Transition-Temperature Oscillations in Thin Superconducting Films

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Ultrathin films of Sn have been grown incrementally on substrates held at 15 K and then studied *in situ* at low temperatures. This process of repeatedly increasing the thickness of a film facilitates the investigation of thickness-dependent physical properties. The superconducting transition temperature has been found to oscillate with a period which was nominally about 4 Å. The latter is approximately a factor of 2 larger than the prediction of simple theoretical models. Oscillations of the normal-state resistance with thickness have not been observed.

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In thin films of thickness t very much smaller than the other two dimensions the projection of the momentum across the thickness becomes quantized. This phenomenon is known as the quantum size effect.[1] The essential features of systems exhibiting quantum size effects follow in the simplest approaches from oscillations in the electronic density of states with thickness which in turn lead to oscillations with thickness of quantities such as the electrical resistance, Hall mobility, magnetoresistance, and the transition temperature T_c of superconducting materials. The latter was first suggested by Blatt and Thompson[2] and most recently discussed by Yu, Stongin, and Paskin.[2] In this Letter we report the observation of large oscillations with thickness of the superconducting transition temperature of ultrathin films of Sn. These results are the clearest demonstration to date of the quantum size effect in superconductors as the amplitude of the effect exceeds that reported earlier by more than a factor of 50.[3]

Films were prepared in an ultrahigh vacuum system pumped by an array of ion pumps with a total speed of 550 l/s. The growth chamber was equipped with a series of commerical Knudsen cells (molecular-beam ovens) used as sources of metal vapor. These cells have 3-cm-diam orifices and were positioned 30 cm from the substrate. A bakable low-temperature apparatus was mounted on top of the growth chamber and served as a sample insertion system. The films, which were defined geometrically by a movable mask and were 5.0 mm $\times 0.5$ mm in size, were grown incrementally on a glazed alumina substrate by repeatedly lowering the low-temperature apparatus into the growth chamber, and opening a shutter, thus exposing the substrate to the vapor source. During growth the substrate temperature was held at 15 K as measured by a thermometer attached to the substrate holder. Four-terminal electrical resistance measurements with the film retracted into the low-temperature apparatus were carried out between successive depositions on the substrate. During growth, the chamber pressure was 5×10^{-10} Torr. The pressure in the vacuum environment of the low-temperature apparatus was not measured, but was undoubtedly much lower. Impurities do not collect on the substrate between depositions because of these low background pressures. In addition, the only residual gas detected in the system was H_2, and because the films were grown with a substrate temperature of 15 K it is possible that any adsorbed H_2 would be desorbed prior to deposition. This assumes the adsorption to be physisorption rather than chemisorption involving bonding between hydrogen and tin. Film thicknesses were calibrated by depositing Sn for an extended period at a fixed rate of 0.25 Å/s and measuring the resultant thick film with a profilometer. The deposition rate was fixed by the temperature of the Knudsen source and was checked *in situ* with a crystal-oscillator thickness monitor. Although the system has the potential to be used for the growth of epitaxial films, for these investigations polycrystalline films were prepared.

In Fig. 1 we show the oscillations of the transition temperature of a set of films as a function of nominal thickness t. Oscillations of the normal-state resistance with thickness were not observed. The increments of material deposited in successive evaporations in this instance were 0.75 Å. For comparsion, the lattice constant of Sn is approximately 5.82 Å. The transition temperatures in the figure were defined operationally as the temperatures at which the electrical resistance fell to less than 0.20 $\Omega/\square$. The current used in all of the measurements was 1×10^{-7} A. The film shown in the figure was initially connected at a thickness of 28.8 Å, but did not exhibit superconductivity until a thickness of 30.75 Å. The nature of the quasireentant superconductivity observed in this thickness

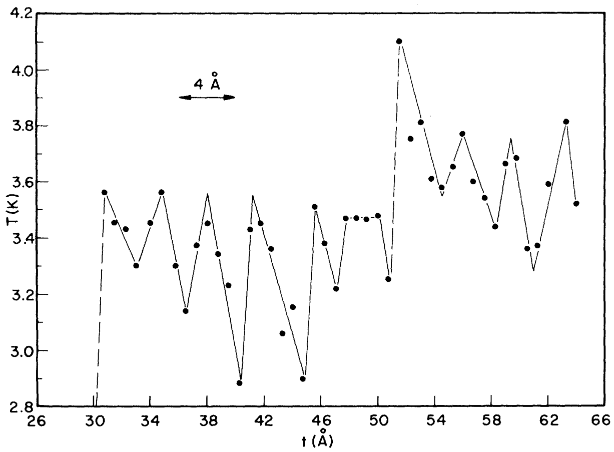

FIG. 1. Variation of the transition temperature T_c of a set of thin Sn films as a function of thickness t. The onset of superconductivity corresponds to a normal-state sheet resistance of the order of 4000 Ω/□. T_c is defined as the temperature at which a film's sheet resistance is < 0.2 Ω/□ at a measuring current of 10^{-7} A.

range and the superconducting fluctuations studied at thicknesses greater than 30.75 Å will be the subjects of future papers.[4] In the case of three other sets of films in which T_c oscillations were observed but which are not shown, the onsets of electrical conduction and superconductivity were observed at slightly different thicknesses. These various critical thicknesses would be expected to be nonuniversal as they depend on precise details of substrate roughness, substrate temperature, and deposition rate which varied slightly from sample to sample.[5]

The oscillatory variation of the superconducting transition temperature with thickness can be understood qualitatively by means of a simple model of the quantum size effect in which the film is modeled by infinite or periodic boundary conditions in the plane, freely moving carriers within the plane, and the requirement that charge carriers not leave the film at its surfaces.[6] This corresponds to an infinite potential well in the vertical direction across the thickness of the film. Under these conditions the energy spectrum splits into subbands denoted by a quantum number s. These subbands are part of a system of overlapping bands shifted relative to one another. Each is populated up to a certain value of the two-dimensional Fermi momentum. The density of states in such a thin film is of the form

$$D(\epsilon) = (m^*/\pi\hbar^2 t)[2t/\lambda_F], \qquad (1)$$

where $[2t/\lambda_F]$ is the integer part of $2t/\lambda_F$.[1] $D(\epsilon)$ then decreases with increasing t as long as $s = [2t/\lambda_F]$, which is the number of filled subbands, stays the same. Here λ_F is the Fermi wavelength and t is the film thickness. At certain values of t a new subband opens up, i.e., $s \rightarrow s+1$ and the density of states increases by $m^*/\pi\hbar^2 t$. This leads to sawtoothlike oscillations of the density of states as a function of t. The period of these oscillations Δt is given by

$$\Delta t = \lambda_F/2. \qquad (2)$$

In semiconductors and semimetals, because of their low carrier density relative to metals, the period can be rather long, which results in the possibility of observing quantum size effects in thicker films than in the metallic case.[1] Because of this, it is also possible to prepare rather easily thin films of such materials with only one subband populated.

Superconductivity is modified as a consequence of the dependence of the density of states on thickness.[1,2] Electrons which are paired have equal and opposite planar momenta, and belong to the same subband denoted by s. The oscillations in the density of states then lead to oscillations as a function of thickness of the gap Δ and of T_c. The simple models give

$$T_c = 1.14\hbar\omega_D \exp[-1/gD(\epsilon)], \qquad (3)$$

where g is the interaction constant, ω_D is the Debye frequency, but where $D(\epsilon)$ is given by Eq. (1). The critical temperature and the gap would decrease monotonically with increasing film thickness, but for the increase in s at certain thicknesses which causes jumps in these parameters. The consequence of Eqs. (1) and (3) is a sawtoothlike variation of T_c as a function of thickness with the amplitude of the oscillations decreasing with increasing film thickness. The fact that $D(\epsilon)$ appears in the argument of the exponential may be the reason why T_c oscillations are large relative to other quantum size effects such as resistance oscillations.[6]

The above considerations, although elementary, contain the essential physical features which lead to transition-temperature oscillations. The effect can only be observed if a number of conditions are met. It is necessary that the discrete energy levels be more widely separated than $k_B T$ and $\hbar/\tau$, where τ is the quasiparticle lifetime. These two conditions are easily satisfied in a material such as Sn at low temperatures. There is also a requirement that the roughness of the surface be small compared with the Fermi wavelength of the carriers and that at least some of the scattering be specular in order for the particles to be quantized in the vertical direction.

There is some disparity in the literature as to the precise nature of the requirements on surface roughness and specular reflection. Jaklevic and Lambe[7] observed quantum-size-effect band splittings in polycrystalline normal-metal films using tunneling. They claimed that the quantum size effect in such a "rough" system results from special states in which the thickness, which is an integer multiple of the lattice spacing, is also an integer multiple of half of the Fermi wavelength. If this interpretation is correct a high degree of smoothness of the surfaces of the film may not be necessary. Falk,[8] in his development of Gor'kov equations for superconductors with planar boundaries, appears to minimize the need for specular scattering at the surfaces as a requirement for oscillations in a time-independent problem such as the variation with thickness of the superconducting transition temperature. In his treatment, the surface roughness increases the effective thickness of the film which results in the replacement of the abrupt jump in T_c by a more gradual change. At a value of s of the order of $\epsilon_F/\hbar\omega_D$ the features are predicted to wash out. The latter considerations may explain why the oscillations are actually observed in the polycrystalline films prepared for the present investigations. The limits of observability with use of any of the above criteria were not tested as the oscillatory behavior was only tracked out to a marginal thickness of 129 Å.

It is useful to evaluate some of the parameters of the theory by use of the free-electron model of Sn. The condition for only one subband to be populated is $n < (3\pi/2)/t^3$, where n is the volume electron density of the material. Taking $n = 14.48 \times 10^{22}/\text{cm}^3$ for Sn we find that t must be less than 3.1 Å. It is clear that many subbands will be populated over the thickness range displayed in Fig. 1. The period of the oscillations from Eq. (2) is 1.9 Å. Examination of Fig. 1 indicates that for the thinnest superconducting films the period of oscillation is about 4.0 Å, and becomes slightly smaller at thicknesses in excess of 50 Å where the average value of T_c abruptly becomes larger. This jump may be an artifact of the processing of the sample, as just before the change manifested itself the sample was momentarily heated to 40 K and sat for a full week at 4 K before additional material was deposited on it. Although the normal-state resistance of the sample did not change as a result of this processing, one cannot rule out the possibility that the heating and waiting had an effect on T_c.

There is also some scatter in the regular oscillation of T_c with thickness beyond 50 Å which suggests the possibility of a finer structure than was resolved. It is possible that in this regime the predictions of the free-electron model might be borne out by more detailed measurements. The flat section of the curve above 46 Å is not the result of a processing artifact as all of the films in the thickness range of 47–50 Å were prepared with no processing errors or delays. The existence of this flat section suggests that there may be an additional, larger-scale modulation of the transition temperature with a period of about 20–25 Å. Such a result might then reconcile the present work with that of Komnik and co-workers[3] who reported much larger periods, but much smaller T_c oscillation amplitudes. The resolution of some of these paradoxes will require more detailed work than reported here.

It is clear that the details of these T_c oscillations are closely related to a number of issues that have been considered in recent years, but which were not known when the simple theories were developed some years ago. In particular, for the thinnest connected films, which have thicknesses and areal coverages just beyond the two-dimensional percolation limit, it is fairly certain that the morphology is highly ramified and that the films probably have a fractal structure.[9] The films in this regime are also thin enough to exhibit a topological phase transition.[10] Furthermore their normal sheet resistances are of the order of a few thousand ohms per square, thus being high enough for weak localization to be relevant.[11] The interplay between these phenomena and the quantum size effect has not been treated theoretically. Localization may be the reason the wavelength of the oscillations with thickness is larger than the free-electron wavelength in the thinner films, as the density of delocalized states may be smaller than that of bulk ordered material. Alternatively it is necessary to remember that the thicknesses quoted here are nominal, resulting from a calibration carried out at thicknesses at which the films certainly grow layer by layer. At thicknesses just beyond the critical thickness the film growth mechanism may be a mixture of areal growth of connected islands and layer-by-layer growth.[12] Under such a circumstance the actual increase of the heights of the connected islands may actually be smaller than the nominal increase in thicknesses determined from the calibration. This hypothesis can, with some difficulty, be checked in a detailed way with Auger-electron spectroscopy to measure the change in the areal coverage with nominal thickness.

In summary, we have observed oscillations in the superconducting transition temperature with thickness in thin, polycrystalline Sn films. The period of the oscillations is approximately twice as large as the prediction of the free-electron model. The amplitudes of the oscillations observed in the present work are about a factor of 50 greater than those reported by previous workers, and as such are the most qualitatively dramatic manifestation of the quantum size effect reported in metals thus far.

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