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New Class of Layered Materials

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A new class of layered materials has been prepared by alternate deposition of two dissimilar metals. Strong experimental evidence is shown that coherent structures with layer thicknesses approaching interatomic spacing can be prepared in this fashion. The experimental x-ray measurements are found to be in good qualitative and quantitative agreement with model calculations.

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Recently there has been renewed interest on the production and stabilization of new materials that do not occur naturally. The engineering of materials with novel physical properties by artifical layering of semiconductors has been extensively studied. It is universally accepted that superlattices can only be produced if the constituents have the *same* crystal structure and *closely matching* lattice parameters. We have prepared a new class of layered ultrathin coherent structures (LUCS) by sequential deposition of ultrathin layers of two *dissimilar* materials. This is the first time that an artificial superlattice structure has been manufactured where the constituents have *different* crystal structures and *large difference* in their lattice parameters. Of course, these experiments have strong implications for the theories that relate to nucleation and physical properties of superlattices.

Alternating layers of metals with a *small* modulation of the composition amplitude were first prepared to study the problem of spinodal decomposition and diffusion in metals by Hilliard and coworkers[1]. More recently, semiconductor superlattices[2] have been prepared by molecular beam epitaxy techniques. These semiconductor superlattices made from two quite similar materials (for instance GaAs and AlAs, where the difference in lattice parameters is ~0.1%) are found to show a high degree of epitaxy. The present work involves metallic systems where the two constituents have a eutectic phase diagram and have *different* crystal structures. I present strong structural evidence (ion mill Auger spectroscopy and x-ray scattering) that LUC's with layer thicknesses approaching interatomic spacing can be prepared in this fashion. I find that the evolution of the x-ray diffraction versus superlattice wavelength is different from what is found in semiconductor superlattices and I present a quantitative explanation for the data based on elementary diffraction theory. The x-ray scattering data implies that the positions of atomic planes (perpendicular to the layers) are correlated ("coherent") from layer to layer giving rise to large diffraction peaks characteristic of the superlattice. It is hoped that in addition to the unique physical properties which are characteristic of layered materials the LUCS will provide additional insight into the role of interfaces for high-T_c superconductivity and into the problem of surface magnetism.

An archetypal example of LUCS is one formed by sequential deposition of Nb (bcc) and Cu (fcc) (the first artificial superconducting superlattice). Samples are prepared on heated single-crystal sapphire substrates with two high-rate (~50 Å/sec) magnetron sputtering guns. The substrate

is held against a rotating table which alternately moves it from one beam of particles to the other. The sputtering rates are controlled by keeping sputtering pressure (0.8 Pa of argon) and power constant. In the present case, the Nb layer thickness was kept equal to the Cu layer thickness.

Ion mill Auger spectroscopy was performed to obtain the depth profile of the chemical composition of the samples. I found that in fact there is a periodic variation of the constituents as a function of depth, although this technique was not sensitive below a layer ($\lambda/2$) thickness of ~ 38 Å.[3] A better technique to study layers in the thickness range of 10–100 Å is an ordinary θ-2θ x-ray diffraction technique.[4] The sample and the detector are rotated synchronously so as to keep the source-sample angle (θ) equal to the sample-detector angle. In this fashion the measurement is only sensitive to changes in scattering function and strains perpendicular (z direction) to the x-y plane of the film (and layers). Figure 1(b) shows the x-ray intensity as a function of 2θ for a sample with a layer thickness $\lambda/2 = 70$ Å. The two peaks are identified as a Cu(111) peak and a Nb(110) peak. In fact, Cu is found to grow in the (111) direction and Nb in the (110) direction under identical growth conditions (the identification is made by use of the higher-order diffraction peaks which are also observed). The lattice parameters for Nb and Cu derived from these peaks are found to be 3.29 and 3.61 Å (within ~ 0.2% of those for the pure materials). Figure 1(a) shows the x-ray intensity as a function of 2θ for a sample with $\lambda/2 = 5$ Å. Not surprisingly there is only one broad peak. The width of this peak overlaps the region where the Nb(110) and Cu(111) peaks are located indicating that this sample has a large distribution of interatomic spacings.

Figure 2 shows the evolution of the x rays for increasing LUCS wavelength (i.e. layer thickness). Figure 2(a) shows one central peak located midway between the pure Nb and pure Cu peaks and two additional satellite peaks symmetrically spaced around the central peak. The experimental systematics shown in this figure has been found for roughly thirty samples. For brevity, only the experimental results for five samples are shown. Notice that there is a continuous, consistent way in which the x rays evolve from the small-λ limit to the large-λ one. Up to eleven distinct peaks were observed and the x-ray linewidths were within factors of 2 of the diffractometer resolution (~ 0.7°). Samples that have been aged for more than six months do not show any no-

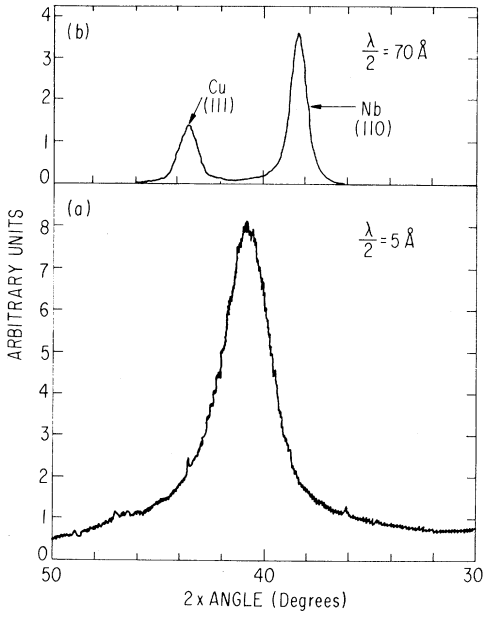

FIG. 1. X-ray diffraction from two samples: (a) One with a large layer thickness (70 Å) and (b) one with a small one (5 Å).

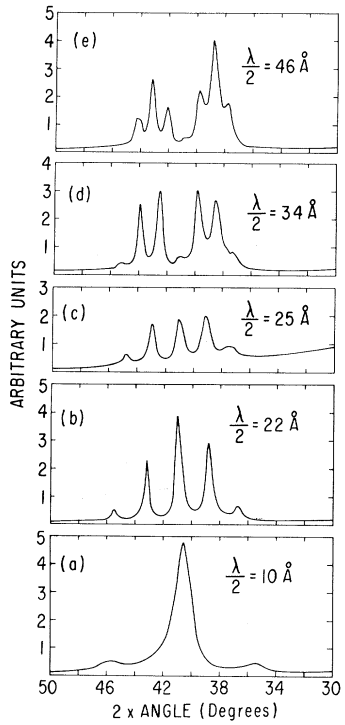

FIG. 2. Evolution of the experimental x-ray diffraction as a function of LUCS wavelength (i. e., layer thickness $\lambda/2$).

ticeable change in their diffraction properties.

To understand the x-ray data I have performed three different one-dimensional model calculations, based on simple scattering theory.[4] The model is shown in the inset of Fig. 3. The distance between the atomic planes is given by the corresponding distances found in the bulk material, except for the closest planes to the interface (δ_1 and δ_2) and the separation (δ) between dissimilar atomic planes, which are varied from model to model.

In the first model (*no adjustable parameters*, $\delta_1 = d_{Cu}$, $\delta_2 = d_{Nb}$, $\delta = d_{Cu}$ or δ_{Nb}) we have summed up the scattering from N atomic planes with N = [total thickness ($\sim 2\mu$)]/($d_{Cu} + d_{Nb}$), where d_{Cu} = 2.083 Å is the separation of the Cu(111) atomic planes and d_{Nb} = 2.34 Å is the separation of the Nb(100) atomic planes. The results of the calculation are shown in Fig. 3. It is found that the width of the experimental x-ray peaks is not determined by finite crystal size effects. The position of the peaks is given by

$$\sin\theta_h = \tfrac{1}{2}h\lambda_x/\lambda, \qquad (1)$$

where h (the "order" of the reflection) is an integer, λ_x = 1.5405 Å is the wavelength of the x ray and λ is the superlattice wavelength.[5] Notice that this model calculation, with *no adjustable parameters*, has the same qualitative features as the experimental data. There is a continuous evolution from the small-λ limit with one central peak and satellites to the large-λ limit where there are two distinct peaks [Cu(111) and Nb(110)] with their own satellites.

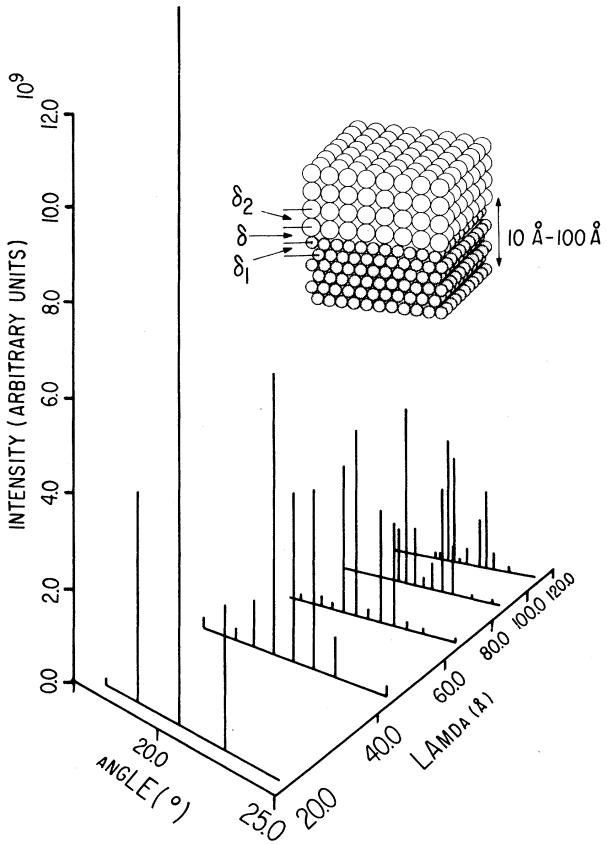

FIG. 3. Calculated x-ray intensity vs angle and superlattice wavelength. The inset shows the model used in the calculations: The interatomic separation is kept the same as in the bulk except for the layers closest to the interface (δ_1 and δ_2) and the separation between dissimilar layers (δ) which might be strained as explained in the text.

An alternative way of thinking about the results is to assume that the x rays reflect from the superlattice, and that the atomic planes in one layer act as a large unit cell, modulating the amplitude of the various orders (h) of reflection. In this fashion Eq. (1) is automatically satisfied. The x-ray intensity is given[4] by

$$I \propto \frac{1+\cos^2 2\theta}{\sin\theta\sin 2\theta}\left|\left\{\sum_{j=1}^{n}\exp\left[-W_{Cu}\left(\frac{\sin\theta}{\lambda_x}\right)^2\right]f_{Cu}(\theta)\sigma_{Cu}\exp\left[i\frac{4\pi}{\lambda_x}x_j\sin\theta\right]\right.\right.$$
$$\left.\left.+\sum_{j=1}^{m}\exp\left[-W_{Nb}\left(\frac{\sin\theta}{\lambda_x}\right)^2\right]f_{Nb}(\theta)\sigma_{Nb}\exp\left[i\frac{4\pi}{\lambda_x}x_j\sin\theta\right]\right\}\right|^2, \qquad (2)$$

where $1+\cos^2 2\theta$ is the polarization factor, $\sin 2\theta$ is the Lorentz factor, $\sin\theta$ is a geometric factor that takes into account that the x-ray beam is smaller than the sample, f_{Cu} and f_{Nb} are the scattering functions of Cu and Nb, σ_{Cu} and σ_{Nb} are the densities of Cu and Nb atoms in the Cu(111) and Nb(110) planes, x_j is the position jth atomic plane, n is the number of Cu planes in one layer, m is the number of Nb planes in one layer, and W_{Cu} and W_{Nb} are the Debye-Waller coefficients.

A fit to the experimental intensities was obtained by use of δ_1 and δ_2 as adjustable parameters and δ calculated from the experimentally determined superlattice wavelength. In this fashion the experimental intensities were fitted to better than 20% for most x-ray peaks. Another possible model is to assume some mixing at the interface and use it to fit the experimental intensities. This will have the effect of changing the exact values

of δ, δ_1, and δ_2. Clearly more experimental work is needed to determine the exact nature of the interfaces. I would like to stress again that the x-ray evidence is conclusive as far as the superlattice nature of the material is concerned.

It should be pointed out that the epitaxy of (111) fcc on (110) bcc metals has been known for some time. Although more than fifteen fcc-on-bcc metallic epitaxial systems have been extensively studied,[6] to my knowledge the Nb/Cu system has not yet been investigated. Based on these previous studies it is thought that there are two possible orientations in the x-y plane, depending on the ratio of the atomic diameters of the two materials. Based on moire-pattern studies and the ratio of the atomic diameters I conjecture that the Nb/Cu system is likely to give epitaxy in the NW (Nishiyama-Wasserman) orientation for which the Cu$[11\bar{2}]$ direction is parallel to the Nb$[1\bar{1}0]$ direction (similarly to nickel-on-tungsten epitaxy). Electron scattering and Laue x-ray scattering experiments are presently underway to check this hypothesis.

Transport and superconducting properties will be the subject of a later publication. I find layer-thickness–limited mean free paths, anisotropic superconducting critical fields,[7] and superconducting transition temperatures smaller than predicted by simple Cooper-limit calculations.[3]

In summary, I have prepared a new class of layered ultrathin coherent structures consisting of two metals that have different crystal structures. The structural evidence indicates that long-range coherence is present. The x-ray data can be qualitatively explained with no adjustable parameters and quantitatively fitted with a one-dimensional model in which the first and last atomic planes in each superlattice layer are strained. Physical properties also imply that the material is layered at the microscopic level, and for the first time a superconducting LUCS has been manufactured.

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