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MULTILAYERED THIN FILM SUPERCONDUCTORS

by

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ABSTRACT

A vapor deposition system for the production of multilayered thin films has been built. The essential idea of the system is to evaporate the materials for both layer types simultaneously and to form the layered structure through the use of a rotating shutter which periodically intercepts one evaporation source and then the other. The system has been used to make Pb-Al layered films. The thicknesses of the individual layers was varied from 60 to 600 Å. Results from a preliminary study of the superconducting properties of the layered films are given.

I. Introduction

A. Enhancing Superconductivity

A superconducting material has zero resistivity in the superconducting state. The superconducting state is stable with respect to a transition to the normal state as long as it is the lower energy state, that is, provided that the critical temperature, T_c , the critical magnetic field, H_c , or the critical current density, J_c , is not exceeded. When enough energy is supplied to a material in the superconducting state either in the form of a rise in temperature, an external magnetic field, or a transport current, the transition to the normal state will occur. The parameters T_c , H_c , and J_c of a superconducting material thus characterize the free energy difference between the superconducting and normal states of that material. By maximizing these parameters the range of conditions over which the superconducting state exists is maximized.

Up to the present time the range of conditions over which the superconducting state has been observed is quite limited; for example, the maximum known T_c is 20.9°K for the compound $Nb_3(Al_{0.8}Ge_{0.2})^1$. Therefore the technological use of superconducting materials is much more limited than one would expect. Sufficient increases of the parameters T_c , H_c , and J_c will lead to big dividends in the technology of electric power transmission, electric motors, high field magnets, and computers.

As a case in point, consider power transmission. Presently electric utilities double their capacity approximately every ten years. It is estimated that by 1990 the demand will be in excess of 10^9 kw and that to meet that demand the electric utilities will

have to install approximately 7.5×10^8 kw of additional generating, transmission, and distribution capacity at an estimated cost of 300-350 billion dollars². The current status of the international studies of superconducting power lines is summarized in a recent article by R. W. Meyerhoff² who also presents a detailed economic analysis of a superconducting line using the material niobium. His conclusion is that for large power levels the capital plus operating cost of a superconducting transmission line is less than 50% of the costs of either resistive cryogenic or conventional underground lines of equivalent power rating. His discussion is based on the known superconducting properties of Nb ($T_c = 9.25^\circ\text{K}$ and $H_c(T=0^\circ\text{K}) = 1,993$ Gauss)³; clearly, if a material with better superconducting properties than Nb could be found, the economic rewards would be even greater. From this one example one begins to see why B. Matthias says that an increase in T_c by a factor of 1.5 over the 21°K of $\text{Nb}_3(\text{Al}_{0.8}\text{Ge}_{0.2})$ would "revolutionize our technology"⁴.

Superconductivity was discovered in 1911 and has been studied extensively since that time. Much is known about the superconducting state. If the reader is unfamiliar with superconductivity, he may consult introductory books such as Lynton⁵ and Rose-Innes and Rhoderick⁶. The fundamentals of superconductivity of bulk materials will not be discussed here.

At the present time superconductors are used in high field magnet technology. The materials used, Nb_3Sn and Nb-Ti, are Type II superconductors. The interaction of a transport current with a magnetic field leads to a Lorentz force which causes a dissipative flux flow condition in a homogeneous Type II superconductor. This dissipative

process is inhibited by the introduction of suitable inhomogeneities which increase the pinning of the fluxoid lattice. The inhomogeneous Type II superconductor is called a hard superconductor. The pinning is very important in determining the critical current and is also very structure sensitive. Thus the critical current of such materials is significantly altered by heat treatment, cold work, and alloying.

Type II superconductors generally have higher superconducting parameters than do Type I superconductors. Thus, the former are more apt to find commercial application. However, although a Type II superconductor can tolerate a large direct current, it is liable to large alternating current losses because the fluxoid lattice is constantly undergoing motion due to the alternating Lorentz force. Hence the Type II superconductor must either be operated at fields below H_{c1} (where the fluxoids do not form) or in a condition of heavy pinning. H_{c1} and the amount of pinning are thus two more parameters to consider when trying to enhance superconductivity.

Because the technological consequences of increasing the superconducting parameters would be so great, a large amount of effort has been devoted towards achieving such increases. The majority of this work has taken place since 1957 when the BCS theory⁷ was published. Unlike previous theories which were phenomenological, the BCS theory was a microscopic theory which explained superconductivity in terms of an electron-phonon interaction leading to an attraction and pairing between two electrons. Many other theories have been brought forth, but actual progress in observing the greatly increased parameters predicted by the theories has been difficult to obtain as Matthias repeatedly points out^{4,8}. Dew-Hughes⁹ makes

the following comments:

Since the discovery of superconductivity in 1911, the number of known superconductors has increased exponentially with time. Maximum known critical temperatures have, however, increased only logarithmically with time over the same period. If the same trend is maintained, it is possible by extrapolation to predict that a material with $T_c = 25^\circ\text{K}$ will be found in about 1990, and 77°K will not be reached until 9000 A.D.!

In view of the slow progress in enhancing superconductivity in bulk materials and of the increasing instability of the new superconducting compounds^{4,10}, other approaches to the problem are in order.

B. Thin Film Superconductors

Bulk superconductors rapidly expend their condensation energy as they attempt to shield out an applied magnetic field (Meissner effect). Specimens of dimensions comparable to the penetration depth, however, can admit flux into their interiors, thus less rapidly using up their condensation energy and so remaining superconducting up to higher fields. Both the London phenomenological theory (based on classical electromagnetism) and the Ginzburg-Landau phenomenological theory (based on a quantum mechanical approach) predict an enhanced critical field H'_c for thin films ($d < \lambda$) of the superconducting material. The relation is of the form:

$$H'_c = k \frac{\lambda}{d} H_c \quad (1)$$

where H_c = critical field of bulk material

λ = penetration depth

d = film thickness

k = a constant on the order of unity for both theories.

A typical penetration depth is of the order of $500\text{\AA}$. The inverse proportionality of H'_c to the film thickness for thin films has been

experimentally verified. See Glover¹¹, p. 183 for results for tin or Lynton⁵, p. 57.

Relation (1) says that as the film thickness approaches zero, the critical field becomes infinite. A fundamental reason why this limiting behavior is not observed is that both of the theories giving rise to (1) were based on the assumption that the free energy in the normal state does not depend on the applied field, H_a ; thus, paramagnetic energy lowering of the normal state, given by $-\frac{1}{2}X_n H_a^2$ where X_n is the normal state paramagnetic susceptibility, was ignored. Since X_n is usually small, the approximation is usually a good one; however, when the critical field becomes on the order of 100 KG, the normal state paramagnetic energy lowering must be considered. This is known as Clogston's criterion¹².

The critical temperature of a well-annealed thin film of a superconductive material is usually close to that of the bulk material. Several mechanisms may cause the critical temperature of a film to differ, however. Among these are: 1) film structure different from that of the bulk, 2) impurities, 3) stress, and 4) proximity effects. Films vapor deposited onto low temperature substrates have a low atom mobility of the condensate so that crystal growth is inhibited leading to a structure different from that of the bulk material. The resulting granular nature of the films frequently causes T_c to rise in superconducting thin films of the soft metals. Hilsch and Buckel¹³ observed T_c 's enhanced from 1.2 to 2.5°K in Al and 1.1 to 8.4°K in Ga. Annealing tends to reduce the enhanced T_c 's towards the bulk value in the cases of both soft and transition metal films. Impurities tend

to reduce T_c , the effect being quite pronounced in the case of good getterer materials like Nb, Ta and V^{14,15}. The effect of stress on critical temperature of thin films has been found to depend on the relative values of the coefficients of thermal expansion of the film and the substrate. The stresses due to differential thermal expansion can reach very high levels in thin films. Enhanced critical temperatures of thin films have been attributed to stress effects^{16,17}. Proximity effects result from intimate contact between a superconductor and another superconductor or a normal metal. T_c was found to decrease in the Pb-Ag system¹⁸, the Sn-Ag system¹⁹, and the Pb-Al system²⁰. Theories to account for these observations have been presented by Douglas²¹ and DeGennes²². However, in 1968 Strongin et. al²³ found that in ultrathin films T_c increases in the Sn-Al system. Their results can be explained by a softening of the phonon spectrum using the theory of McMillan²⁴.

The critical currents of thin films are frequently much higher than the J_c of the bulk superconductors. The critical current density of NbN films at 150 KOe was observed to increase an order of magnitude to 3×10^5 Amps/cm² when the film thickness was reduced from 10^5 Å to 10^2 Å²⁵. In the case of Nb₃(Al_{0.8}Ge_{0.2}) the critical current density of a 2000 Å thick film at 60 KOe was 2 orders of magnitude higher than the J_c of the bulk material²⁶.

It is generally agreed that surfaces contribute greatly to pinning of the flux lines; Lowell²⁷ gives a summary of the experimental evidence. There is no general agreement for the surface pinning contribution^{28,29,30,31,32}. Kramer and Das Gupta argue that crystal defects near the surface are more effective pinning centers than

the same defects in the bulk. At any rate, it seems clear that increased surface to volume ratio leads to increased pinning.

Summarizing, in comparing bulk superconductors to thin films of the same material, one can expect about the same T_c for both and enhanced H_c , J_c and pinning in the thin film.

C. Multilayered Thin Films

A considerable amount of study of thin film two layer composites consisting of a superconducting layer and a normal layer has been done by E. Guyon and the Orsay group on Superconductivity^{33,34,35,36}. The results can be summarized as follows: When a normal metal N is deposited upon a superconducting layer S with good electrical contact between the two, the superconducting properties in S are attenuated while there is an induced superconductivity in N. These phenomena are called proximity effects; other work on proximity effects in two layer films was mentioned in the section on thin films. Proximity effects are related to the "leakage" of Cooper pairs from the producing reservoir S to the unfavorable receiving one N. The thickness of the leakage region is typically 100 to 1000 Å³³.

In 1967, Cohen and Douglass³⁷ predicted on theoretical grounds that a superconducting-dielectric barrier-superconducting (SBS) three layer sandwich would have a greatly enhanced T_c when the S layers were about 60 Å thick and the B layer separating them was about 10 Å thick. Their theory was based on pairing across the dielectric barrier. While the dielectric barrier was predicted to weaken the electron-phonon interaction, it was also expected to greatly weaken or even reverse the sign of the effective Coulomb

interaction thus leading to an enhanced critical temperature. This theory was immediately tested by Strongin et. al.³⁸ using dielectric SiO_2 barriers and the superconducting metals Al, Zn, In, Sn and Pb. Increases in T_c were indeed observed; in Al- SiO_2 -Al sandwiches, T_c 's of as high as 5.7°K were found (the T_c of bulk Al is 1.2°K). The enhanced T_c 's were attributed to the presence of the dielectric layer. However, in further work Strongin et. al.³⁸ found similar enhanced superconductivity in layered metallic films of Al-Cu. Thus the need for the pairing across dielectric barriers in the Cohen-Douglass theory³⁷ was eliminated. The results were explained by the McMillan theory²⁴ which attributes the enhanced T_c to the lowering of phonon frequencies in the layered film structure which leads to increased electron-phonon coupling. The changed phonon spectrum of thin layered films seems to offer an explanation of enhanced T_c 's in "soft metal" films but in other types of films effects such as the density of states and the metal-insulator boundary must be considered.

Gamble et. al.⁴¹ reported layered transition metal dichalcogenide superconductivity when the layers were separated to accommodate organic molecules between them. A theory of these results has been given⁴².

Work on thin film layered composite superconducting materials on cylindrical substrates has been done by D. Snowden^{43,44,45,46} of Gulf General Atomic in connection with work on superconducting power transmission lines. He has worked on methods of preparation of superconducting compounds such as Nb_3Sn and $\text{Nb}_3(\text{Al, Ge})$ by simultaneous vapor deposition of the elements in proper stoichiometric

ratios. Such depositions must be done with carefully controlled evaporation rates⁴⁶. Snowden found that his Nb_3Sn films had superconducting properties characteristic of the bulk materials. However, by forming a composite of layers of Nb_3Sn and a second material to act as fluxoid pinning planes, the critical current density was enhanced by a factor of 2 to 4 over that of the bulk material⁴⁴. Snowden is no longer working on these layered composite materials; the work is being continued by a group under R. H. Hammond at Stanford University⁴⁷.

Preliminary results of an experimental study of pinning effects in superconducting inhomogeneous Pb-Bi films has been given by H. Raffy and J. C. Renard⁴⁸. They prepared films with spatially modulated concentrations of impurities by two source vacuum evaporation. The Pb evaporation rate was held constant and the Bi evaporation rate was a sinusoidal function of time. The resulting Bi concentration in the Pb-Bi alloy films varied sinusoidally along the direction perpendicular to the film plane. The total film thicknesses were typically 60,000 Å and the periods of the concentration variations ranged from 700 to 2000 Å. In parallel magnetic fields Raffy and Renard found that the modulation of concentration produced large increases of the critical current density compared to the critical current density of a homogeneous film. The largest critical current density values corresponded to the largest values of the amplitude of the modulation of concentration. Samples which were homogenized by annealing had critical current densities comparable to those of homogeneous samples. The authors noted that the periods of concentration modulation, which are analogous to the film thick-

nesses of layered films, were of the order of magnitude of the coherence length and penetration depth of the superconducting samples. The coherence length and the penetration depth are two characteristic superconducting lengths and are discussed in references 5 and 6.

L. Dobrosavljevic⁴⁸ has recently published a theoretical paper concerning the critical fields of layered superconducting systems. He considered the layered system as a single but anisotropic superconductor and applied the linear Ginzburg-Landau equation for an anisotropic superconductor which was developed by Wertmaher⁵⁰. An important parameter in the theory is the Ginzburg-Landau coherence length. In the limit of thin (compared to the coherence length) normal layers of thickness d_n and thin superconducting layers of thickness d_s , Dobrosavljevic predicts that $H_{C2}(T)$ is independent of the period $d = d_s + d_n$ and depends on d_s and d_n only by way of the ratio d_s/d_n . He further predicts the same type of H_{C2} dependence for alternating layers of two superconductors with nearly the same transition temperatures.

D. Synthetic Hard Superconductors

In 1962 Bean, Doyle, and Pincus⁵¹ formed a synthetic hard superconductor by forcing molten H_g (a Type I superconductor) in porous Vycor glass. The resulting composite material had a T_c within three tenths of a degree of the critical temperature of bulk mercury but both the critical current density and critical magnetic field were substantially enhanced.

Since that time J. P. H. Watson of Corning Glass Works Research and Development Laboratories has studied the superconducting pro-

perties of metal impregnated porous glass composite materials^{52,53,54,55,56}. Watson formed the porous glass by leaching a phase separated alkali-borosilicate glass to remove the boron rich phase and leave the body porous. When viewed in an electron microscope the resulting glass structure appeared to be a collection of randomly packed 300 Å diameter silica spheres with pores between the spheres. By varying the leaching conditions, samples with pore sizes between 30 Å and 250 Å in diameter were produced. The next step was to develop a filamentary network of metal by forcing molten metal into the pores of the glass under hydrostatic pressure conditions. Watson worked with the metals In, Pb, Bi, Sn, Cd, Ga and alloys of these metals. A typical sample was 10 mm in diameter and 10 mm high⁵². Typical impregnation conditions for In were to squeeze on a porous glass sample surrounded by molten In at 200°C with a pressure of 70,000 psi (4760 atm) which caused about 70% of the pore volume to become filled with indium⁵².

Watson found that his synthetic hard superconductors had substantially increased critical fields and critical current densities when compared to the corresponding bulk metal properties. The critical temperatures were also enhanced somewhat but usually the amount was only on the order of tenths of a Kelvin degree. The large degree of enhancement of the critical field of these porous glass composites became apparent with the early work on indium. For a sample with a 65 Å pore diameter the magnetic field for the normal-superconducting transition was 25,770 Oe at 2.67°K which is some 156 times greater than the 176 Oe critical field for bulk indium at 2.67°K⁵². On this same sample the critical temperature was 4.24°K

compared to the bulk indium value of 3.41°K.

Because he was able to vary the pore size of his porous glass, Watson was able to investigate the dependence of the superconducting parameters upon the size of the filamentary metal network. In general he found that T_c , J_c , and H_c all increased as the pore size decreased, that is, as the strands comprising the filamentary metal network became thinner. The results for the critical field dependence on the pore size are worthy of special attention. An example of such results for indium is shown in Figure 1 (see also Figure 6 of reference 53). For values of the reduced critical temperature below $t = 0.6$ ($t = T/T_c$) the critical field is proportional to the inverse of the pore size. Note that this relation is essentially the same as that of expression (1) which applied to thin films. By assuming that the mean free path was proportional to the pore size, Watson was able to show that his results for $t < 0.6$ were essentially in agreement with the predictions of De Gennes⁵⁷ and Maki⁵⁸, for dirty Type II superconductors. In further work Watson was able to give an explanation for the critical field behavior of his porous glass composites in terms of the granular superconductor theories of Abeles et al⁵⁹ and Parmerter⁶⁰. A granular superconductor is one consisting of small superconducting grains which are separated spatially but connected by electron tunneling.

Working with Pb-Bi-Sb ternary and Pb-Bi binary systems Watson found critical magnetic fields in the neighborhood of 200 K Oe at 0°K. He also observed critical current densities of 2×10^5 A/cm² in low magnetic fields for Pb - 30% Bi samples⁴⁰.

Although almost all of the behavior of Watson's porous glass superconductors was that typical of a dirty Type II superconductor

Figure 1. The critical field H versus sample pore diameter at various values of the reduced temperatures. After Watson, reference 53.

(that is, a hard superconductor), he did note some Type I behavior in samples with the largest pore size⁵³. Such Type I behavior is expected for bulk forms of the metals Watson studied.

E. Choice of System

Of the superconducting parameters it would seem to be most desirable to increase the critical temperature. This is true not only because T_c is the most restrictive condition but also because the critical field and critical current are both decreasing functions of the reduced temperature, τ ($\tau = T/T_c$). However, as mentioned previously, the progress in enhancing T_c has been very slow in comparison to progress in raising the other superconducting parameters. Matthias⁴ offers a rather convincing fundamental reason why T_c is proving so difficult to enhance beyond the present peak of 21°K. In the phonon mechanism of the BCS theory, superconductivity arises from a deformation of the crystal lattice by a conduction electron. Large interactions between the electron and the phonon, which would lead to a high T_c , require a very deformable lattice. Unfortunately, a very deformable lattice tends to be unstable. The instability of the high temperature superconducting compounds was encountered some time ago and has proven to be a major stumbling block in the search for higher T_c 's^{4,10}. Matthias, the leading expert in the field of enhancing T_c by the synthesis of new metastable phases, feels that higher T_c 's will be found but that the increase will be limited to 5 to 10°K unless new mechanisms for superconductivity are found⁴.

Several other mechanisms for superconductivity have been proposed although they have not yet been observed. These include the

exciton mechanism proposed by Ginzburg^{61,62,63} and Bardeen et al⁶⁴ and the organic mechanisms of Little⁶⁵. Metallic hydrogen may be a superconductor with a high transition temperature^{66,67}. In addition, the very recent work at the University of Pennsylvania indicates that some organic solids have some but not all of the properties associated with superconductivity⁶⁸.

McMillan³² has predicted a maximum value of T_c for the phonon mechanism of superconductivity to be 40°K (in thin films of V_3Si). Even if this value could be obtained, it is not clear how large the economic rewards would be in some applications. For example, analysis at Westinghouse in connection with the design of a superconducting 5 MW generator has shown that the operational costs of He and H_2 cooled machinery are nearly the same⁶⁹. Thus, for significant economic savings T_c would have to be raised to liquid nitrogen temperatures. Based on progress to date such a large enhancement of T_c seems unlikely.

In view of the situation concerning enhancing T_c and recalling the large improvements in the other superconducting parameters for thin films and synthetic hard superconductors, it seems more promising to concentrate on the improvement of the latter parameters.

Watson's work on porous glass superconductors is highly interesting and promising in that the parameters depend inversely on the pore size. However, the pore size is limited to values between 29 Å and 250 Å. There are several other drawbacks to this approach as well. The uniformity of the pore size caused problems for Watson when he attempted to study the critical current density as a function of pore size⁵⁴. The nature of the superconducting normal interface is complicated. And beyond these drawbacks to a scientific study

of porous glass composites; problems with the flexibility of the fibers can be expected to complicate the technological applications of such materials.

On turning to thin films one can adopt the point of view that each thin film is in fact a two component sandwich consisting of the film and its substrate. By stacking many such sandwiches on top of each other while preserving the enhanced superconductivity properties, one can make three dimensional composite materials with enhanced superconducting properties compared to the bulk materials. In the course of a study of spinodal decomposition Cook and Hilliard developed a method of producing many hundreds of alternating layers of two materials by simultaneous vapor deposition of the two components^{70,71,72}.

Studying thin film composites has several advantages over the study of porous glass. The size of the layers can be more easily controlled and varied. Cook and Hilliard were able to make individual layers as thin as $7 \text{ \AA}$ in the Au-Ag system⁷⁰. The superconducting-normal interface is planar so that interpreting the results from a basic studies point of view is not as complicated. The effects of various substrates and substrate temperatures can be investigated relatively easily. Many types of materials can be vapor deposited so that possible systems of study are not limited to glass and the soft metals which can be squeezed into the glass. And from a technological point of view, a wire or tape of a multilayered composite materials can be easily fabricated. By employing a system of differentially pumped vacuum deposition systems such a composite could be produced continuously. The technology of similar continuous

evaporation systems has already been developed⁷³. Thin films also have the advantage that extreme brittleness can be controlled by choosing a backing which has a larger coefficient of thermal expansion than the brittle component and which therefore will put the superconductors in compressive stress upon cooling. The Nb₃Sn tape developed by Hanak^{74,75} of RCA for use in windings of superconducting magnets is produced by continuous deposition onto an appropriate substrate to overcome brittleness problems.

The multilayer approach also has the advantage that such layered systems are those for which Ginzburg's theoretical exciton mechanism of superconductivity is expected to be observed^{61,62,63}. Bardeen et al⁶⁴ have also proposed a model for the exciton mechanism and are hoping to observe it in metal-semiconductor layers which are in intimate contact so that substantial tunneling can occur.

Having decided to study multilayered superconducting films using an experimental production technique similar to that of Cook and Hilliard, the next decision was which system to study. The Pb-Al system was chosen for several reasons. First, it was found that Pb could easily be evaporated at controlled rates with a resistance heated source and Al could be evaporated easily and smoothly with an electron beam gun. Second, Pb and Al are almost totally immiscible in each other at room temperature so that a layered structure is not likely to rapidly degrade by diffusion. Third, Pb-Al two layer structures have been studied in connection with proximity effects^{76,77}. Thus, a possible base for theoretical analysis was available.

The SiO₂-Pb system was another attractive system. SiO₂ was

readily evaporated with an electron beam gun and the prospect of comparing the characteristics of an SiO_2 -Pb layered film with those of Watson's lead porous glass superconductors was alluring.

The objectives of the present study were to design and build a two source vapor deposition system capable of producing multi-layered thin films, to produce such films in a controlled manner, and to study the superconducting properties of the films.

II. Design & Construction of Vapor Deposition System

A. Scheme of Evaporation

The essential idea of the vapor deposition system is to evaporate materials for both types of layers simultaneously. A rotating shutter is used to alternately mask one evaporation source and then the other. This scheme is patterned after that used by Cook and Hilliard to make alternating layered films of silver and gold^{70,71}. Their system employed two electrical resistance heated evaporation sources. Alumina coated tungsten baskets were used and typical evaporation rates ranged from about 60 to 600 Å/min.

The present system uses one electrical resistance source and one electron beam gun source. The latter is a very versatile and powerful method of evaporation capable of evaporating almost any material⁷⁸. The resistance source is limited to materials which are relatively easy to evaporate. The other major difference between the present system and that of Cook and Hilliard is that here two quartz crystal thickness monitors are used to measure the amount of materials vapor deposited.

B. Vacuum System

The basic vacuum system is essentially an Edwards "Speedivac" 4" pumping system. The major components of this system are a mechanical roughing pump, a high speed oil diffusion pump, a freon cooled Chevron baffle, and a liquid nitrogen cooled cryotrap. The mechanical pump is a Model ED 250, 2 stage pump with an ultimate vacuum of 1×10^{-3} Torr. This pump is used primarily as a backing or fore pump for the diffusion pump which is a Model E04. Cooling water is required for the diffusion pump. The unbaffled pumping speed is 600 liters/sec

and the ultimate vacuum is 10^{-10} Torr. The Chevron baffle is a Model CB4 and includes a freon cooled refrigeration unit capable of attaining temperatures less than -15°C . At such temperatures the chevrons provide an effective baffle for trapping backstreaming oil vapor thus preventing the vapor from entering the chamber. The liquid nitrogen cryotrap is mounted directly above the baffle and the diffusion pump and provides the dual functions of helping prevent diffusion pump oil vapor from backstreaming into the vacuum chamber and of pumping out condensable vapors which may be present in the vacuum chamber.

Measurement of the pressure in the vacuum chamber is accomplished by the use of a Model 1 Control Unit and its associated Pirani and Ionization Gauges. Pressures in the range of 1 Torr to 10^{-8} Torr can be measured. The Pirani Gauge Head, Model M6A, is positioned in the backing line and measures rough pressures in the range from 1 Torr to 10^{-3} Torr. The ionization gauge head, Model IG5M, is mounted on a 2 3/4" conflat Flange and bolted to a mating flange on the feedthrough collar of the vacuum chamber. Pressures from 10^{-3} Torr to 10^{-8} Torr can be measured with the ionization gauge.

The 18" diameter stainless steel baseplate of the vacuum chamber has a rectangular groove in it in which fits the Viton O-Ring which forms the seal between the baseplate and the feedthrough collar. The latter is constructed of stainless steel and contains 6 ports, two with 4" conflat flanges and 4 with 2 3/4" conflat flanges.

The system as described thus far was present at the start of this study. It was essentially in working condition except that new roughing lines had to be made and seven holes in the welds of

the feedthrough collar had to be found and filled. The rest of the system to be described below was built in the course of this study.

An 18" diameter 18" high pyrex glass cylinder with ends open and ground for vacuum service and two Viton L-shaped gaskets provide a demountable vacuum chamber. The 20" diameter top plate of the chamber is made of $\frac{1}{2}$ " thick stainless steel and has a smooth surface on the lower side so that a vacuum seal with the L-gasket on top of the glass cylinder can be obtained. Due to the limited number of ports on the feedthrough collar, the top plate was designed with four additional ports on the ends of which are 2 $\frac{3}{4}$ " conflat flanges. There is also a 1" hole in the top plate in which a hand operated rotary motion feedthrough is located. An implosion shield consisting of a steel framework and a wire mesh surrounds the glass cylinder. The various components of the vacuum system are shown in Figures 2, 3, 4, 5 and 6.

C. Evaporation Sources

1) Resistance Source

The resistance source consists of a tungsten wire basket and an aluminum oxide crucible as shown in Figure 7. Power for the heating of the filament is supplied by a 20 amp Powerstat variable transformer whose output is passed through a 6 volt, 250 amp transformer. Current is transferred from the transformer to the feedthrough collar by two $\frac{1}{4}$ " copper rods and into the vacuum chamber by a Varian 954-5008 dual medium current feedthrough mounted on a 2 $\frac{3}{4}$ " conflat flange. These components appear on Figures 2, 5, and 6. Inside the vacuum chamber the current feedthroughs are suitably extended so that when the filament is held between the two the

Key For Components In Figures 2,3,4,5 and 6

- A) Thickness Monitor
- B) Recorder
- C) Electron Beam Gun Power Supply
- D) Control Module for Electron Beam Gun
- E) Powerstat for Resistance Source
- F) Transformer for Resistance Source
- G) Copper Rods to Resistance Source
- H) Thickness Monitor Transducer
- I) Water Cooling Lines for Thickness Monitor
- J) Tantalum Heat Shield Enclosing Resistance Source
- K) Stainless Steel Funnel
- L) Stainless Steel Wall
- M) Bearing for Shutter Shaft
- N) Electron Beam Gun
- O) Water Cooling Line for Electron Beam Gun
- P) High Voltage Feedthrough for Electron Beam Gun
- Q) Signal and Water Feedthrough for Thickness Monitor Transducers
- R) Motor to Drive Pinwheel
- S) Variable Speed Control for Pinwheel Motor
- T) Medium Current Feedthrough for Resistance Source
- U) Copper Coil Cold Trap
- V) Sample Holder Cyostat
- W) Air Admittance Valve
- X) Implosion Shield
- Y) Liquid Nitrogen
- Z) Vacuum Gauge Control Unit

AA) Liquid Nitrogen Dewar

BB) Feedthrough Collar

CC) Top Plate Assembly

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7. Tungsten basket and crucible of the resistance source.

evaporation source is at its proper location. See Figure 3. To obtain higher evaporation rates a tantalum radiation heat shield surrounds the basket and crucible. In addition a stainless steel cylinder is located directly above the source. This acts as a funnel to channel a greater percentage of the evaporate upwards. See Figure 3.

2) Electron Beam Gun Source

The second source is a Varian 980-1105 6KW electron beam gun. A beam of electrons is produced by a hot tungsten filament held at a high negative potential and is accelerated into a grounded crucible. The beam is magnetically deflected 210° from its point of origin into the crucible by a permanent magnet. Beam sweep is accomplished manually or automatically by an electromagnet assembly. The electron beam gun can achieve temperatures in excess of 3500°C (the gun is water cooled so it does not melt itself) and evaporates all types of materials placed in its crucible - refractory, dielectric, magnetic, and conductive. See Figures 3 and 8.

The power supply for the electron beam gun is a Varian 98-1123 consisting of the power supply itself and a small remote control module. The latter allows the operator to adjust the filament current and the beam sweep. In the automatic mode the beam is moved about the crucible at a fast or slow (1 or 20 Hz) rate while in the manual mode the operator has full control of the beam position.

The power supply for the control module (see Figure 6) is connected to the gun via two separate feedthroughs. One is Varian 954-5012 8 pin instrumentation feedthrough which allows control of the beam sweep. The other is a specially made feedthrough which has

Figure 8. Schematic of the electron beam gun.

two water and two high voltage feedthroughs all mounted on the same 4" conflat flange. Due to the limited number of ports on the feedthrough collar, this special feedthrough was designed to allow the other 4" flange to be left open. Thus, a second electron beam gun can be added to the system with a minimum of disruption to the present system. (The present electron beam gun only uses 3 of the 8 pins of the instrumentation feedthrough so that a second gun can use the remainder.)

It is very important that the electron beam gun be sufficiently cooled. As a safeguard, a water flow switch is connected in series with the power supply to form an interlock switch which is closed when sufficient cooling water passes through the gun.

D. Thickness Monitors

Two Kronos QM-320 Thickness Monitors are used to measure the amount of materials vapor deposited. See Figure 6. These monitors operate on the principle that the frequency of oscillation of a quartz crystal is influenced by the mass of materials deposited on its surface. More specifically, the period of oscillation, or reciprocal of frequency, changes in a manner that is directly proportional to the change in mass. Therefore, if the area of deposition on the crystal is clearly defined, the density of the deposit is known, and the proportionality constant is established, the thickness of deposition can be quantitatively and directly measured by noting the resulting change in period of oscillation. The resolution of the monitors is $1 \text{ \AA}$ on the most sensitive range. An analog output of 0 to 5 volts allows the thickness to be displayed on a recorder as well as on the four digit thickness display Nixie tubes.

The monitor heads are located in the vacuum chamber at approximately the same distance from the evaporation source as is the substrate. Cooling water is required for the monitor heads; the cooling lines for both are connected in series. The coaxial feedthroughs for transmitting the thickness signals out of the vacuum system and both water feedthroughs are on the same 2 3/4" conflat flange so that only one of the ports on the feedthrough collar is needed for operation of the thickness monitors.

The lifetime of each quartz crystal is limited and spent crystals must be periodically replaced. A crystal test function is built into the thickness monitor allowing the operator to know how much life is left in the crystal simply by depressing a switch.

E. Sample Cryostat

The films are evaporated onto a holder which is about 6" above the evaporation sources and centered between them. The holder is designed as a cryostat which is used to cool the sample holder with liquid nitrogen during deposition. The cryostat is welded onto a 2 3/4" conflat flange which is bolted onto a mating flange on one of the top plate ports. See Figure 4. A schematic of the cross section of the cryostat is given in Figure 9; note that the space between the tube holding the liquid nitrogen and the outer support tube is part of the vacuum chamber so that heat transfer is reduced.

F. Other Components

A polished stainless steel wall is mounted onto the baseplate of the vacuum system and functions primarily to keep the two evaporation sources separated. The wall also blocks the line of sight between the thickness monitor for one evaporant and the evaporation

Figure 9. Sample Cryostat

source of the other. A stainless steel block is mounted on top of the wall which serves as a bearing for the lower of the pinwheel shaft. See Figure 3.

The pinwheel is made of stainless steel shim stock and is driven from above by a small motor with a variable speed control. See Figure 2. The rotary motion is transmitted into the vacuum chamber via a Varian 954-5026 magnetically coupled feedthrough which is mounted onto one of the ports on the top plate.

A sample shield is located inside the vacuum chamber so that the sample can be shielded from evaporants during warm up periods. The shield is driven by hand by a rotary motion feedthrough which can be raised and lowered as well as rotated. This feedthrough is mounted on the 1" hole in the top plate.

G. Coldtrap

In order to keep the pressure low during evaporation a large coldtrap is located inside the vacuum chamber which helps freeze out evaporant that does not hit the sample substrate. This trap consists of 18 turns of 3/8" diameter copper tubing wound into a coil. See Figures 2 and 4. During evaporation the coldtrap is filled with liquid nitrogen which is transmitted by two feedthroughs mounted onto the remaining two ports on the top plate. These feedthroughs are designed similarly to the sample cryostat; that is, two coaxial tubes are welded into a conflat flange with the space between them evacuated to reduced heat transfer. See Figure 10.

Figure 10. Liquid nitrogen feedthroughs

III. Experimental Procedures

After construction of the vapor deposition system, the first step was to test the two evaporation sources for constancy of evaporation rates with time for given power inputs. It was found that the resistance source evaporated lead at rates from 500 $\text{\AA}/\text{minute}$ to 5000 $\text{\AA}/\text{minute}$. The rates were measured with the thickness monitor sensor head located 7" from the source; approximately the same source to substrate distance was used later during evaporation of the multilayered films. The evaporation rates were controlled by the setting of the Powerstat and were found to be constant with time to within several percent after a stabilization period of a few minutes. The evaporation rate for a given filament current, that is, a given input power, for the electron beam gun was found to vary considerably with time. However, by manually adjusting the filament current knob on the control module of the electron beam gun power supply constant evaporation rates were obtained. Aluminum was evaporated at rates varying from 600 $\text{\AA}/\text{minute}$ to 6000 $\text{\AA}/\text{minute}$. The 6000 $\text{\AA}/\text{minute}$ rate of evaporation from the electron beam gun was obtained at filament currents of about 0.55 amps; the gun is capable of filament currents of 1.0 amp.

Other materials in addition to Pb and Al were evaporated. Tin was found to evaporate at constant rates from the resistance source although the rate for a given power setting was lower than the rate for lead at the same power. Niobium, tin, and silicon dioxide were evaporated from the electron beam gun. As with aluminum, the filament current had to be manually adjusted in order to obtain constant evaporation rates. Rates of evaporation of SiO_2 were found to be dependent upon the type of charge placed in the electron beam gun

crucible. Higher rates were obtained using a powdered charge compared to the rates using a charge comprised of chunks of SiO_2 . Nb was the most difficult material to evaporate. The power requirements were much higher; the evaporation rates attained were roughly 1/5 of the rates for Al. A more serious problem when evaporating Nb was that trapped gases escaped at irregular intervals causing the evaporation rate to be uneven. The latter problem was partially solved by 'soaking' the charge at low filament currents thus allowing some of the trapped gases to escape before evaporation.

Although the source to substrate distances and the source to thickness monitor sensor head distances were nearly the same, it was necessary to calibrate the deposition system so that the relationship between the film thickness deposited on the thickness monitor sensor head and the film thickness on the substrate mounted in the sample cryostat could be determined. This calibration was obtained by the following procedure: a thin layer of Al was evaporated onto a sapphire substrate. The Al coated substrate was then partially masked and a layer of Pb evaporated. The thickness of the Pb layer as measured by the thickness monitor was noted. The resulting film on the substrate thus had a step in it and the thickness of this step could be determined through the use of the interference microscope. When two reflecting surfaces are brought into close proximity, interference fringes are produced. The fringes show a displacement as they pass over the step of the film which is directly related to the height of the step; thus the method provides a direct determination of the film thickness. The principles and techniques of the use of interference fringes to measure film thickness are described elsewhere^{79,80}. An example of the fringes observed in the course

of the present study is given in Figure 11. The actual Pb film thickness on the substrate was thus measured directly and compared with the thickness as measured on the Pb thickness monitor. The procedure was then repeated using a layer of Pb upon which a layer of Al was evaporated with a step in it so that the Al thickness could be calibrated. After the system was calibrated it was very important that the geometry not be changed; otherwise the system would have required another calibration.

The substrates used for the multilayered film depositions were sapphire discs 1" in diameter and .023" to .026" thick. The substrates were supported against the copper block of the cryostat by the copper nut of the cryostat. A thin coating of thermal grease was used to ensure good thermal contact between the block and the substrate. The substrate was masked so that the multilayered thin films produced were 1/2" long by 1/8" wide and had 4 narrow extensions on one side to facilitate attaching leads onto the specimen during subsequent testing.

The details of procedures during the evaporation runs are given in Appendix A. The thicknesses of the Pb and Al layers were controlled by varying the evaporation rates and the speed of the rotating shutter. Typical evaporation times varied from 5 to 10 minutes resulting in total film thicknesses of from 10,000 Å to 35,000 Å. Layer thicknesses were varied from 60 Å to 600 Å; the sum of the Pb layer thickness and the Al layer thickness, which will be referred to as the period of the specimen, was varied from 160 Å to 1000 Å. The rates of evaporation, shutter speeds, layer thicknesses, periods, and ratios of layer thicknesses for various specimens are given in

Figure 11. Interference Fringes.

Appendix B. The films there are all Pb-Al layered films and were made with the sample cryostat at liquid nitrogen temperature. The only exceptions to the latter statement were specimens 48 and 50 which each had a layer of aluminum evaporated onto them at room temperature before the multilayered structure was evaporated with liquid nitrogen in the cryostat. During evaporation of specimen 49, no attempt was made to control the cryostat temperature; it is safe to presume that the substrate was initially at room temperature and that its temperature rose somewhat during deposition. The modifications to the evaporation procedure for these three specimens were made in an attempt to obtain better film to substrate adherence. Whether better adherence was in fact obtained is not clear.

Several Pb-SiO₂ multilayered films were produced which had thickness characteristics similar to those of the Pb-Al films listed in Appendix B.

During evaporation of the multilayered films the pressure in the vacuum chamber was in almost every case between 2×10^{-5} and 5×10^{-5} Torr regardless of the base pressure of the vacuum system before the evaporation began. The pressure rise to this level was primarily associated with the electron beam gun; it was possible to evaporate Pb alone from the resistance source at pressures of less than 1×10^{-6} Torr. During initial evaporations the pressure rose to the 10^{-4} Torr range. Installation of the copper coil coldtrap (See Figures 2 and 4) which was filled with liquid nitrogen during subsequent evaporations had the effect of reducing the pressure during evaporation by roughly an order of magnitude.

The superconducting properties of the specimens were tested at the National Magnet Laboratory located on the campus of the

Figure 12. Experimental setup at the National Magnet Laboratory.

Massachusetts Institute of Technology in Boston. The experimental apparatus used there are shown in Figure 12. The magnets used were capable of generating fields of up to 150 KGauss. The facilities also include a pumping and regulating system with which it was possible to pump on the helium dewar to attain temperatures of as low as 1.4°K. At temperatures of above 1.8°K the regulator easily controlled the temperature to within 0.02°K for time periods of about 30 minutes. During testing at zero and small magnetic fields both the vapor pressure of the helium in the dewar and germanium resistance thermometers were used to measure the specimen temperature; the agreement between the two was excellent. At higher fields only the vapor pressure could be used to measure temperature since the germanium thermometer is adversely affected by a magnetic field greater than 10 KGauss⁸¹.

The thin film specimens were mounted in a specially designed holder which allowed two specimens to be placed in the dewar at one time. This holder consisted essentially of a copper block on the end of a stainless steel tube through which the lead wires were run. The top of the tube was filled with epoxy which formed a vacuum tight seal so that the dewar could be pumped on to attain temperature less than 4.2°K. The flange for the dewar top was modified by adding a Quik-Connect so that the entire holder could be raised or lowered thus ensuring that the specimen was located in the homogeneous part of the magnetic field. A close-up view of the copper block end of the specimen holder with a specimen mounted in it is shown in Figure 13. The germanium thermometers were mounted in holes in the sides of the copper blocks and packed with thermal grease to ensure good thermal contact.

Figure 13.

The resistances of the specimens were measured by attaching four leads, two for current and two for voltage. Considerable difficulty was encountered in keeping the wire leads fastened to the specimen as the specimen was cooled in liquid helium. The problem was due basically to poor adhesion between the substrate and the film. In the first attempt #20 copper wires were attached to the specimen by the use of silver paint but during cooling thermal contraction caused the parts of the film directly under the wires to break away from the substrate thus causing open circuits. The problem was partially overcome by using much finer #34 copper wires and later almost totally solved by using 5 mil gold wires.

The transition temperatures of the specimens were determined by measuring the resistance as a function of temperature. Critical fields were observed by measuring the specimen resistance while sweeping the magnetic field. The fields were swept in both increasing and decreasing directions. The transition between the normal and superconducting states was usually marked by a sharp change in specimen resistance. Critical currents were measured in zero magnetic field by applying enough current to the specimen to drive it normal. Tests were also run in various fixed magnetic fields in which the current was varied upwards until the specimens were driven normal and then downwards until they became superconducting again.

IV. Results and Discussion

A. Critical Temperatures

The critical temperatures of the multilayered films are given in Table 1. The values ranging from 1.54°K to 2.27°K are accurate to within .03°K. The values for specimens 47 and 48 were obtained by extrapolation of critical field versus temperature curves (see for example Figure 15) and are less certain. Note that Table 1 states that the critical temperature of specimen 48 is greater than 5.4°K. This was measured by pressurizing the dewar. It is worth noting that the critical temperatures of pure, bulk Al and Pb are 1.2°K and 7.2°K respectively.

The critical temperatures were measured in zero magnetic field both as the temperature was being increased and as it was being decreased. The transition temperatures were found to be 0.01°K to 0.03°K less when measured while the temperature was decreasing as compared to when the temperature was increasing. See Table 2 for data for sample 38. Table 2 shows that in addition to being weakly dependent on the direction of temperature change, the transition temperature depends on the current being passed through the specimen. As expected⁸⁵, the transition temperature increases with decreasing current. Again the dependence is weak; at low enough currents the dependence should become immeasurably small. The more accurate values of the transition temperature are obtained with smaller measuring currents⁸⁶.

Table 1 lists thickness characteristics and room temperature resistances of the films as well as critical temperature. There appears to be no quantitative correlation between the various

Table 1. Critical Temperatures of Multilayered Thin Films

Sample	Ratio d_{Al}/d_{Pb}	Period $d_{Al}+d_{Pb}$	d_{Al}	d_{Pb}	Total Thickness	T_c	Room Temp Resistance
		Å	Å	Å	Å	°K	Ohms
28	2.4	445	311	130	27,800	1.54	0.4
29	1.1	7.6	368	348	35,800	1.81	2.4
32	1.7	626	395	231	34,400	1.86	0.6
33	2.2	465	318	147	27,950	2.03	1.6
34	0.6	411	151	260	21,450	1.92	20
37	1.3	162	90	72	13,130	1.76	38
38	0.7	401	99	150	14,530	2.27	21
47	0.1	703	83	620	24,720	>4.2*	260
48	0.3	694	173	521	17,340	>5.4**	8
50	0.6	187	72	115	20,980	2.01	8.8

* Determined by extrapolation to be 6.8°K

** Determined by extrapolation to be 6.0°K

Table 2. Critical Temperature for Specimen 38

Temperature	Current(Amps)	T_c (°K)
Decreasing	1×10^{-3}	2.18
Increasing	1×10^{-3}	2.18
Decreasing	1×10^{-4}	2.25
Increasing	1×10^{-4}	2.28
Decreasing	1×10^{-5}	2.27
Increasing	1×10^{-5}	2.29

parameters of the Table. However, the qualitative relationship between the ratio of the layer thicknesses and the critical temperatures is what one would expect. As shown in Figure 14, as the thickness ratio d_{Al}/d_{Pb} becomes small (that is, the film is mostly lead) the transition temperature increases and approaches the $7.2^{\circ}K$ value which one would expect for a film comprised totally of Pb. Similarly, as the ratio becomes large, the transition temperature decreases towards the $1.2^{\circ}K$ value which would be expected for aluminum films.

B. Critical Fields

It is well known^{5,6} that the critical field of a superconductor is strongly dependent on temperature and current. Thus when talking about critical fields it is important to specify the temperature (or the reduced temperature which is defined as $t = T/T_c$) and the current in order to be able to make meaningful evaluations. Table 3 lists typical values of the critical fields of the films along with the conditions at which the values were measured. The critical fields of bulk Al and Pb (at $t=0$) are 99 gauss and 803 gauss respectively⁵.

Note that the critical fields were determined both as the field strength was being swept upwards and as it was being swept downwards. The curves were almost reversible, the difference being that the critical fields were often slightly higher when determined in an increasing field as compared to a decreasing field. Recall that in the determination of critical temperatures a similar result was found; namely that the value of T_c was found to be higher when the temperature was being increased as compared to when it was being

Figure 14. Critical temperatures versus layer thickness ratios.

Table 3. Critical Fields of Various Specimens

Sample	Temp. °K	$t = \frac{\text{Temp}}{T_c}$	Test Current Amps	Critical Field Kilogauss	
				Up*	Down*
33	1.89	0.93	1×10^{-5}	4.0	3.0
	1.89	0.93	1×10^{-6}	3.0	2.0
	1.97	0.97	1×10^{-6}	1.6	1.6
	1.97	0.97	1×10^{-7}	1.3	1.3
38	1.86	0.82	4×10^{-3}	4.5	4.0
	1.86	0.82	6×10^{-3}	4.0	3.8
	1.86	0.82	8×10^{-3}	3.4	3.3
	1.86	0.82	10×10^{-3}	3.0	2.8
47	4.20	0.62	1×10^{-3}	18.5	18.0
	4.20	0.62	1×10^{-7}	30	30
	2.60	0.38	1×10^{-3}	26	25
	2.60	0.38	1×10^{-7}	38	38
	1.60	0.24	1×10^{-3}	30	29
	1.60	0.24	1×10^{-7}	45	--
48	4.20	0.70	1×10^{-3}	4.3	4.2
	4.20	0.70	1×10^{-5}	5.8	5.5
	1.73	0.29	1×10^{-3}	6.0	6.0
	1.73	0.29	1×10^{-4}	8.8	8.7
34	1.60	0.83	1×10^{-5}	15	15
	1.60	0.83	1×10^{-6}	18	18

* Up or down refers to the direction in which the field was being swept during the observation of the transition.

decreased. Examination of Table 3 shows that the difference in the two determinations of the critical fields often becomes smaller or disappears altogether as smaller test currents are used (at a given value of the reduced temperature, t).

The critical fields listed in Table 3 vary widely among the specimens. Comparing the critical fields with the film thickness characteristics of the various films (Table 1) leads to no apparent correlations among the various parameters. There is a relationship between the room temperature resistance of the film and its critical field. In general, as the resistance goes up the critical field increases. This result was to be expected; Berlincourt and Hake⁸⁷ found that the critical fields of various materials depended directly upon the normal state resistivity. In addition, the critical field in the Ginzburg-Landau theory^{5,6} depends on the parameter K which in turn depends on the normal state resistivity of the specimen. The trend observed here that the critical field increases with increasing normal state resistance is the qualitative relationship which is to be expected; quantitative predictions would require further work.

It is well known^{5,6} that the critical field of a superconductor as a function of temperature follows the approximate relationship:

$$H_c(T) = H_0[1-(T/T_c)^2] \quad (2)$$

where $H_c(T)$ = critical field at temperature T

H_0 = critical field at $T=0$

T_c = critical temperature of the superconductor.

Results obtained in the present study for the temperature

dependence of the critical field of Sample 47 are given in Figure 15. Note that the critical field depends on the current being passed through the specimen. The curves are of the expected shape. By extrapolating the curves to zero temperature and zero field, one can obtain values of H_0 and T_c which can then be used in relation (2) along with the measured data points. For example, if the curve for $i=1 \times 10^{-3}$ in Figure 15 is extrapolated, H_0 and T_c can be determined to be 31 KGauss and 6.8°K. Using these values and the data points shown, one finds that relation (2) is obeyed to within about 5%.

Figure 15 is essentially a phase diagram. The material is in the superconducting state below the curve and in the normal state above the curve.

C. Critical Currents

The currents required to drive the superconducting films into the normal state were found to be low. For example, at a temperature of 1.91°K ($t=.94$) and zero magnetic field, sample 33 was driven normal by a current of 8×10^{-3} Amps which corresponds to a critical current density of only 90 Amps/cm². Critical current densities of from 10 to 100 Amps/cm² were typical of the films studied in this work. These values are very low compared to those of Watson's porous glass superconductors⁵⁵ (10^3 to 10^5 Amps/cm²) and those of Raffy and Renard's⁴⁸ spatially modulated alloy films (10^5 Amps/cm²). Sufficient data was not obtained to draw conclusions on the critical current density as a function of the film thickness parameters for the multilayered Pb-Al films.

A very interesting curve emerged from experiments on sample

Figure 15. Critical field versus temperature for specimen 47.

48 in which the critical current was determined as a function of various constant applied magnetic fields. The results are shown in Figure 16. Note the existence of the peak in J_c at a field of 0.25 KGauss. This appears to be a manifestation of the so called "peak effect" (see for example Reference 88). It is interesting to note that Raffy and Renard⁴⁸ observed the peak effect in their spatially modulated layered films which are fundamentally similar to the Pb-Al multilayered films of the present study. Explanations of the peak effect in terms of flux pinning have been given by Webb⁸⁹ and Kramer⁸⁸. However, it should immediately be pointed out that the observation of the "peak effect" here as shown on Figure 16 depends really on only one experimental data point. Even though the author has no grounds to doubt the validity of that data point, more data should be acquired before further consideration of the "peak effect".

An anomaly appeared in a few of the tests on sample 48. While holding the field fixed and sweeping the current to determine the critical current, the curve took the peculiar form shown in Figure 17 which is a reproduction of the original data. Note the easily discernable existence of two nearly vertical lines on each curve. These would seem to indicate two transitions. This strange behavior was observed only for this specimen and only at fields of 1.5 KG (as in Figure 17), 1.25 KG, and to a lesser extent at a field of 1.75 KG. The author has no convincing explanation of this behavior; to the best of his knowledge there was nothing different from the rest of the tests on this sample or the tests on the other samples which would account for the strange observa-

Figure 16. Critical current density versus magnetic field for specimen 48.

Figure 17. Reproduction of original data for specimen 48.

tions in this particular case. One possible explanation is that the peaks are associated with heating effects. Professor E. Kramer has observed similar effects while working with niobium; based on his experience the double peaks are quite possibly due to contact heating of the film - silver paint - gold wire junctions.

No measurements of the superconducting properties of the Pb-SiO₂ films were obtained. Not too much effort was expended in trying to obtain the data due to a shortage of magnet time at the National Magnet Laboratory. This shortage of time also prevented testing of some of the Pb-Al films which are listed in Appendix B.

V. Suggestions for Future Work

A. Improvement of the Deposition System

1) Feedback System to Control Deposition Rates

The rates of evaporation could be more accurately controlled by the use of electronic feedback systems. For the electron beam gun source, which needs to be continually adjusted to keep a constant evaporation rate, the basic idea of an electronic feedback system could be simple. The 0 to 5 volt analog output from the rate monitor can be differentiated by an operational amplifier and the resulting signal used to drive the electron beam gun power supply whose circuits include provision for an external control signal. While the rate of evaporating lead from the resistance source is constant to within several percent, the deviation could be reduced to about one-half of one percent by using a silicon controlled rectifier feedback system similar to that of Cook⁷¹.

2) Sample Cryostat

The present sample cryostat could be modified to allow deposition of several samples during a given pumpdown cycle. Suitable positioning of the sample mask would then allow the several samples to be deposited simultaneously or sequentially. Another improvement over the present cryostat would be to install on it a simple resistance heater and a temperature measuring device which would allow the effect of the substrate temperature on the properties of the resulting films to be investigated.

3) Improved Pressure During Deposition of Films

Reduction of the pressure inside the vacuum chamber during deposition is an obviously desirable improvement. It could be

accomplished by increasing the pumping capacity of the system. One way to do this without adding any new pumps would be to remove the chevron cooled baffle which is located immediately above the diffusion pump. The liquid nitrogen cold trap would still be left in the system to cut down on back-streaming oil vapor from the diffusion pump. Another approach to reducing the pressure during evaporation would be to make a second cold trap similar to the coil suspended from the top plate which was found to have a highly beneficial effect on reducing the pressure. The second cold trap would also be made from copper tubing and would be fitted below the pin-wheel along the baseplate of the vacuum chamber. It is worth noting when discussing improved vacuum of the system that several components in the system, such as the thickness monitor heads and the electron beam gun magnets, cannot be baked. Thus ultrahigh vacuums are not possible unless extraordinarily long pumping times are employed.

4) Installation of a Second Electron Beam Gun

The system was designed so that a second electron beam gun can readily replace the resistance heated evaporation source. Addition of the second gun would require only the gun itself and a special water-high voltage feedthrough flange like the one presently in use. No additional instrumentation feedthrough is needed since the open pins on the present feedthrough could be used, and a second Varian 6kW gun would fit without relocation of any of the present components.

5) Improved Sample Holder for Testing Specimens

The sample holder which was used to measure the superconducting properties of the specimens could be greatly improved by

making several relatively small changes. The first would be installation of a multipin connector at the top of the stainless steel tube where the leads emerge. Then by simply attaching a mating connector after the sample holder is in place, one would be ready to test the specimens. In addition to saving time, the connector would guard the lead wires where they emerge from the epoxy filled end of the tube and are most vulnerable; during the present study the lead wires did in fact once break off thus negating many hours of prior work. The design and installation of a protective shield to cover the copper block end of the sample holder would protect both the sample and the joints between the sample and the gold wires as the holder is lowered into the thin neck of the helium dewar.

6) Others

Presently removing and replacing the top plate of the vacuum chamber requires two people. Installation of a hoist would greatly facilitate this operation.

By rearranging the roughing and backing lines of the vacuum system and the coolant lines of the refrigeration unit, the vacuum chamber could be isolated from the continuous vibrations to which it is constantly subjected due to the present arrangement which has all these components mounted in the same cabinet.

Stainless steel shim stock fitted inside the glass cylinder in such a way that windows allowed one to look inside the vacuum chamber during evaporation would greatly reduce the amount of cleaning of its inner surface between evaporations. Rotation of the shim stock between successive evaporations would then mean cleaning the glass cylinder much less frequently while allowing

visual access to the chamber during all evaporations.

By obtaining two X-Y recorders, two nanovoltmeters, and two precision current sources, it would easily be possible to test both of the specimens mounted on the sample probe at one time. This should nearly double the efficiency during testing of the superconducting properties of the films.

A. Experimental

1) Improvement of Calibration of System

If new materials are to be evaporated, the system will need to be calibrated. In doing so it is essential to do the calibration deposition under the same conditions as will be present later during multilayer film deposition. That is, the system geometry and substrate temperature must be the same. In addition a careful calibration would control the rates of evaporation and shutter speed as well. The accuracy of the interference microscope method of measuring the actual film thickness could be significantly improved. Suggestions on how to do so are given by Chopra⁷⁹ and the references he cites.

2) X-Ray Studies of Layered Thin Films

X-Ray studies of the layered thin films would help characterize the concentration profiles of the films. Such studies are desirable as an independent check on the layer thicknesses and on the degradation of the layered structure due to diffusion. Techniques of such studies are discussed in references 48, 82, and 83.

3) Proximity Effect Studies

Proximity effects in Pb-Al single sandwich films have been studied experimentally by Hauser and Theurer²⁰. Theory has been

developed^{21,22} to explain the results of the experiments which were conducted by evaporating lead films of varying thicknesses onto an aluminum film 4400 Å thick. The subject is reviewed by Deutscher and de Gennes⁸⁴. Further work on the Pb-Al system might well involve comparison of the results obtained for the multilayered films with the theory developed for the single sandwich films. Such work would perhaps result in a more detailed explanation of Figure 14.

4) Critical Fields in Layered Superconducting Systems

Dobrosavljevic⁴⁹ has recently published a theoretical paper which concludes that in the thin film limit and under certain other conditions, $H_{c2}(t)$ for multilayered superconducting systems will be independent of the period $d = d_1 + d_2$ (d_1 = layer thickness of component 1, d_2 = layer thickness of component 2) of the layers and will depend on d_1 and d_2 only through the ratio d_1/d_2 . This theory could easily be checked using the present two source deposition system and making specimens for which Dobrosavljevic's conditions are met (essentially these conditions require proper layer thicknesses and transition temperatures of the two materials).

5) Critical currents and Pinning Effects

By modifying the present evaporation system so that one component is evaporated at a constant rate while the other has its rate modulated by a shutter, it would be possible to study pinning effects in superconducting inhomogeneous film. Preliminary results of such studies have been published by Raffy and Renard⁴⁸. To modify the present system to produce such films would be easy requiring merely that the pinwheel be offset a few inches.

6) Thin Film Analogy to Watson's Work on Porous Glass

It would be very straight forward to evaporate thin film layered structures of SiO_2 and Pb. Study of such a layered system could be highly interesting in the light of what is known from Watson's work on porous glass superconductors.

7) Other

With the present system it is possible to produce multilayered thin films of any one material which can be evaporated from the 6 KW electron beam gun and another material which can be evaporated from the resistance sources. By using the thickness monitors and varying the shutter speeds and the evaporation rates, it is possible to characterize the films produced. In thinking about future research one should not limit his thinking solely to the superconducting properties of multilayered films. Mechanical behavior, transport phenomena, ferromagnetism, and optical properties of the multilayered thin films might well be worthy of consideration.

Appendix A. Procedures for Operation of Deposition System

- 1) Ensure that vacuum chamber is clean.
- 2) Load the electron beam gun crucible and the basket of filament source with materials to be evaporated.
- 3) Turn on thickness monitors and depress test function switch momentarily. The amount of crystal life used is displayed on the Nixie tubes of the thickness monitors. If necessary, change quartz crystals. This change is accomplished by unscrewing the top of the thickness transducer, removing the old crystal, and inserting a new one. (New crystals may be obtained from Kronos; they are Model XT-7044). Turn off thickness monitors.
- 4) Place substrate and any desired mask in place on the sample cryostat; a small amount of Cry-Con Grease may be used to cause the substrate to adhere to the underside of the copper block. The grease also helps ensure good thermal contact between the substrate and the cryostat. The Cry-Con Grease is made by Air Products and Chemicals, Inc., Allentown, Pa. Screw the copper nut onto the end of the cryostat to hold the substrate firmly in place.
- 5) Check that the connectors between the copper coil coldtrap and its two feedthroughs are tight. Thermal cycling has an adverse effect on the vacuum tightness of these fittings.
- 6) Ensure that the top of the feedthrough collar is clean and that the "L" gaskets are in proper position. Then place the glass cylinder on top of the feedthrough collar. The implosion shield fits sufficiently tightly around the glass cylinder that the cylinder and the shield can be handled as one component.

- 7) Check to see that the underside of the top plate is clean and then place top plate on glass cylinder being careful to seat the pinwheel shaft in the bearing on top of the stainless steel wall. The upper "L" gasket and the top plate should be in continuous contact; any small gaps can be closed by sliding the "L" gasket upwards slightly. The top must be rotated into proper position - that is, so that the substrate is at the same position relative to the evaporation sources as it was during calibration of the system. This step is essential if one is to be able to characterize the film thickness.
- 8) With the roughing line, foreline, and butterfly valves all closed, start the mechanical pump. Allowing this pump to run for about 15 minutes to warm up will lead to faster pumpdown of the vacuum chamber. Open roughing line valve and pump down the vacuum chamber to a pressure of about 10^{-2} Torr as indicated by the Pirani gauge.
- 9) Close roughing line valve and open the foreline valve to rough out the diffusion pump. Turn on the main water valve to send cooling water to the diffusion pump. Water cooling for the diffusion pump is important; failure to cool will result in necessity of changing pump oil as well as severely reduced pumping ability. Turn on diffusion pump heater which automatically turns on the cooling unit of chevron baffle at the same time.
- 10) After about 30 to 40 minutes the diffusion pump oil reaches its proper operating temperature. Open the butterfly valve to begin high vacuum pumping of the vacuum chamber.
- 11) After about 5 minutes switch on the ionization gauge. The IG5M gauge head has the same characteristics as the IG3 gauges so that

pressures are read on the black (upper) scale of the readout meter not on the red (lower) scale. Note that this black scale has a full scale deflection value of 5, not 10. Initially the pump down rate is relatively fast; under normal conditions the pressure should be down to about 1×10^{-5} Torr after 30 minutes of pumping.

- 12) Assuming that the system is leak free, the base pressure to which the system will pump down is determined by the cleanliness of the vacuum chamber and the pumping time. Since the pressure will rise substantially during evaporation, pumping to pressures much below 1×10^{-8} Torr is not really worthwhile.
- 13) Connect the insulated copper tubing lines from the liquid nitrogen dewar to the feedthroughs for the copper coil coldtrap. Fill both the diffusion pump coldtrap and the copper coil coldtrap with liquid nitrogen. The combined effect of these two traps should reduce the pressure in the system by roughly an order of magnitude.
- 14) Open the valves for cooling water for the thickness monitors and the electron beam gun. Sufficient water for the latter is critical. Unless enough water goes through the water flow switch which is in series with the electron beam gun, the power supply for the gun will not supply power.
- 15) Rotate the sample mask so that it covers the sample holder and then apply power first to one evaporation source and then the other to melt and outgas the materials to be evaporated. Premelting the materials in this fashion results in smoother evaporation during later depositions. The resistance source is heated simply by setting desired level on the powerstat. Operation of the electron beam gun is more complicated. Details of operation are

given in the instruction manual supplied by Varian (#87-400 279, March 1972).

- 16) The thickness monitors must be scaled according to materials to be evaporated. Instructions for doing so are given in the operation manual for the monitors (Kronos QM 300 series Film Thickness Monitor Operation and Service Manual, 1971). The scaling takes only a few minutes since all that is required is the clipping of pins on a scaling header comb bus bar. New headers can be obtained from Kronos; the part number is 163204.
- 17) Turn on thickness monitors and allow to warm up and stabilize for about 15 minutes.
- 18) Mount pinwheel drive motor on top plate, adjust the o-ring belts, and clamp the motor in place. Hook up the variable speed control of the motor.
- 19) Add liquid nitrogen to cryostat by pouring it from a small dewar through a funnel. Allow sufficient time for thermal equilibrium to be attained.
- 20) Apply desired power to evaporation sources. The resistance source should be turned on first because it takes longer to reach a constant evaporation rate.
- 21) After desired rates of evaporation have been attained, turn on pinwheel motor and then manually rotate the sample shield away from the sample holder. Be careful not to rotate the shield into position where it shields one of the thickness monitor transducers.
- 22) After deposition rotate the sample shield to again cover the sample holder. Remove power from evaporation sources. Do not turn off cooling water to electron beam gun immediately. This

is important if very high melting point materials such as niobium are evaporated.

- 23) To remove sample from vacuum chamber go through the above steps in reverse order. After closing the butterfly valve between the vacuum chamber and the diffusion pump, turn off the diffusion pump heater. Leave the foreline valve open for 20 to 30 minutes with the mechanical pump still on so that the diffusion pump oil cools properly. Then close the foreline valve, turn off the mechanical pump, open the air admittance valve, and open the roughing valve to bring the vacuum chamber back to atmospheric pressure.

Sample	Pb Rate Å/min	Al Rate Å/min	Shutter Speed RPM	Total Rev	Total Thick Å	Pb Layer Thick Å	Al Layer Thick Å	Period $d_{Al} + d_{Pb}$ Å	Ratio d_{Al}/d_{Pb}	Notes
24	1750	1170	7.0	70	29,200	250	167	417	0.67	1
27	1010	1470	5.5	55	24,850	185	267	452	1.45	
28	820	1960	6.3	63	27,800	130	311	445	2.40	
29	1740	1840	5.0	50	35,800	348	368	716	1.07	
31	2680	1065	6.5	65	37,440	412	159	571	0.38	
32	1270	2170	5.5	55	34,400	231	395	626	1.70	
33	885	1910	6.0	60	27,950	147	318	465	2.16	
34	1700	980	6.5	52	21,450	260	151	411	0.58	
35	1055	1005	5.7	42	15,470	188	180	368	0.96	
36	660	1120	5.5	55	17,810	120	204	324	1.70	
37	830	1040	11.5	81	13,130	72	90	162	1.25	
38	1735	1150	11.5	58	14,530	150	99	401	0.66	
39	700	820	11.5	69	9,100	61	71	132	1.16	
45	3325	1675	5.0	25	25,000	665	335	1000	0.50	
46	1640	1160	4.8	38	22,390	346	242	588	0.70	
47	3115	420	5.0	35	24,720	620	83	703	0.13	
48	2605	865	5.0	25	17,340	521	173	694	0.33	2
49	1565	1245	5.4	43	22,450	291	231	522	0.80	3
50	1835	1160	16.0	112	20,980	115	72	187	0.63	2

Notes:

- 1) Alignment of system slightly off
- 2) Layer of Al deposited at room temperature before rest of deposition
- 3) No nitrogen in cryostat during entire deposition

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