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LAYERED ULTRATHIN COHERENT STRUCTURES (LUCS)

by

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LAYERED ULTRATHIN COHERENT STRUCTURES (LUCS)*

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ABSTRACT

We describe a new class of superconducting materials, Layered Ultrathin Coherent Structures (LUCS). These materials are produced by sequentially depositing ultrathin layers of materials using high rate magnetron sputtering or thermal evaporation. We present strong evidence that layers as thin as 10 Å can be prepared in this fashion. Resistivity data indicates that the mean free path is layer thickness limited. A strong disagreement is found between the experimentally measured transition temperatures T_c and the T_c's calculated using the Cooper limit approximation. This is interpreted as a change in the band structure or the phonon structure of the material due to layering or to surfaces.

INTRODUCTION

One of the most fascinating areas of solid state physics is the artificial production and stabilization of new materials that do not occur naturally. The possibility of fine tunning band structures, phonon spectra etc. by artificially layering materials seems very attractive and promising. In particular, layered superconductors have been studied for some time.[1] The study of layered superconductors can shed light on the role of the interfaces on surface superconductivity and on the Cooper limit problem.

We have prepared ultrathin layers of niobium (Nb) and copper (Cu) with layer thicknesses ranging from 10 Å - 2500 Å. It is found that in fact this system grows in layered form and that diffusion does not destroy the LUCS structure. We find extremely good reproducibility in the sample preparation, mean free paths limited by layer thicknesses and T_c's smaller than predictions based on a simple Cooper[2] limit calculation.

SAMPLE PREPARATION AND CHARACTERIZATION

Samples can be prepared in two completely different ways. Figure 1 shows the experimental setup for

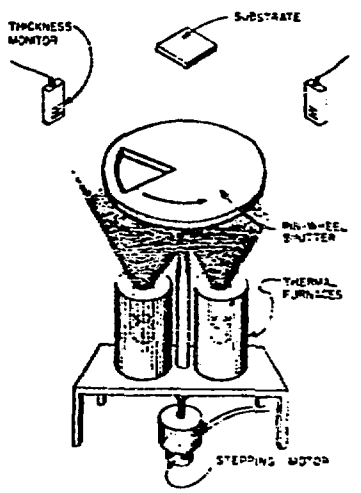

Figure 1. Experimental setup using two thermal furnaces.

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thermal evaporation[3] of LUCS. Two thermal evaporation sources are closely located to each other. The substrate on which the sample is prepared is located between the two sources roughly 15 inches above them. A rotary shutter exposes the substrate alternately to the two evaporated metal beams. The evaporation rates in each thermal source are controlled and monitored using a quartz crystal based feedback system. This system is used for the preparation of samples that are used in our tunneling studies.

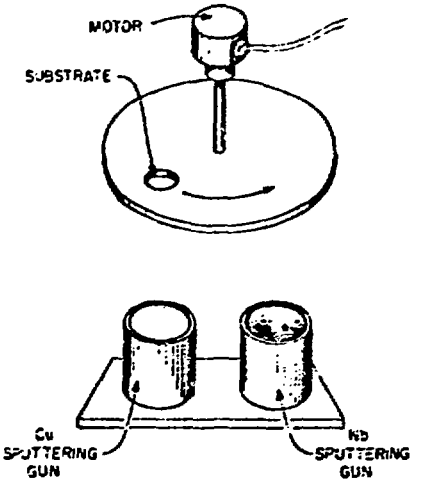

Figure 2. Experimental setup using two sputtering guns.

The sputtering system is based on two high rate magnetron sputtering guns. The two guns are located roughly 15 inches from each other. The substrate is held against a rotating table which alternately moves it from one beam to the other. The sputtering is performed with 6 mtorr of argon pressure and the sputtering rates are controlled by keeping sputtering pressure and power constant. Since the energy of sputtered atoms is distributed in a much narrower range (due to thermalization by the Ar sputtering gas) the sputtered sample growth is closer to a single crystal than the thermally prepared samples. On the other hand, the preparation of tunnel junctions is difficult in sputtering systems where high energy ions can destroy the tunneling barrier. To illustrate the methodology we will describe the properties of sputtered Nb/Cu LUCS.

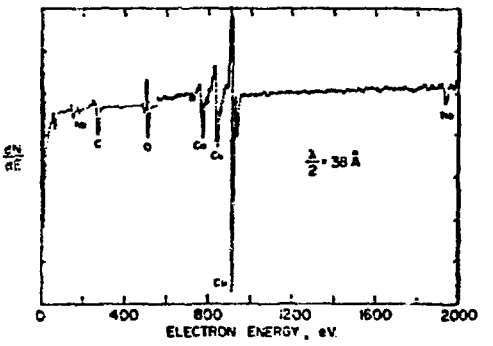

Figure 3. Auger spectrum for a 38 Å Nb/Cu LUCS

To characterize the sample Ion Mill Auger Spectroscopy was performed. Auger spectroscopy allows the study of the composition of the films 15 Å - 30 Å from the surface. This, in combination with ion milling, allows depth profiling of the chemical composition. It should be pointed out that since the escape depth of the Auger electrons is larger than one atomic layer it is expected that this measurement will be characteristic of an average composition over the escape depth. Figure 3 shows a derivative curve of the number of Auger electrons as a function of energy for a sample having a layer thickness $\lambda/2$ = 38 Å, and overall thickness of 1 μm.

Notice the presence of characteristic peaks of Carbon, Oxygen, Niobium, and Copper. Back-streaming from the diffusion pump is probably responsible for the residual Carbon. The large Cu peak indicates that the first layer is of Cu.

To depth profile the chemical composition of the samples, they are bombarded with 1 KeV Xe ions. This slowly mills the surface of the films, while simultaneously the Auger spectrum is analyzed. Figure 4 shows a graph of the peak to peak height of the Cu LMM Auger electron at ~ 910 eV versus time. Since the ion milling is presumed to be performed at a constant rate this graph illustrates the change in Cu concentration versus depth. We should point out that attempts to depth profile films with $\lambda \leq 30$ Å were unsuccessful. This probably is due to the fact that the energetic Xe ions stir up the surface of the material. In addition the Auger electrons have an escape depth somewhere in the neighborhood of 30 Å so this kind of a measurement becomes insensitive for determining chemical compositions for films with smaller layer spacings. Figure 4 shows that the variation in Cu concentration is periodic with depth.

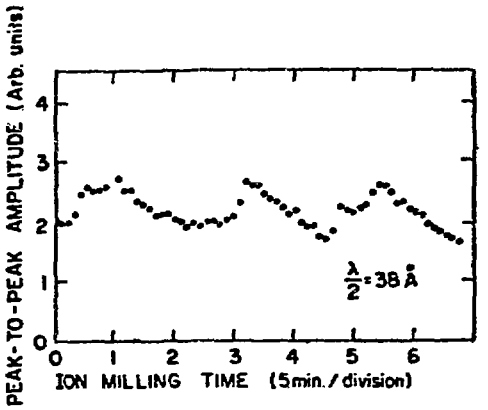

Figure 4. Depth profile of the Cu concentration for the Nb/Cu LUCS shown in Figure 3.

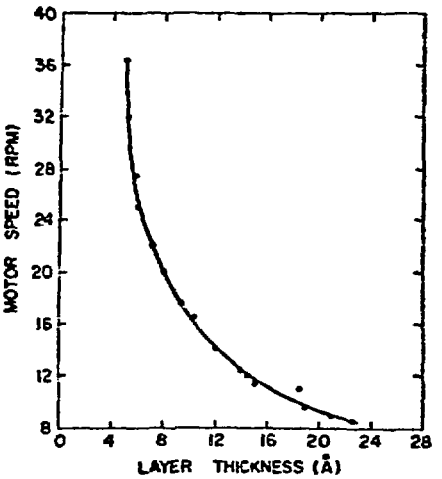

Figure 5. Superlattice wavelength versus speed of driving motor.

Detailed X-ray studies also indicate that the material is layered. A detailed account of the diffraction and Laue patterns will be published elsewhere.[4]

The reproducibility of sample preparation is indicated in Figure 5, where the superlattice wavelength derived from X-ray measurements is plotted against the speed of the driving motor.

Notice that the wavelength is proportional to the inverse of the motor speed indicating that sputtering pressure and power fluctuations do not significantly affect the results.

TRANSPORT PROPERTIES

The layered nature of the Nb/Cu LUCS manifests itself also on the various transport properties. Figure 6 shows the variation of

residual resistivity versus the inverse of the layer thickness. As expected, the resistivity depends linearly on $1/\lambda$ indicating that the mean free path is limited by the layer thickness.

The superconducting coherence length ξ of the Nb/Cu LUCS can be calculated from the coherence length $\xi = 380$ Å[5] of pure Nb and the mean free path ℓ found from resistivity using $\xi = \sqrt{\xi_o \ell^5}$ valid for a dirty superconductor. For a layer thickness of 10 Å the coherence length is found to be $\xi = 62$ Å. It is interesting to note that in the normal state this material will behave as decoupled layers of metals because the electrons are confined to move inside each layer. On the other hand, below the transition temperature, this material should behave as a homogeneous superconductor since $\xi > \lambda$.

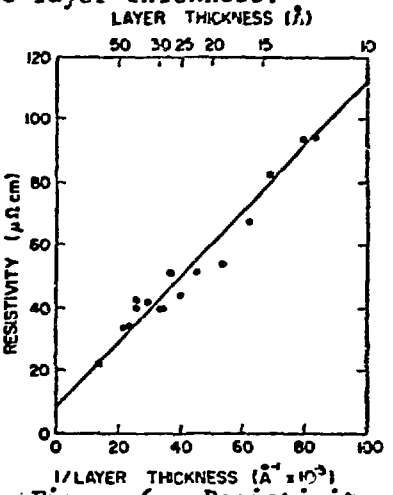

Figure 6. Resistivity of Nb/Cu LUCS versus inverse layer thickness.

The existence of a superconductor where $\xi > \lambda$ allows a direct comparison of experiment to Cooper limit calculation of the effective electron-phonon coupling (N_oV). It was shown many years ago by Cooper[2] that N_oV for a material such as our Nb/Cu LUCS will be given by the average of the two attractive interactions.

$$(N_oV)_{Nb/Cu} = \frac{N_1V_1(N_1d_1) + N_2V_2(N_2d_2)}{N_1d_1 + N_2d_2} \qquad (1)$$

where 1 and 2 refer to Nb and Cu respectively and $d = \lambda/2$ is the thickness of either Nb or Cu. Notice that if $d_1 = d_2$ (our case), N_oV will be independent of thickness as long as $\xi > \lambda$. A lower limit for the transition temperature of such a sandwich can be calculated from[7]

$$1.45\ T_c = \theta_D \exp(-1/N_oV) \qquad (2)$$

where the density of states in each material can be determined from the experimentally measured specific heat coefficient γ using.

$$N_o = 3\gamma/2\pi^2k_B^2 \quad . \qquad (3)$$

The various parameters used in the calculation of T_c are shown in Table 1.

TABLE I

Relevant parameters for Nb and Cu

Element	Z	γ [mJ/moleK^2]	N_o [states/eVcm^3]	V [eVcm^3]	θ_D [°K]	T_c [°K]	N_oV
Nb	5	7.66[8]	0.90×10^{23}	0.34×10^{-23}	241[9]	9.2	0.306
Cu	1	0.69[8]	0.125×10^{23}	0.512×10^{-23}	342[8]	<0.01	0.072[10]

We find using Eqs. (1), (2), and (3) and the value from Table I that the transition temperature of the Nb/Cu LUCS should be $T_c = 5.4$°K in the short wavelength limit ($\xi > \lambda$). Experimentally it is found that below $\lambda/2 = 20$ Å the transition temperature of the Nb/Cu LUCS is almost layer thickness independent and that $T_c \tilde{=} 2.5$°K. The strong disagreement, of over a factor of two, between experiment and theory implies that layering strongly affects the band structure and hence V or N_o in these layered materials. Since Nb has a peak in the density of states at the Fermi surface we expect layering to affect more strongly N_o than V which would imply changes in the phonon structure.

In summary, we have been able to prepare Layered Ultrathin Coherent Structures (LUCS) where the layer thickness approaches interatomic spacings. All measurements to date, structural as well as transport, indicate that the material is layered at the atomic level. Resistivity measurements show that the mean free path is layer thickness limited. The disagreeement between the T_c's theoretically calculated and the ones experimentally determined imply the possibility of strong band structure effects.

A more detailed account of X-ray results, critical field versus temperature and angle, and T_c versus wavelength will be published elsewhere.

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REFERENCES

1. Myron Strongin et. al., Phys. Rev. Letters 21, 1320 (1968).
2. L. N. Cooper, Phys. Rev. Letters 6, 689 (1961); IBM Journal 6, 75 (1962).
3. J. E. Hilliard in Modulated Structures - 1979, edited by J. M. Cowley, et. al., AIP Conference Proceedings No. 53, pg. 407.
4. Ivan Schuller to be published.
5. C. Kittel, Introduction to Solid State Physics, pg. 425, Fourth Edition, J. Wiley and Sons, Inc., N.Y. (1971).
6. P. G. deGennes, Superconductivity of Metals and Alloys, pg. 225, W. A. Benjamin, Inc., N.Y. (1966).
7. G. Gladstone, M. A. Jensen, and J. R. Sehrieffer in Superconductivity, Edited by R. D. Parks, Marcell Dekker, Inc., N.Y. (1969).
8. K. A. Gschneider, Sol. St. Phys. 16, 275 (1964).
9. Y. Heine, Phys. Rev. 153, 674 (1967).
10. E. Krätzig, Sol. St. Commun. 9, 1205 (1971).