+Nd)]+\exp[iQ(a_1+a_2+2Nd)]+\cdots+\exp\left[iQ\left[\sum_{j=1}^{M-1}a_j+(M-1)Nd\right]\right]\right\}, \tag{1}$$

where M is the number of bilayers in the sample, and Q is the scattering vector assumed to be in the perpendicular direction to the multilayer.

We will concentrate here only on an uncontrollable random type of disorder excluding long-range drifts in the preparation conditions and systematic changes such as those produced by interdiffusion. The type of random variations possible are the following: (a) at a particular point in the x-y plane of the film, the thickness of each amorphous layer might vary around an average value $\bar{a}$; (b) there might be lateral thickness variations ("roughness") along the plane of the film due to substrate imperfections, island growth, lateral diffusion, etc.

The x-ray linewidths will be affected by the disorder in the following ways (assuming for simplicity that the crystalline layer thickness does not vary):[7]

(1) Noncumulative disorder (as is the case for thermal motion[8,9]) in which the position of the layers randomly fluctuates around the mean value $\bar{a}$. As a consequence the position of the Rth layer which appears as the exponent of the Rth term in expression (1) is given by

$$R\bar{a}+RNd+\Delta a_R\ , \tag{2}$$

where Δa_R is the change of the position of layer R from its average position $R\bar{a}+Nd$. In general Δa_R is assumed to be randomly distributed in a Gaussian distribution. This is similar to the treatment of thermal fluctuations and therefore the linewidth is not affected, only the intensity decreases as the effective Debye-Waller coefficient as long as Δa_R is given by a Gaussian distribution.

(2) Cumulative disorder which is possibly the main effect in multilayers.[6,10] In this case, the exponent of the Rth term in expression (1) is given by

$$R\bar{a}+RNd+\sum_{j=1}^{R}\Delta a_j \ . \tag{3}$$

The main difference between formulas (2) and (3) is that in the second case the random fluctuations of one layer affect the fluctuations in the other. This is the main reason why this type of disorder will affect the linewidth and relative intensities considerably.

(3) Surface roughness (incoherent) which should be averaged laterally (x-y) over the sample.

(4) The finite-crystal-size coherence length which also affects the linewidth in a known fashion.

The scattering intensity for perfect crystalline layers is given by

$$I(Q)=A(Q)A^*(Q)=f^2(Q)\frac{\sin^2(NQd/2)}{\sin^2(Qd/2)}\left(M+2\left\{\sum_{j=1}^{M-1}\cos[Q(a_j+Nd)]+\sum_{j=1}^{M-2}\cos[Q(a_j+a_{j+1}+2Nd)]\right.\right.$$
$$\left.+\sum_{j=1}^{M-3}\cos[Q(a_j+a_{j+1}+a_{j+2}+3Nd)]\right.$$
$$\left.\left.+\cdots+\cos\left[Q\left(\sum_{j=1}^{M-1}a_j+(M-1)Nd\right)\right]\right\}\right) . \tag{4}$$

Assuming a Gaussian distribution for the a_j around $\bar{a}$ with a width c^{-1} and averaging the intensity over this distribution,[11,12]

$$I(Q)=\langle A(Q)A^*(Q)\rangle=f^2(Q)\frac{\sin^2(NQd/2)}{\sin^2(Qd/2)}\left[M+2\sum_{j=1}^{M-1}(M-j)\exp(-Q^2j/4c^2)\cos[Qj(Nd+\bar{a})]\right] . \tag{5}$$

For $c^{-1}=0$ formula (5) reduces to the simple expression for a step model.

The effect of the disorder is to give intensities which are *not* Debye-Waller-like. On the other hand if the averaging is performed on the scattering amplitudes[10,13]

$$I(Q)=\langle A(Q)\rangle\langle A^*(Q)\rangle$$
$$=f^2(Q)\frac{\sin^2(NQd/2)}{\sin^2(Qd/2)}\left[\exp[(M-1)x]\frac{\sinh(Mx)}{\sinh x}\right.$$
$$+2\sum_{j=1}^{M'}\cos(2jy)\left(\exp[(M-1-j)x]\frac{\sinh[(M-j)x]}{\sinh x}-\exp[(j-1)x]\frac{\sinh(jx)}{\sinh x}\right)$$
$$\left.+2\sum_{j=0}^{M'}\cos[(2j+1)y]\left(\exp[(M-1-j)x]\frac{\sinh[(M-j-1)x]}{\sinh x}-\exp(jx)\frac{\sinh(jx)}{\sinh x}\right)\right] ,$$

with

$$\begin{cases}x=-Q^2/4c^2,\\ y=Q(Nd+\bar{a}),\end{cases} \tag{6}$$

and

$$M'=\begin{cases}(M-1)\text{ for odd }M\ ,\\ M/2\text{ for even }M\ .\end{cases}$$

At this point we should remark that the incoherent diffuse scattering (i.e., the difference between the average of the scattering function squared and the average of the intensities) is quite large at high angles so care should be exercised if a comparison is to be made between low- and high-angle intensities. Of course, dynamical effects are also present which further complicate this comparison.

Figure 1 shows the effect of cumulative disorder in the amorphous layer on the high-angle diffraction peaks as calculated using formula (5). A perfect multilayer with no variation in the thickness of the amorphous layer ($c^{-1}=0$) shows well-developed superlattice peaks at *high angles*. As the disorder increases the lines broaden and merge together. When the disorder changes from $c^{-1}=0.05\bar{a}$ to $c^{-1}=0.07\bar{a}$ all trace of superlattice modulation peaks disappears and the high-angle diffraction spectrum is merely given by the finite-crystal-size-limited diffraction peak from the crystalline Pb component.

In order to check some of these ideas we have performed diffraction experiments on a variety of crystalline Pb–amorphous Ge multilayers.[14] The Pb-Ge multilayers were prepared on liquid-N_2-cooled sapphire substrates in a molecular-beam-epitaxy apparatus (1×10^{-8} Torr during evaporation) using a rate-control technique which employs a quadrupole mass spectrometer in a feedback mode. This technique allows a control which is better than 5% on the rate with a time constant of 3 msec, as has been described earlier.[14] The starting materials were 99.999%-pure Pb and 99.9999%-pure Ge. The x-ray measurements were performed on a 2-kW DMax II Rigaku diffractometer equipped with a variable-temperature stage and low-angle capabilities. The high quality of the layered structure is proven by the existence of up to 13 low-angle multilayer peaks and by the fact that the even-order peak intensities

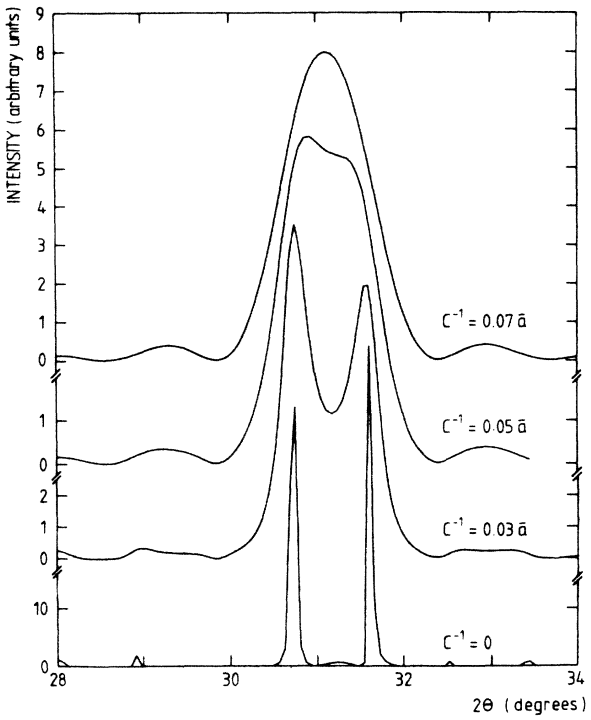

FIG. 1. Simulated high-angle θ–2θ x-ray spectra for different values of thickness distribution width c^{-1} for $d = 2.87$ Å, $N = 25$, $\bar{a} = 30$ Å, and $M = 13$.

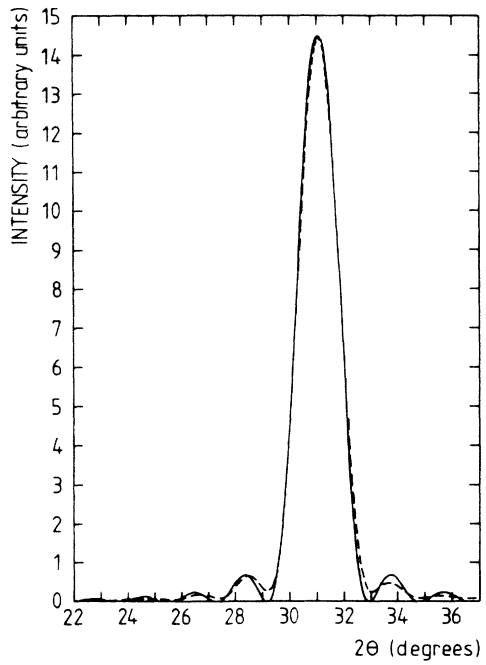

FIG. 2. Experimentally measured θ–2θ x-ray spectrum (dashed line) for a Pb (49 Å)–(Ge 59 Å) multilayer fitted to Eq. (5) with $c^{-1} = 0.04\bar{a}$ (solid line).

are of smaller amplitude than the odd-order ones in equal-thickness multilayers. Independent transmission electron microscopy and electron diffraction measurements on transverse cross sections prepared using ion milling, also showed distinct well-separated layers. The details of the temperature behavior of the x-ray diffraction and electron microscopy results will be the subject of a future publication. The amount of roughness, however, is very hard to quantify from such electron microscopy measurements.

Figure 2 shows the experimentally measured diffraction data from a Pb (49 Å)–Ge (59 Å) multilayer with $M = 51$. The diffraction data at high angles show one broad peak centered at the Pb (111) position. Measurements for a variety of thicknesses of the Pb films confirmed that the linewidth of this peak is given by the finite size of the Pb layer. This figure also shows a fit to Eq. (5) with $c^{-1} = 2.0$ Å, which corresponds to a disorder of about 4%. We have performed additional Debye-Scherrer diffraction measurements from a sample peeled off the substrate and confirmed that only crystalline Pb is present, without any traces of oxides or crystalline Ge phases.

Earlier measurements on Cr-C, Ni-C, W-C,[15,16] Fe-Ge,[17] and Nb-Ge (Ref. 18) (crystalline-amorphous) multilayers also show the existence of one broad peak due to the finite size of the crystalline component. Therefore, in all these multilayers the cumulative disorder is larger than about 5% of the layer thickness. The conclusions drawn here are equivalent to the statement that the individual Pb layers scatter incoherently[4,17,18] with the additional quantitative conclusion regarding the amount of disorder required to obtain incoherent scattering. Moreover, if the amount of cumulative disorder is assumed to be the same for all crystallites in the x-y plane the conclusions will not change. This is so because lateral (x-y) plane roughness adds incoherently (for scattering Q vector in the z direction) and so only the total intensity of the peaks changes, not their relative intensities or shapes. We should remark at this point that generally the rate control in all preparation methods available to date (power control for sputtering, quartz crystal, mass spectrometry, electron impact emission spectroscopy for electron beam gun evaporators, etc.) is larger or of the order of 5%. The error in the rate control, therefore, is sufficient to wipe out higher-order multilayer peaks. Of course, growth phenomena, such as diffusion, island growth, etc., will also contribute to further smear out the multilayer peaks.

We would like to thank J.-P. Locquet, L. Mertens, Y. Lepetre, D. B. McWhan, C. P. Flynn, and A. J. Eades for useful discussions. This work was supported by the Belgian Interuniversity Institute for Nuclear Sciences, the U. S. Department of Energy-BES-Materials Sciences under Contract No. W-31-109-ENG-38, and U. S. Office of Naval Research Contract No. N0014-83-F-0031. One of us (M.G.) was partially supported by the Belgian Interuniversitair Instituut voor Kernwetenschappen. International travel was supported by NATO Grant No. RG 85/0695.

[1]For an early review, see D. de Fontaine, in *Atomic Arrangements Studied by X-Ray Diffraction,* edited by J. B. Cohen and J. E. Hilliard (Gordon and Breach, New York, 1966).

[2]For a recent review, see D. B. McWhan, in *Synthetic Modulated Structure Materials,* edited by L. L. Chang and B. C. Geissen (Academic, New York, 1985), Chap. 3.

[3]A. Segmüller and A. E. Blakeslee, J. Appl. Cryst. **6**, 19 (1973).

[4]I. K. Schuller, Phys. Rev. Lett. **44**, 1597 (1980).

[5]E. Spiller and A. E. Rosenbluth, Proc. SPIE Int. Soc. Opt. Eng. **563**, 221 (1985).

[6]J. M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1975), Chap. 7.

[7]Since the crystalline layers can only change in a discrete fashion (i.e., the thickness can only be given by an integer number of atomic planes) we believe the effect of randomness on the crystalline component is only to change multilayer peak *intensities,* not to broaden the lines.

[8]A. Guinier, *X-Ray Diffraction in Imperfect Crystals, and Amorphous Bodies* (Freeman, San Francisco, 1963), p. 186.

[9]H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures* (Wiley, New York, 1974), p. 144.

[10]D. B. McWhan, M. Gurvitch, J. M. Rowell, and L. R. Walker, J. Appl. Phys. **54**, 7 (1983).

[11]I. S. Gradzshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1965).

[12]Similar results have been obtained by Cowley (Ref. 6) using a generalized Patterson function.

[13]In order to allow for a direct comparison between (5) and (6) we have expanded the intensity formula of Ref. 10 into a Fourier sum. We have checked that this also broadens the x-ray lines and that the behavior is not Debye-Waller.

[14]W. Sevenhans, J.-P. Locquet, and Y. Bruynseraede, Rev. Sci. Instrum. **57**, 937 (1986).

[15]E. Spiller, A. Segmüller, J. Rife, and R. P. Haelbich, Appl. Phys. Lett. **37**, 1048 (1980).

[16]E. Ziegler, Y. Lepetre, I. K. Schuller, and E. Spiller, Appl. Phys. Lett. **48**, 1354 (1986).

[17]C. F. Majkrzak, J. D. Axe, and P. Boni, J. Appl. Phys. **57**, 3657 (1985).

[18]S. T. Ruggiero, T. W. Barbee, Jr., and M. R. Beasley, Phys. Rev. B **26**, 4894 (1982).