STRUCTURAL AND ELECTRONIC PROPERTIES OF Pb/Cu MULTILAYERS

D. Neerinck, K. Temst, H. Vanderstraeten, C. Van Haesendonck, Y. Bruynseraede, Laboratorium voor Vaste Stof-Fysika en Magnetisme, Katholieke Universiteit Leuven, B-3030 Leuven, Belgium
A. Gilabert, Laboratoire de Physique de la Matière Condensée, Université de Nice, Parc Valrose, F 06034 Nice Cedex, France
Ivan K. Schuller, Physics Department-B019, University of California-San Diego, La Jolla, California 92093, U.S.A.

Abstract

We have performed extensive structural and electronic transport measurements of Pb/Cu multilayered structures. The high-angle x-ray diffraction spectrum indicates the presence of continuous interfacial disorder. In the low-angle x-ray spectrum, pronounced minima occur at positions given by $q = 2\pi/\Lambda$, where Λ is the bilayer thickness. This is in sharp contrast to the results for Pb/Ge (crystalline/amorphous) multilayers, where minima are observed at positions $q = 2\pi/t_{Pb}$ with t_{Pb} the Pb thickness. These low-angle x-ray spectra can be explained by taking into account lateral coherence and continuously distributed thickness fluctuations. The effect of this interfacial disorder on the electronic properties is investigated by measuring the low-temperature resistivity and the superconducting transition temperature of the multilayers. The calculated values for the elastic mean free path in the individual layers confirm the presence of strong interfacial scattering. The thickness dependence of the critical temperature is explained by taking into account an interfacial barrier with penetration probability $\sigma \simeq 0.5$.

1 Introduction

Artificially prepared metal/metal and metal/semiconductor multilayers and superlattices have received considerable attention during the last decade [1]. The investigation of the structural quality by means of x-ray diffraction and the novel electronic transport and magnetic properties of these systems have been the subject of extensive theoretical and experimental work [2,3]. In this paper we report on the effect of interfacial disorder on the structural, normal and superconducting properties of Pb/Cu multilayers. These multilayers can be considered as an ideal testing system for the physical properties of incoherent artificially layered structures: their thermodynamic phase diagram indicates that no solid solution or intermetallic compound is formed; the absence of substantial interdiffusion gives rise to sharp interfaces; the extremely large lattice mismatch between Pb and Cu (27%) induces an important structural disorder at the Pb/Cu interface.
The samples were made in a UHV chamber by electron-beam evaporation using a quadrupole mass spectrometer for rate control [4]. Two series of Pb/Cu multilayers have been prepared on oxidized Si(100) substrates. The first series of samples, with individual layer thicknesses below t=200 Å, were made on liquid nitrogen cooled substrates. The continuity limit for the individual Pb- and Cu-layers, as confirmed by SEM measurements, is about t=40 Å. The second series of samples, with thicknesses ranging between t=200 and t=600 Å, were made at room temperature. All samples consist of 10 bilayers with equal Pb- and Cu-layer thickness. The first and final deposited layer for each sample was Cu. The resistance was determined using a four point dc measurement. The four point pattern was defined fotolithographically using a lift-off technique. The critical temperature was defined as the midpoint of the resistive transition.

2 Structural investigation

Layer uniformity of the thick samples, evaporated at room temperature, was investigated by Rutherford Backscattering, since low-angle x-ray diffraction becomes less sensitive for thicker films. The correspondence between the oscillations in the yield versus energy spectrum and the layer sequence indicates two-dimensional layer-by-layer growth.

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The structure of the thin samples, evaporated at liquid nitrogen temperature, was investigated by $\theta - 2\theta$ x-ray diffraction measurements. The measurements were performed on a computer controlled Rigaku DII Max goniometer with a rotating anode and 12 kW maximum power output. The high-angle spectrum of a Pb/Cu (40 Å/40 Å) multilayer is shown in Fig. 1. The spectrum only shows the broad Pb(111) and Cu(111) peaks, indicative of the usual (111) texture in fcc materials. The lack of superstructure in the high-angle diffraction spectrum results from the severe structural mismatch between the two components of the multilayer. The large geometrical difference in lattice parameter a_o between Pb (a_o=4.95 Å) and Cu (a_o=3.61 Å) leads to an extended disordered interface. This interface structure has its effect on the distribution of thickness fluctuations. In superlattices with a small lattice mismatch, these fluctuations are constrained to be an integer times the interplanar spacing of the constituents. Consequently, the fluctuation distribution is discrete, leading to coherent interfaces. In systems with a disordered interface [5,6] however, such as in Pb/Cu, the fluctuation distribution is continuous. It has been shown, that the presence of only a few Å of continuous interfacial disorder is sufficient to wash out all superlattice peaks, whereas the discrete distribution has a minor effect on the high-angle spectrum [7-9].

The experimental low-angle x-ray spectrum for the Pb/Cu (40 Å/40 Å) multilayer is shown in Fig. 2a. Besides superlattice peaks, the spectrum has 8 secondary peaks, caused by the limited number of bilayers (10), in accordance with simple kinematic theory [2]. However, this spectrum shows a new feature : the presence of several minima. These minima, indicated by arrows, occur at positions $q = n2\pi/\Lambda$, where q is the scattering vector ($q = 4\pi sin\theta/\lambda$ in the $\theta - 2\theta$ arrangement, with λ the x-ray wavelength), n is an integer and Λ is the superlattice period ($\Lambda = t_{Pb} + t_{Cu}$). We have used the optical multilayer theory based on the Fresnel equations, equivalent to the full dynamical theory, as a framework to calculate the low angle diffracted intensity. The recursive formulation approach we adopted is outlined in detail in Ref. 10. This theory describes the multilayer as a stack of homogeneous layers, each characterized by its complex refractive index $\hat{n} = 1 - \delta - i\beta$. We have introduced a continuous Gaussian distribution of individual layer thicknesses. The half width of the distribution 1/c was identical for Pb and Cu. Furthermore, the observed diffraction minima could only be explained by the introduction of lateral in-plane coherence. This coherence is taken into account by summing the reflected amplitudes of all atomic rows within a certain distance. The intensity as a function of angle is then calculated as follows :

$$I(\theta) = |\sum R(\theta)|^2 \qquad (1)$$

This procedure is repeated typically 100 times to average out numerical noise. Fig. 2b shows a simulated x-ray spectrum obtained from a numerical calculation with the following parameters: t_{Pb} : 42.87 Å, t_{Cu} : 37.512 Å, 1/c = 1.5 Å and 100 atomic rows of lateral coherence. The secondary multilayer peaks and the diffraction minima at $q = n2\pi/\Lambda$ are clearly visible. The origin of these minima is the occurrence of deep minima in the bilayer x-ray diffraction spectrum, which is superimposed upon the multilayer spectrum. The bilayer minima can be explained using an optical analogue. For a homogeneous thin film of thickness t, reflection minima occur at incidence angles

$$2tsin\theta = n\lambda, \; n = 1, 2, 3, ... \qquad (2)$$

where λ the x-ray wavelength. For the $\theta - 2\theta$ x-ray diffraction geometry, this condition can be written as

$$q = n2\pi/t, \; n = 1, 2, 3, ... \qquad (3)$$

Since Pb and Cu have nearly equal optical constants ($\delta_{Pb} = 2.7 \times 10^{-5}, \delta_{Cu} = 2.423 \times 10^{-5}$, neglecting absorption), a Pb/Cu bilayer can be considered as one homogeneous film of thickness Λ. Consequently, reflection minima in the bilayer spectrum will occur at $q = n2\pi/\Lambda$. This bilayer spectrum has to be combined with the multilayer spectrum, caused by the yet different Pb and Cu layers. Although this layering gives rise to multilayer peaks at $q = n2\pi/\Lambda$, the diffraction minima at exactly the same positions, which are a bilayer effect, seem to prevail in the spectrum.

This is in contrast with crystalline/amorphous Pb/Ge multilayers, where the observed

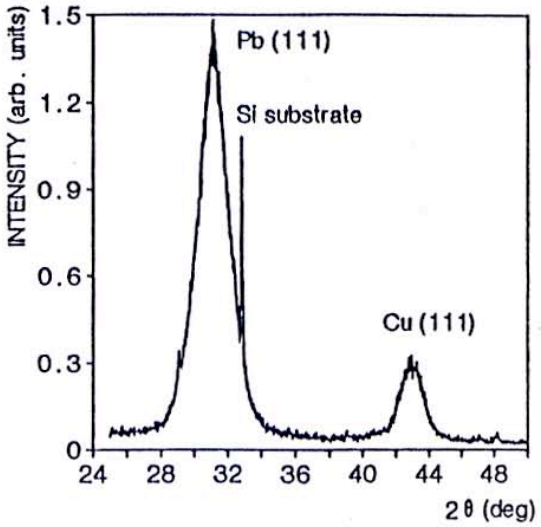

Fig. 1 : High angle x-ray diffraction spectrum of a Pb (40 Å)/Cu (40 Å) multilayer.

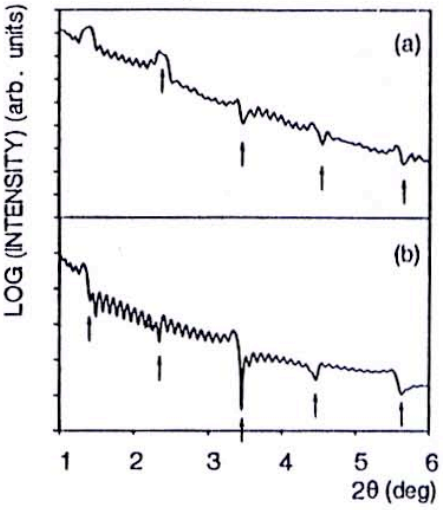

Fig. 2 : (a) Low angle x-ray diffraction spectrum of a Pb (40 Å)/Cu (40 Å) multilayer. (b) Numerical calculation of the low angle diffracted intensity using the recursive optical formula.

reflection minima occur at $q = n2\pi/t_{Pb}$, with t_{Pb} the Pb- thickness. Since the Ge-layers are essentially non-scattering, a Pb/Ge bilayer can be considered as one single Pb-film, having reflection minima at $q = n2\pi/t_{Pb}$. Mathematically, the amorficity of the Ge-layers is taken into account by putting the atomic scattering power f equal to zero. Since δ is directly proportional to f, $\delta_{Ge} \simeq 0$, leading to a large difference in optical constants between Pb and Ge in a crystalline/amorphous Pb/Ge multilayer. In this case, there is no coincidence of the multilayer peaks, occurring at $q = n2\pi/\Lambda$, and the bilayer minima.
We may summarize by stating that the x-ray diffraction spectra of Pb/Cu multilayers indicate the presence of a continuously disordered interface structure. No superlattice peaks occur at high angles due to this continuous disorder; the low-angle spectrum can be explained by introducing continuous thickness fluctuations in the optical theory.

3 Normal transport properties

The low temperature multilayer resistivity, $\rho_{4.2K}$, of Pb/Cu multilayers with equal Pb and Cu thickness, shows no saturation at the small thickness limit as observed in Nb/Cu[11], Nb/Al[12] and Nb/Ti[13], down to the continuity limit. Saturation does occur for large thicknesses, but the saturation value is higher than the bulk resistivities of Pb and Cu. This is due to the poor structural quality of Pb/Cu sandwiches and will be discussed later. We have analysed our multilayer resistivity data using Gurvitch's parallel resistors model [12], without taking into account resistivity saturation. The assumption of independent parallel resistors seems justified in the case of Pb/Cu multilayers because of the disordered interface inhibiting coherent electron transport in the modulation direction. The resistivities of single thin films, due to electron-phonon scattering, measured at 300 K, ($\rho_{th} = \rho_{300K} - \rho_{4.2K}$=21.04 $\mu\Omega cm$ for a 220 Å Pb film and ρ_{th}=2.08 $\mu\Omega cm$ for a 600 Å Cu film) are in good agreement with the published bulk values of 21 $\mu\Omega cm$ and 1.7 $\mu\Omega cm$ [14], respectively. From the calculated individual layer resistivities we determined the electron mean free paths (MFP) using the free electron ρl-values (ρl_{Pb}=1200 $\mu\Omega cm$Å and ρl_{Cu}=851 $\mu\Omega cm$Å)[12]. The MFP's are plotted in Fig. 3 as a function of layer thickness. Individual layer thicknesses differed slightly from the designed thicknesses and were calculated exactly from x-ray diffraction data. For comparison, the MFP of Pb films in Pb/Ge multilayers deposited on liquid nitrogen cooled substrates, is also shown in Fig. 3. The good correspondence between the MFP of Pb in Pb/Ge and Pb/Cu multilayers, taking into account

the somewhat different experimental circumstances, supports the application of the parallel resistors model. The fact that the MFP of Pb is higher than the Pb layer thickness is not surprising since we essentially determine the MFP in the direction parallel to the layers, which is not limited by the finite layer thickness.
The solid line in Fig. 3 is a fit to the data using Fuchs' single film model[15]. The fit to the MFP of Pb yields a value of p=0.11 (p is the fraction of electrons that are specularly reflected at the interface) and a bulk Pb residual resistivity $\rho_{4.2K}$=1.97 $\mu\Omega cm$. The low value of p indicates that diffuse surface scattering (or interfacial scattering in this case) is very important, again consistent with the use of the parallel resistors model. The value of 1.97 $\mu\Omega cm$ is in reasonable agreement with the measured residual resistivity of $\rho_{4.2K}$=2.34 $\mu\Omega cm$ in a 1000 Å Pb film as well as values reported in the literature for similar films [16]. The value of p for the Cu-layers is p=-2.5, indicating that Fuchs' model is not applicable for the Cu-layers. Assuming maximum diffuse scattering at the surface or the interface (p=0) is not sufficient to explain the observed thickness dependence of the resistivity. Moreover, the bulk Cu resistivity, $\rho_{4.2K}$=4.74 $\mu\Omega cm$, extracted from the fit, is too high if compared to reported values [17]. We believe that the low MFP of Cu at large thicknesses results from the poor structural quality of the multilayer samples with respect to single films. Deposition of a Cu layer on a Pb layer can affect the structural growth of Cu, thereby increasing its resistivity in comparison with Cu films deposited on silicon oxide substrates. This explanation is confirmed by the fact that the residual resistivity of a single 600 Å Cu film is $\rho_{4.2K}$=3.05 $\mu\Omega cm$, about half the resistivity of a Cu film in a Pb/Cu(600 Å/600Å) multilayer.

4 Superconducting properties

Many experiments on normal/superconductor sandwich structures have been performed to investigate the reduction of the critical temperature T_c of a superconductor in proximity with a normal metal [18]. In Fig. 4, the transition temperature of Pb/Cu multilayers is shown as a function of the individual layer thickness. We have analyzed our data using the model of Entin-Wohlman et al. [19], who introduced McMillan's barrier penetration probability σ [20] by including generalized boundary conditions in the diffusion approximation of De Gennes-Werthamer [21]. The effect of a barrier with $0 < \sigma < 1$ is to increase T_c with respect to the De Gennes- Werthamer value where no barrier is present ($\sigma = 1$). The calculation of Entin-Wohlman et al. leads to a modified implicit equation for the critical temperature :

$$\frac{D_N N_N}{D_S N_S} k_N \tanh(k_N d_N) = k_S \tan(k_S d_S) + \frac{L_0}{\sigma} (k_S \tan(k_S d_S)) (k_N \tanh(k_N d_N)) \quad (4)$$

where $D_S(D_N)$ and $N_S(N_N)$ are the diffusion coefficient and the density of states at the Fermi level in the superconducting (normal) layers, d_S and d_N are the layer thicknesses, and k_S and k_N satisfy equation 12 in Ref. 21. The characteristic length $L_0 = 2l_N^2/d_N$, where l_N is the MFP in the normal layer [19]. Since the theory applies only to sandwiches, d_N and d_S are put equal to half the actual thickness to calculate T_c for the multilayer [17]. The measured resistivities, as extracted with the parallel resistors model, were first fitted with Fuchs' theory. This thickness dependence of the resistivities was then inserted in the implicit relation to determine T_c, with only σ as an adjustable parameter. The solid line in Fig. 4 is the fit to the T_c data assuming the same σ for all thicknesses. The fit yields a value for σ of 0.49, in close agreement with σ values for bilayers prepared under UHV conditions [18]. An analysis of our data with McMillan's tunneling model [20], valid in the clean limit, has shown that it is impossible to get a reasonable agreement assuming the same σ for all thicknesses. At low thicknesses, the De Gennes-Werthamer approximation is no longer valid and we obtain the Cooper limit for equal thickness Pb/Cu bilayers [22], as shown by the arrow.
In summary, we have investigated the effect of the presence of a continuously disordered interface, as indicated by x-ray diffraction, on the electronic properties of Pb/Cu multilayers. Analysis of low temperature resistivities with the parallel resistors model and Fuchs' theory indicate strong interfacial scattering. The critical temperature of the multilayers can be explained taking into account an interfacial barrier with penetration probability about 0.5.

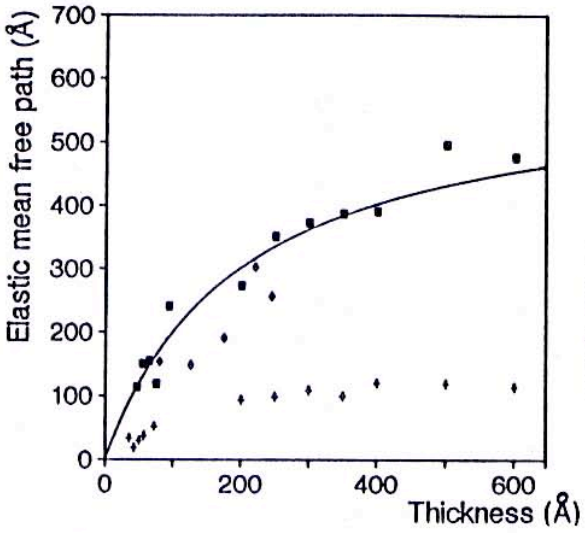

Fig. 3 : Elastic mean free path versus film thickness for Pb (■) films and Cu(+) films in Pb/Cu multilayers. Also shown is the mean free path for Pb(◇) films in Pb/Ge multilayers. The solid line is a fit to Fuchs' theory.

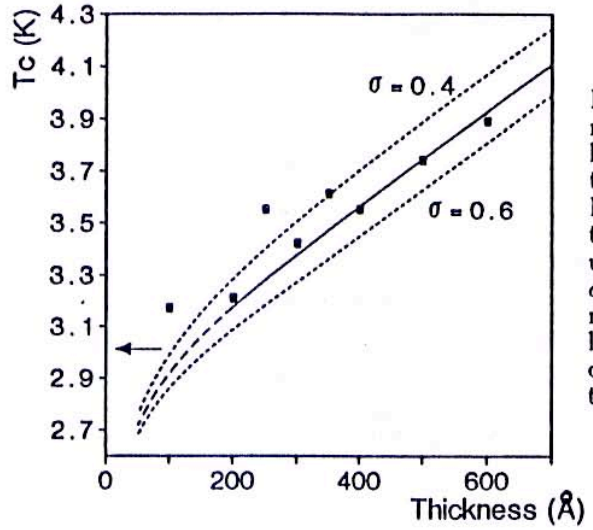

Fig. 4 : Critical temperature for Pb/Cu multilayers as a function of individual layer thickness. The arrow indicates the Cooper limit value for equal layer Pb/Cu bilayers. The solid line is a fit to the theory of Entin- Wohlman [19] using a barrier penetration probability σ=0.49. The broken line indicates the region where this approximation is no longer valid. The upper dotted line is a calculation for σ = 0.4, the lower dotted line for σ = 0.6.

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