

NON-LATTICE MATCHED METALLIC SUPERLATTICES

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Abstract

We describe the main highlights from our work on metallic multilayers and superlattices prepared from non-lattice matched components that do not form solid solutions in the thermodynamic phase diagram.

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Introduction

The structure and properties of metallic multilayers and superlattices have been the subject of intense research in recent years.¹ Many studies have concentrated on combinations of materials which are lattice matched, Cu/Ni being the archetypal system under study.² Most systems that are lattice matched also form solid solutions in their thermodynamic binary phase diagram.³ In order to obtain sharp interfaces, it is hoped that by keeping the preparation temperature low, minimal interdiffusion will occur, due to kinetic limitations.

To minimize interdiffusion and with the hope of obtaining sharp interfaces, our studies have concentrated on combinations which do not form solid solutions in their thermodynamic phase diagram.⁴ These systems however are not lattice matched, and in general they do not grow as single crystals in the plane of the film. However, in some cases they exhibit sharp interfaces, good layering and coherent atomic stacking. We will describe here the structure and properties of some of these systems. Some combinations exhibit coherent atomic stacking over many layers (i.e., superlattice structure) although the reasons for this type of growth is not understood at this time.

Some of the interesting effects exhibited by these superlattices include: dimensional crossover in superconducting superlattices,⁵ development of magnon bands in magnetic superlattices,⁶ metal-nonmetal transition in the electrical transport,⁷ and anomalous softening in the elastic properties.⁸ We have also used superlattices to study a variety of problems related to the crystallization of amorphous semiconductors in contact with a metal,⁹ interfacial anisotropy in magnetic films,¹⁰ the dependence of the superconducting penetration depth on mean free path,¹¹ and the stability of W/C multilayers.¹²

The range of problems that can be studied using metallic multilayers makes this an extremely interesting and fruitful area of research. Here we will describe some selected highlights from our work on metallic multilayers.

Sample Preparation and Characterization

Multilayered metallic samples can be prepared using sputtering¹³ or thermal evaporation (in ultrahigh vacuum known as molecular beam epitaxy, MBE)¹⁴ from multiple sources. In the sputtering technique, the temperature controlled substrate is generally moved alternately from one sputtered beam to the next. In the thermal evaporation technique, the temperature controlled substrate is stationary and the various particle beams are interrupted by various shutter configurations (individual shutters above each source, or a single rotating one, in our case).

Sample characterization is a major concern because many of the properties depend on a variety of structural properties such as interdiffusion, sharpness of interfaces, crystallinity, roughness, etc.¹⁵

A first extremely useful characterization tool we have developed and applied successfully to multilayered metallic samples is commonly designated as Microcleavage Transmission Electron Microscopy (MTEM).¹⁶ In this

technique, the multilayer-substrate combination is cleaved perpendicular to the substrate. In this fashion, a wedge shaped fragment is collected on a microscope grid and then oriented so that the electron beam propagates parallel to the layers. The layers are quite easily visible in this type of measurement as shown in figure 1 for a sputtered NbN(50 Å)/AlN(150 Å) sample. We have applied this technique quite successfully to a large number of combinations,¹⁶ although apparently MTEM can only be applied if one of the components of the multilayers is a brittle material. To further characterize the layered growth small angle x-ray diffraction can be used. This is especially important if MTEM is difficult to apply. For instance, Fig. 2 shows the small angle θ - 2θ x-ray diffraction from an MBE grown Pb(50 Å)/Ge(50 Å) multilayered sample.⁹ The position of the x-ray diffraction peaks is determined by the multilayer periodicity; the interpretation of the intensities is however more cumbersome. The reason is that kinematical treatments are complicated by dynamical corrections,¹⁷ whereas intrinsically dynamical treatments such as the Fresnel formalism require the knowledge of optical constants of very thin films and their dependence on thickness. In any case, the existence of a large number of small angle peaks, together with the fact that the even numbered diffraction peaks are much smaller in intensity than the odd ones, implies that the samples are well modulated with a nearly square modulation profile.

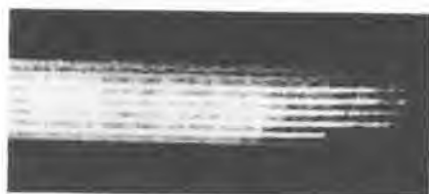


Fig. 1. Microcleavage transmission electron microscopy image of a NbN(50 Å)/AlN(150 Å) multilayer clearly showing the layered nature of the sample.

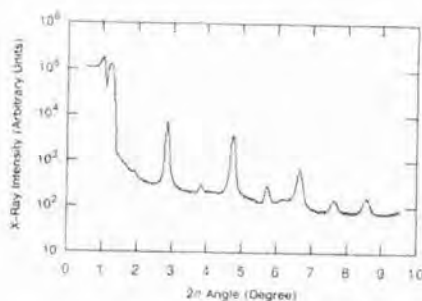


Fig. 2. Small angle x-ray diffraction from a Pb(50 Å)/Ge(50 Å) superlattice. The weak nature of the even-numbered peaks is an indication of good square-wave modulation.

From the large number of combinations that have been grown in a layered structure, some also exhibit a coherent stacking (i.e., "superlattice" structure). If the atomic planes (parallel to the substrate) are stacked so that the perpendicular coherence length is much larger than the layer thickness, superlattice peaks appear around the high angle θ - 2θ x-ray diffraction.⁴ This is shown nicely for a Nb(22 Å)/Cu(22 Å) superlattice (Fig. 3). In order to understand the structure of these superlattices we have performed a number of different model calculations and compared the experimentally measured and theoretically calculated x-ray diffraction intensities. These type of detailed comparisons¹⁸ have shown that for Mo/Ni, Nb/Cu, and V/Ni the interface width has an upper limit of two atomic planes with minimal interdiffusion. In all cases in which we have grown superlattices from combinations that do not form solid solutions in their phase

diagram, and that are not lattice matched, the in plane structure is polycrystalline. On the other hand, in the classical Cu/Ni system which is lattice matched (and which forms a continuous set of solid solutions) we have quite easily grown single crystal superlattices. Figure 4 is the electron diffraction image from a Cu/Ni superlattice showing the single crystal nature of the superlattice.¹⁹ At the present time it is not clear to us whether lattice matching is a sufficient and/or necessary condition for superlattice growth or whether thermodynamic phase diagrams play a more important role than has so far been recognized. It is interesting to note also, that epitaxial growth has been observed and studied in a large variety of combinations with or without lattice matching.²⁰

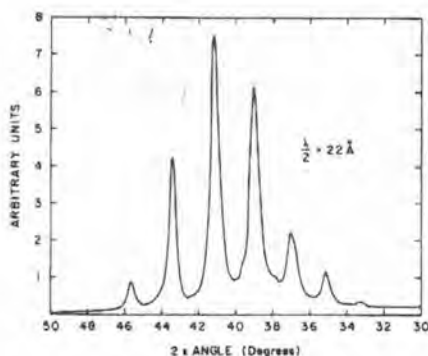


Fig. 3 High angle x-ray diffraction from a Nb(22 Å)/Cu(22 Å) superlattice. The spacing of these peaks is directly related to the modulation wavelength (44 Å).



Fig. 4. Electron diffraction from a Cu/Ni superlattice. The absence of rings indicates the single-crystal nature of the sample. The weaker spots surrounding the six main spots are due to the layering.

Normal State Properties

The electrical resistivity parallel to the layers can give valuable information on the amount of interfacial scattering present. In order to determine whether interfacial scattering is present we have measured the electrical resistivity parallel to the layers in a series of Nb/Cu samples.⁷ A calculation using free electron theory to obtain the mean free path in these systems is not sufficient since this type of calculation relies heavily on a number of parameters which are a-priori unknown, and may well vary with layer thickness. For this reason, systematic studies as a function of layer thickness are necessary. As shown in Fig. 5, the electrical resistivity scales with the inverse of the layer thickness (up to the maximum metallic resistivity) indicating the existence of a substantial amount of interfacial scattering. Since the resistivity is dominated by interface scattering it can be concluded that the majority of electron states do not extend over more than one layer. Consequently it is unlikely that superlattice effects in the electronic structure (e.g., Fermi surface nesting) of these materials play an important role, and that other anomalies observed in

these superlattices (for instance, elastic anomalies)² cannot be explained as due to electronic superlattice effects. More likely they are due to single film effects.

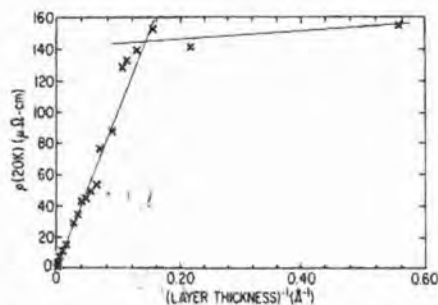


Fig. 5. Electrical resistivity at 20°K of Nb/Cu superlattices as a function of inverse layer thickness ($d_{\text{Nb}} = d_{\text{Cu}}$), showing the effect of scattering from the interfaces.

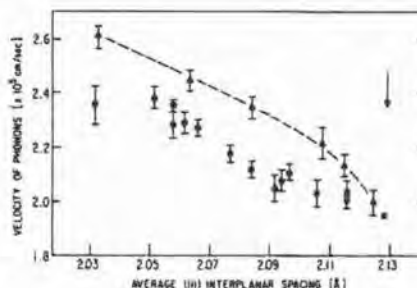


Fig. 6. Phonon velocities as a function of interatomic spacing. The dots are experimental results, the triangles are the results of a molecular dynamics calculation.

The elastic constants of these superlattices are found to be quite anomalous;⁸ as a function of layer thickness a shear modulus (measured by Brillouin scattering) softens considerably contrary to what would be expected if each layer were to possess its bulk properties. This softening has been correlated with experimentally observed lattice expansions perpendicular to the layers.¹⁸ Figure 6 shows the measured shear phonon velocity as a function of the measured interatomic spacing (dots) together with a no adjustable parameter molecular dynamics (MD) calculation²¹ (triangles). Since the Brillouin scattering experiment measures a surface mode whereas the MD is for a bulk mode, a scaling factor between 0.85 and 1 must be incorporated bringing theory and experiment into agreement. Since no adjustable parameters were used in the calculation the agreement is considered to be excellent. Although the anomalous elastic behavior is well explained by the observed lattice expansion, the origin of the expansion is unknown at the present time. It is, however, clear that purely epitaxial strains at the interfaces together with Poisson's ratios cannot explain the data.

Superconductivity

Multilayers and superlattices are ideal model systems for the study of superconductivity. The reason for this is that the characteristic length that determines the superconducting properties is the coherence length (ξ) which is much longer than any characteristic structural length. Therefore small structural imperfections are not expected to influence the superconducting properties much.

One of the most extensively studied phenomena is that of "dimensional crossover".²² For this, a set of two dimensional (i.e., $d_s < \xi$) superconducting layers are separated using a nonsuperconducting element (metal⁵ or

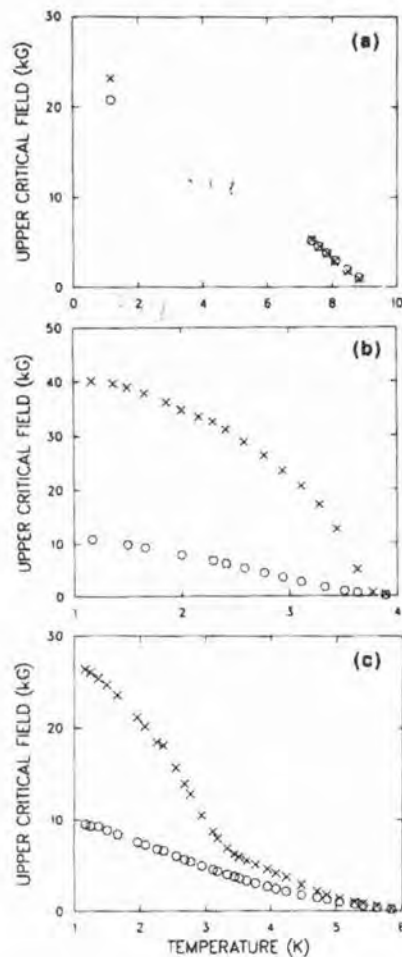


Fig. 7. Parallel (crosses) and perpendicular (circles) upper critical fields in Nb/Cu superlattices as a function of temperature. (a) for a single film of $d_{Nb} = 8500 \text{ Å}$ shows 3D behavior, (b) for a single film of $d_{Nb} = 191 \text{ Å}$ shows 2D behavior and (c), for $d_{Nb} = 172 \text{ Å}$ and $d_{Cu} = 333 \text{ Å}$ illustrates dimensional crossover.

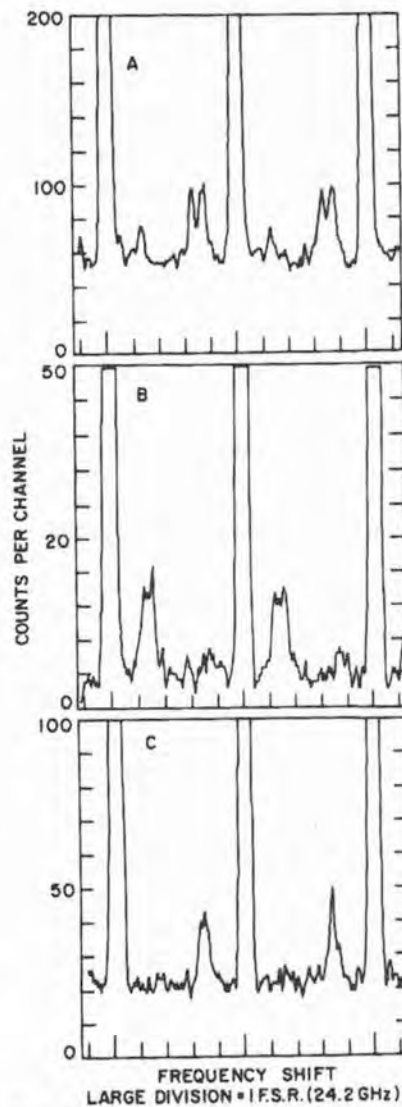


Fig. 8. Brillouin spectra from magnons in Mo/Ni superlattices. (a) $d_{Ni} = 3d_{Mo} = 249 \text{ Å}$, $H = +0.93 \text{ kG}$; (b) $d_{Ni} = d_{Mo} = 160 \text{ Å}$, $H = -0.83 \text{ kG}$; and (c) $3d_{Ni} = d_{Mo} = 300 \text{ Å}$, $H = +0.93 \text{ kG}$.

semiconductor²²). If the layers are well separated (i.e., nonsuperconducting material is thick) the behavior of the parallel upper critical field (H_{c1}^{\parallel}) is typically square-root-like (crosses Fig. 7b) as for a two dimensional (2D) superconductor. If on the other hand the "separator" thickness is very small, the 2D superconducting layers couple strongly together, and the behavior is typically three dimensional (3D) (i.e., linear) Fig. 7a. Since ξ is strongly temperature dependent it is possible to prepare samples that at high temperatures, where ξ is long, are 3D like (i.e., H_{c1}^{\parallel} linear vs. T) and at low temperatures, where ξ is short, the behavior is 2D (i.e., H_{c1}^{\parallel} square-root vs. T) (Fig. 7c).²³ The exact dependence of H_{c1}^{\parallel} on the thicknesses, temperature and ratio of density of states²⁴ has been extensively explored in a variety of experiments which are in good agreement with theoretical calculations. The perpendicular critical field (circles in Fig. 7) on the other hand, depends only on properties parallel to the layers. Because of this, the perpendicular critical field is linear for all thicknesses as shown in Fig. 7.

Magnetism

Many of the magnetic properties of magnetic/normal metal superlattices can be explained as being due to simple thin film effects.²⁵ For instance in the case of Mo/Ni both the saturation magnetization (M_s) and the Curie temperature (T_c) decrease with decreasing Ni thickness. This is expected since the properties of Ni depend sensitively on the number of nearest neighbors. Although, in principle, these measurements can be performed in single films, superlattices offer a technical advantage. Because the thin film is repeated many times the volume of sample available for measurement is much larger than in a single film and therefore the signal available is larger than otherwise. Moreover, in-situ measurements are not necessary since the contamination of the surface of the film is only a small portion of the total sample volume.

A very interesting effect that we have studied⁶ is that of the development of magnon bands due to dipolar coupling in Mo/Ni superlattices. It has been shown theoretically,^{26,27} and simultaneously observed experimentally, that the surface magnon modes of individual Ni layers, because of the coupling across the Mo layers, split into an overall surface mode for the superlattice plus a band of bulk like modes. In spirit this effect is similar to the development of electronic bands in crystals from the individual atomic electronic states.

Figure 8 shows typical Brillouin spectra from samples in the regime where a) the thickness of the magnetic Ni layer (d_{Ni}) is larger than the nonmagnetic Mo layer (d_{Mo}), b) $d_{Mo} = d_{Ni}$ and c) $d_{Mo} = 3d_{Ni}$. This figure shows that as the ratio of Ni to Mo is increased, the surface like mode splits off from the rest. The frequency of the magnons as a function of applied field (H), scattering vector (Q), and saturation magnetization M has been found to be in good agreement with theoretical predictions and independent D.C. magnetization measurements. For instance, Fig. 9 shows the Q dependence of the mode frequencies for a variety of samples. The dots are experimental points and the full lines are theoretical calculations.

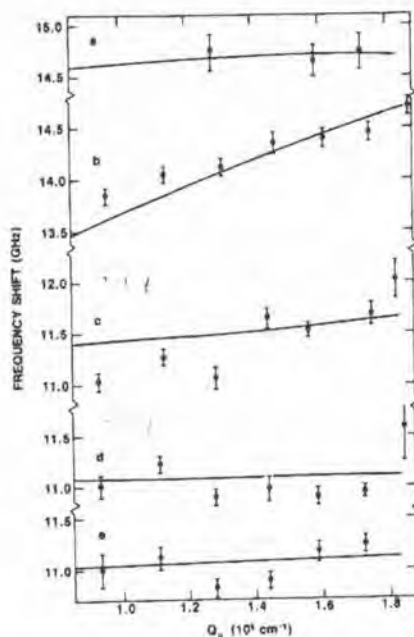


Fig. 9. Wavector dependence of the magnon frequencies -- dots, experimental points; full lines theoretical calculations.
 (a) $d_{Ni} = d_{Mo} = 2500 \text{ \AA}$,
 (b) $d_{Ni} = d_{Mo} = 550 \text{ \AA}$,
 (c) $d_{Ni} = d_{Mo} = 250 \text{ \AA}$,
 (d) $d_{Ni} = d_{Mo} = 100 \text{ \AA}$, and
 (e) $d_{Ni} = 249 \text{ \AA}$, $d_{Mo} = 83 \text{ \AA}$.

Summary

Our results show that high quality multilayers can be grown by sputtering and molecular beam epitaxy techniques. If the constituents are not lattice matched and do not form solid solutions, the reasons for the growth into superlattices is not understood. For some limited cases (Mo/Ni, Nb/Cu, V/Ni, Ag/Co) high quality superlattices can be grown quite easily although the in plane structure is polycrystalline. If the constituents form solid solutions and are lattice matched the growth into single crystalline superlattices is possible although more interdiffusion is likely. All this points out that detailed, high quality characterization using electron microscopy and diffraction techniques together with theoretical studies of film growth is imperative.

The physical properties in nonlattice matched superlattices exhibit anomalous elastic constants and a metal-nonmetal transition in their normal state properties. By changing the relative coupling across a normal material we have observed dimensional crossover in superconducting superlattices and the development of magnon bands in magnetic superlattices. We have performed a variety of other studies (not described here) including the study of crystallization of amorphous semiconductors, interdiffusion, ion beam mixing, dimensional effects on the melting of two-dimensional metals, etc.

The recent effort in the fabrication of multilayers and superlattices has opened up a large area of research; to use these as model systems, to prepare novel materials and devices, and to study new physical phenomena.

The possibilities are practically endless and only limited by our imagination. We believe in future years this will be a fruitful and growing area of research.

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