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RECENT ISSUES IN METALLIC SUPERLATTICES

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After a brief historical summary, I describe the most recent issues in the field of metallic superlattices. It is shown that the physics of metallic superlattices is controlled by different length scales and therefore structural characterization at the appropriate length scales must be an important ingredient in these studies. Quantitative structural refinement methods are outlined and two recent examples from magnetism and high temperature superconductivity are described. A summary of the most important unsolved issues are outlined and an extensive list of references is provided.

Keywords: A. magnetic films and multilayers, A. superconductors,
A. thin films

Introduction

Metallic superlattices and multilayers have been studied for almost sixty years[1] in a variety of contexts. In the early stages of the field, relatively thick multilayers were prepared because preparation techniques were limited by the thickness control and vacuum capabilities. In the early stages of the use of evaporation techniques in high vacuum many of the studies were dedicated to growing lattice matched Cu/Ni multilayers to study magnetic[2] or elastic[3] properties, Pb/Mg multilayers to study short length scale diffusion[4] or a variety of low-temperature superconducting layers to search for new mechanisms of superconductivity.[5] This paper is a brief review of recent advances in the field and of some of the important unanswered issues and includes some of the most recent review articles.[6-11] An attempt was made to include sufficient references from which a complete picture of the literature in the field may be obtained. Nevertheless, in such a short article it is impossible to properly review all of the vast available literature, and I apologize for any omissions which are solely my oversight.

Preparation and Structural Properties

The main techniques that have been used for the growth of metallic superlattices are sputtering and Molecular Beam Epitaxy (MBE), although recently laser ablation has also been used, mostly for the growth of high temperature superconducting multilayers. A comparison of the two main techniques shows that they are complementary. MBE is cleaner, can be done in an Ultrahigh Vacuum (UHV) environment, allows for in-situ characterization but it is hard to rate-control and is also very slow, thus allowing only the growth of a small number of samples. Sputtering on the other hand, permits the growth of large volumes, is easy to rate-control and allows tunability of the energy distribution of particles arriving at the substrate, although the presence of sputtering gas makes this a much "dirtier" process, with the consequent exclusion of ***in-situ*** structural characterization techniques. It is probably fair to state that the structural and physical properties of metallic superlattices prepared by both techniques are comparable, if the same care is taken in the growth. Probably the reason for this is that, contrary to semiconductors, most of the properties of metals are relatively insensitive to small amounts of contamination.

The number of metallic multilayers and superlattices that have been grown to date is enormous[6-12] and it would be impossible to summarize them in this brief review. Metallic superlattices have been grown from a large variety of combinations involving metallic elements, independent of the relationship between their crystallographic structures. The reason is that, elements that are closely lattice- matched and have the same crystal structure generally have ***equilibrium*** thermodynamic phase diagrams forming continuous sets of solid solutions.[13] Therefore, systems that are lattice-matched, are driven thermodynamically towards interdiffusion, although thin film growth is kinetically limited. On the other hand, it has been known for many years that lattice matching is not a necessary condition for epitaxy.[14] Moreover, if the components of the superlattice do not form alloys, it may be expected that they will be more segregated. In agreement with these ideas, lattice mismatched metallic superlattices were grown for the first time from the eutectic Nb-Cu system[15] in the beginning of the 1980s. An important issue to highlight is that the growth of a superlattice is somewhat different than that of a bilayer. The structure is not only affected by the momentary substrate and temperature on which a layer is growing, but may also change while layers are grown at higher levels. The reason is that generally growth is performed at elevated temperatures, and therefore annealing and interdiffusion may occur in the buried layers. Because of this it is important to characterize the structure once the whole superlattice was grown.

The term superlattice was coined originally to describe a multilayer in which long range (larger than one bilayer thickness) structural coherence exists in the direction perpendicular to the growth. The conceptual difference between what is meant by a multilayer and a superlattice is blurred because in the absence of imperfections crystalline multilayers ***always*** exhibit structural coherence perpendicular to the layers. Although this distinction describes a very clear physical situation and has very well defined observable consequences, it has been customary to use the two terms indistinctly.

The structural characterization techniques that have been applied extensively to metallic superlattices are a variety of surface techniques combined with Ion Milling. These techniques provide complementary information, although in all cases some form of simulation or refinement[16-20] is required to extract quantitative, structural information close to the atomic level from the data. A comparison of the length scales relevant for structural characterization tools and physical properties is shown in figure 1.

Figure 2 shows a schematic classification of the major types of defect structures present in superlattices together with the particular feature affected in their X-ray diffraction spectrum. The distinction between interdiffusion and roughness is artificial, since at the atomic level the concept of interdiffusion is somewhat meaningless. For practical purposes the distinction between interdiffusion and roughness depends on the lateral X-ray diffraction coherence length (typically ~ 200 Å). At short length scales, smaller than this lateral diffraction coherence length, an interface with roughness "looks" as a homogeneous interface with an average scattering function given by the relative proportion of the constituents. In a naive interpretation, interdiffusion affects only the peak intensities, layer thickness fluctuations broaden the peaks, rocking curve widths are affected by the angular

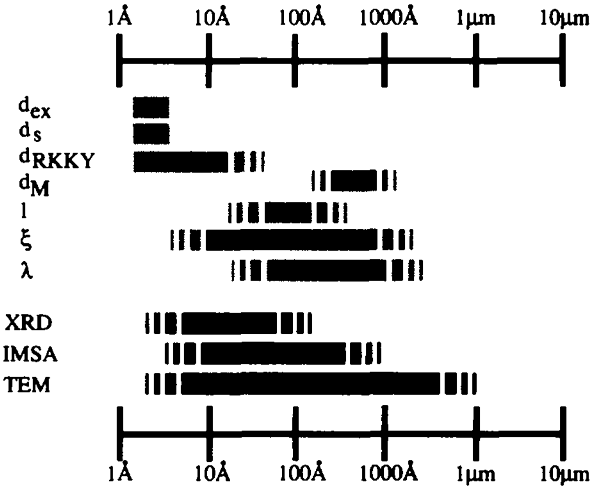

Fig.1 Comparison of structural characterization techniques used for superlattices with length scales relevant for the physics of superlattices. Broken lines indicate the region of uncertainty. d_{ex} = exchange length, d_s = screening length, d_{RKKY} = RKKY length, d_M = magnetic dipolar length, ℓ = mean free path, ξ = superconducting coherence length, λ = superconducting penetration depth. XRD = X-Ray Diffraction, IMSA = Ion Mill Surface Analysis, TEM = Cross sectional Transmission Electron Microscopy.

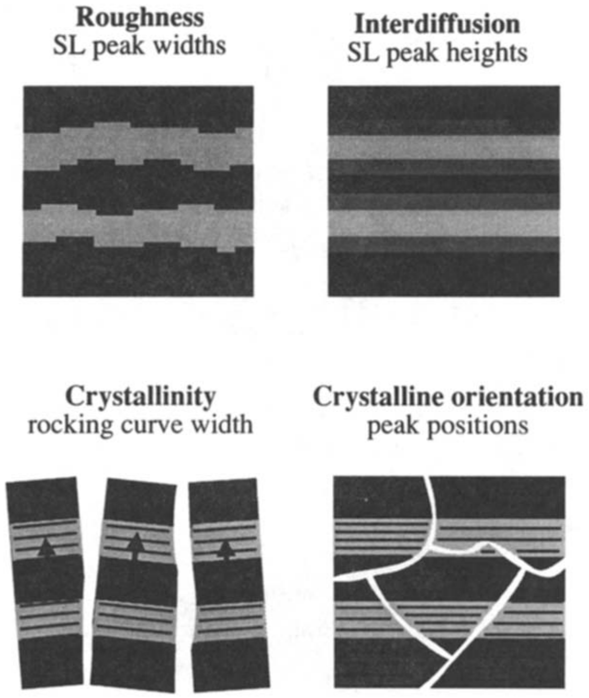

Fig. 2 Classification of disorder features present in a superlattice.

distribution of crystallites and crystalline orientation and interatomic spacing change the peak positions. In realistic situations, however, there is no such clear distinction between the particular type of disorder and its effect on a particular feature; **all** diffraction features are affected to some degree.

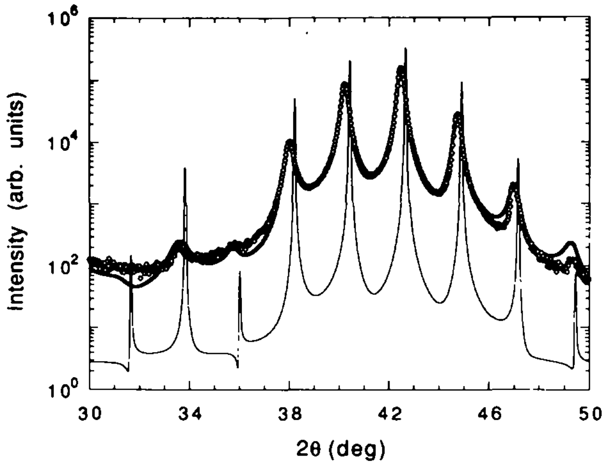

Fig. 3 Measured x-ray diffraction profile of a Mo/Ni superlattice (circles) and calculated spectra (thin line) from a perfect superlattice. Thick line is the result of the refinement procedure described in the text.

To illustrate the type of quantitative studies needed, I will describe here the type of refinement analysis we applied very successfully to X-ray diffraction spectra from metallic superlattices.[20] The approach used for superlattices is very similar in spirit to the well-known Rietveld refinement[21] which has been applied for many years to the determination of the structure of complex materials. The procedure consists of a nonlinear fitting scheme in which the parameters of a model are determined ("refined") by a nonlinear optimization scheme. Although philosophically the two approaches are similar, they differ in the details of the mathematical approach and the computational implementation. As an example of the application of this technique to a real system, figure 3 shows the θ-2θ (i.e. scattering vector in the growth direction) XRD from a Mo/Ni superlattice (dots). A comparison of the data with a model assuming a perfect superlattice (thin solid line) is in ***qualitative*** agreement, but in clear ***quantitative*** disagreement; although the number of peaks and their relative intensities resemble the data, their positions, intensities and line shapes are in clear quantitative disagreement. A refinement of this data as outlined above gives excellent quantitative agreement (thick solid line) and provides a number of disorder parameters which are otherwise inaccessible. This technique provided reliable disorder parameters in situations where the answer was known *a-priori*.[20]

General Considerations

Metallic multilayers serve as ideal systems in which structural parameters can be modified artificially, with the consequent change in their physical properties and thus providing stringent tests for theories.[22-25] It should be kept in mind that for different physical phenomena different characteristic lengths may be important, as illustrated in figure 1. Since the characteristic lengths vary widely in magnitude, the length scale over which the structural properties of a superlattice must be known also varies. In order of increasing sample ***complexity***, the physical phenomena in superlattices can be classified as: single film, interface, proximity, coupling and superlattice effects. Since multilayers consist of a multiple stack of single layers an additional practical advantage of studies in multilayers is that samples can be handled and manipulated

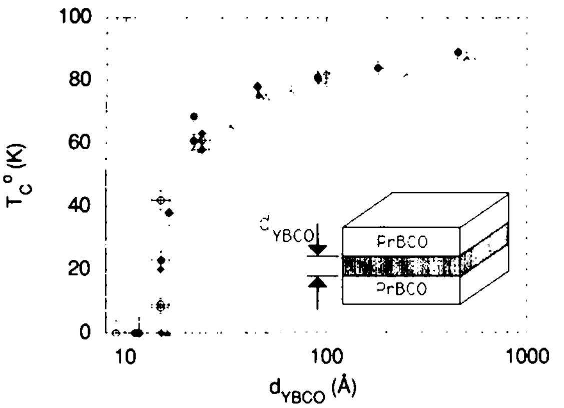

Fig. 4 T_c of single layer of YBCO as a function of thickness (d_{YBCO}) sandwiched between buffer layers.

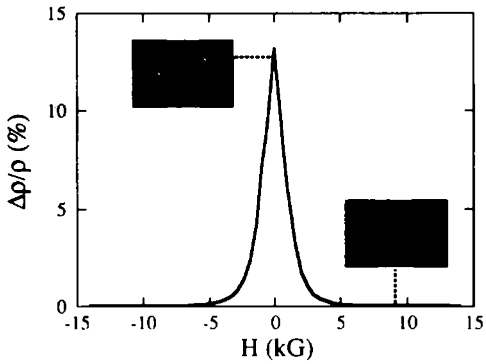

Fig. 5 Giant Magnetoresistance from an Fe/Cr superlattice, the insets illustrating the magnetic configuration of two adjacent Fe layers.

without the additional complications due to surface contamination. Single film effects are due to the restriction in geometry, dimensionality studies in conventional superconductors being a classical example[26] studied for many years. Proximity effects occur due to the coupling of two unlike materials, for instance a superconductor and a normal material, again classic examples of this type are encountered in the field of conventional superconductivity.[5] The recent interest in magnetic superlattices is in great part motivated by studies of magnetic coupling across normal materials.[27-33] Note that all the phenomena described above require at most three layers; a superlattices in fact is not needed. Superlattice effects which were the main motivator in the original stages of the field, have been observed only in two circumstances for metals; in the structure[15] and for the development of magnon bands in magnetic superlattices coupled via dipolar coupling.[28]

The following sections will be dedicated to two examples in which superlattices have played a major role and still are the subject of very intense research; high temperature superconductivity and magnetism.

Superconductivity

The field of superconductivity is a very fertile field for studies using metallic superlattices.[34-37] The reason is that the superconducting coherence length in some cases can be very long and therefore interesting studies can be performed even if the structure is not controlled at the atomic level. In the field of high temperature superconductivity, the situation is more stringent since the coherence length in these materials can be as short as 2-3Å.[37]

One of the important problems which have been studied extensively using superlattices is the superconductivity of a single unit cell.[38,39] The main motivation behind these studies is the fact that many theoretical models used to describe high temperature superconductivity rely on the superconductivity of a properly doped single layer of CuO_2. This problem also beautifully illustrates the importance of structural measurements in studies of physical properties. These studies require the preparation superlattices consisting of a single unit cell of a ceramic superconductor sandwiched between normal materials. Two important issues must be addressed: the integrity of the single unit cell and the effect the nonsuperconducting component has on the properties of the superconductor. These problems have not been solved at the present time. The integrity of a single unit cell, the length scales of the imperfections, the amount of interdiffusion, etc. are the subject of considerable controversy.[40-42] To illustrate the type of information that it is being investigated, figure 4 shows the superconducting transition temperature as a function YBCO layer thickness sandwiched in between PrBCO (nonsuperconducting) layers, measured in our laboratory. In this particular study, a single unit cell is not superconducting; however other studies have claimed that in fact a single unit cell is superconducting with transition temperatures ranging between 12-20K.[37-39, 42] In all cases, however, in addition of the structural issues raised above, it should be also ascertained whether proximity effects and/or coupling across the normal PrBCO affects the results which may be the reason for the discrepancies found in the literature. It is safe to state, therefore, that this problem is still open and should be further investigated.

Magnetism

Metallic superlattices are playing an ever increasing role in the field of magnetism both from the research as well as the applied points of view.[43] Many studies have been dedicated to studying dimensionality effects, interfacial, properties,[44] anisotropy,[45] the relation between structure and magnetism,[46] temperature dependences[47] and to the search for magneto-optical[48-49] and electronic[50] applications.

The recent increased activity in the field was motivated by discovery of Giant Magnetoresistance (GMR)[25] in coupled[32] Fe/Cr superlattices. This discovery has generated an enormous interest in the field of metallic superlattices in general, in the basic mechanism responsible for the effect[51-52] and possible magnetoresistive applications. The basic idea of the effect is that in zero field adjacent Fe layers are antiferromagnetically aligned, whereas in high fields the alignment is ferromagnetic. This, together with spin dependent scattering (not spin-flip)[51] gives rise to additional scattering in zero field as compared to high field, as shown in figure 5. The mechanism of the coupling, which was found to be oscillatory for many non magnetic materials,[33] has been the subject of much recent theoretical activity, although it is not a *sine-qua-non* condition for GMR.[53] Although these studies have received considerable attention many questions remain, principally about the connection between structure and GMR.[54]

Open Questions

In spite of the intense activity in the field, by many laboratories, a large number of unanswered questions remain and maybe the subject of future investigations. Here I will list just a few which seem to recur through the literature repeatedly. There is a need to establish clear cut quantitative criteria by which structural results between different laboratories can be compared. As far as structure is concerned, the connection between different structural and growth parameters must be investigated and quantified. For instance, is there a connection between crystalline orientation and interfacial roughness ? Are those systematic variations of structure in the growth direction? What are the length scales for lateral roughness? In the field of superconductivity, many unanswered questions remain: what is the superconducting property of a single CuO_2 layer, what is the effect of crystalline anisotropy on superconductivity,[55] what is the origin of the long range coupling across the normal PrBCO, and why is there a difference in the properties of superlattices and single layers are just a few of the obvious questions. In the field of magnetism the situation is similar; the issue of dead interfacial layers has not been settled, are there dimensional transitions as a function of layer thickness, what is the origin of the interfacial anisotropy and its connection to structure, what determines the strength of coupling and how is this affected by interfacial structure, are there magnetic proximity effects which modify the results, are just a few of the questions which arise. An important issue which is generic to all superlattices and have a great impact on the range of theories allowed is the presence of extended wave functions across the superlattice. Is there a direct experimental observation possible to ascertain whether extended wave functions in the perpendicular direction exist or whether they are destroyed by the interfacial disorder which is invariably present? It should be stressed that the obvious theoretical prediction, which is the presence of minigaps in the electronic spectrum has never been observed.

We have come a long way, although as Antonio Machado , the Spanish poet said, "the road is made while walking" so many more questions have been raised than answered.

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