PHYSICAL REVIEW B VOLUME 13, NUMBER 11 1 JUNE 1976

Experimental search for excitonic superconductivity*

D. L. Miller,† Myron Strongin, and O. F. Kammerer
Brookhaven National Laboratory, Upton, New York 11973

B. G. Streetman†
Department of Electrical Engineering and Coordinated Science Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 16 October 1975; revised manuscript received 29 January 1976)

A search for excitonic superconductivity in a thin-film structure of the type proposed by Ginsberg and Allender, Bray, and Bardeen was undertaken. Ultrathin layers of Pb, In, and Tl were deposited on PbTe, and layers of Pb and In were deposited on Te. Substrate preparation and film deposition were accomplished in an ultrahigh-vacuum system with integral cryostat, and were monitored by low-energy electron diffraction and Auger electron spectroscopy. *In situ* measurement of crystalline, epitaxial Pb films as thin as 10–15 Å deposited on PbTe showed a strong film-substrate interaction; however, no excitonic enhancement of T_c was observed. A simple proximity-effect model is presented to explain the observed decrease in T_c for the thinner films, and the influence of the substrate on the superconductivity of ultrathin films is discussed. Several aspects of these experiments involving the transition temperatures of In and Tl films are unexplained.

I. INTRODUCTION

The search for superconductivity at high temperatures has always been an area of priority for both experimentalists and theoreticians involved with superconductivity. Metallurgical and materials approaches have had considerable success, obtaining T_c's above[1] 22 K in what promise to be usable materials, yet the need for still higher T_c's obviously exists. Among the more speculative approaches to obtaining high-temperature superconductors, the excitonic mechanism proposed by Little[2] and Ginsberg[3] and more recently developed further by Allender, Bray, and Bardeen[4] (ABB) has been considered one of the more feasible experimental possibilities. This paper reports an experimental effort to investigate the possibility of an excitonic mechanism in a metal-dielectric layer structure as suggested by ABB. Although no excitonic effect was observed, information was gained about the interaction between ultrathin superconducting films and conducting substrates, and this experiment should provide a guide for future experimental investigations of an excitonic mechanism.

The motivation for attempting this type of search in a serious manner at this time was provided by both theoretical and experimental advances in areas relevant to the experiment. ABB had produced calculations with enough detail using realistic parameters that some confidence in the observability of an effect under favorable conditions seemed justified on the basis of theory. Additionally, it was demonstrated experimentally that surface-sensitive techniques such as low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) could be combined with ultra-thin-film deposition equipment to produce and characterize the extremely thin ordered films required by the calculations of ABB.[5,6] Thus the decision was made to look for excitonic superconductivity in a planar structure consisting of an ultrathin metal film deposited in intimate contact with a suitable clean crystalline dielectric. This configuration has the advantages over sandwich or granular methods of putting the metal and dielectric together intimately in that the structure can be prepared sequentially, monitoring the physical properties of the substrate and the film as each is prepared. It also avoids the difficulties involved in growing a film of the dielectric material. Thus the dielectric can be obtained in bulk with characteristics suitable for the experiment, and then an appropriate surface prepared on it. This surface can be monitored before film deposition, and the metal deposition observed and controlled to obtain an appropriately thin and well-characterized film. It was felt that only by carefully observing and controlling each step of the sample preparation would useful information be obtained, in the event of a failure to observe excitonic superconductivity.

Since the ideal conditions set forth by ABB can in practice only be approximated, a particular configuration of materials was chosen as an experimental goal. It was felt that if a crystalline, strain free, pure, continuous, uniform film of 10 Å or less thickness of a soft superconducting metal such as Pb were deposited on an atomically clean surface of single-crystal PbTe, a reasonable test of the theory should result. A substrate surface structure (atomic placement) essentially unchanged from the bulk positions was desired since it was felt that a crystal with a restructured surface would not be likely to exhibit at the surface the band-structure properties for which the crystal was chosen. The use of a pure, crystalline film of a soft superconductor like Pb would make unwanted enhancements of T_c due to such well-known thin-film effects as strain or impurities highly unlikely, and would reduce the chance of masking any small excitonic enhancements. Epitaxy of the film on the substrate was considered desirable because it indicates some measure of interaction between the crystalline film and substrate short of forming actual surface compounds. Crystalline PbTe was chosen as a substrate material because of a combination of availability and a favorable band structure. These conditions have been discussed more extensively previously,[4,7] and the experimental details of substrate and film preparation will be published elsewhere.[8] Only those experimental details necessary to allow an evaluation of this experiment as a test of excitonic superconductivity will appear here.

II. APPARATUS

The apparatus used in this experiment has been discussed in detail elsewhere,[9,10] so that only a general outline of the features most important to understanding the experiment will be presented here. As the experiment progressed toward the goal configuration, the apparatus existed in several states. Initial studies of Pb, In, Tl, and Sn films were made by depositing these metals onto a PbTe substrate at 77 K, observing film and substrate crystallinity and cleanliness with LEED and AES, and then removing the samples from the vacuum chamber to a liquid-helium cryostat for measurement of T_c.[7,9] This simple apparatus was useful for studying film growth and epitaxy, and pointed out the necessity of avoiding agglomeration of the films as they were warmed to room temperature. Several evaporations were also made onto crystalline InSb substrates, and with evaporated Ge overlayers, but with unpromising results.

An intermediate stage of the experiment was performed with single-crystal Te as a substrate. Although not originally considered as favorable a substrate material as PbTe, Te had the considerable advantage from an experimental standpoint of being easy to prepare as a substrate. Typical methods considered for cleaning the surface of a compound crystal such as PbTe were vacuum cleaving or sputter etching. In vacuum cleaving, it is difficult to consistently provide relatively large flat areas free of steps. Such steps or ledges could cause shadowing of some substrate areas and lead to discontinuous films with incomplete resistive superconducting transitions. Sputter etching of the substrate inside the cryogenic shielding necessary for obtaining low temperatures succeeds only in depositing extra contamination from the shields onto the substrate. It was therefore decided to use a single-crystal Te substrate, which could be cleaned easily by heating in vacuum to 275 °C, while a more complicated apparatus for use with PbTe was constructed. The apparatus used for the Te substrates consisted of an ultrahigh-vacuum chamber containing a liquid-He cryostat with a shuttered aperture for entrance and exit of the LEED and AES electron beams, electron bombardment heating for substrate cleaning by sublimation, and spring probes for *in situ* resistive measurement of T_c.

The final apparatus used to obtain *in situ* T_c measurements of ultrathin films deposited on sputter-cleaned PbTe crystals is discussed in detail elsewhere.[10] This apparatus was a modification of the previous designs and allowed the sample to be removed from the cryogenic shields for sputter cleaning while retaining the cryogenic and surface analysis capabilities of the earlier designs. *In situ* measurements of superconductivity were made using a four-point probe resistive method. The low resistivity of the PbTe substrates at low temperatures ($< 10^{-3}\ \Omega$ cm) made contact to the films relatively easy, even at the smallest thickness. Temperature measurements were made with Au-Fe thermocouples soldered to the back of the PbTe substrates with Au-Tl alloy. Although this soldering procedure caused some inaccuracy in the thermocouple readings, the indicated temperature could be checked against the T_c of thick Pb films at 7.2 K. From this it was estimated that the temperature of the metal film was known with an accuracy of ±0.1 K.

III. SUBSTRATE AND FILM PREPARATION AND CHARACTERIZATION

As already mentioned in Sec. II, different methods were used to clean the Te and PbTe substrates. The Te crystals were cleaned simply by heating an air-cleaved crystal in ultrahigh vacuum, relying on the relatively high vapor pressures of Te (10^{-4} Torr at 275° C) to sublime away the surface faster than contaminant gases could arrive and stick. A low pressure was maintained near the sample by cooling the surrounding heat shields to 77 K during the cleaning procedure. This minimized outgassing of the shields due to radiactive heating, and provided a convenient pumping surface for the sublimed Te. In this way, excellent LEED patterns of the Te $(10\bar{1}0)$ surface used as a substrate were obtained, which indicated an unreconstructed $(10\bar{1}0)$ plane of the hexagonal Te crystal. AES was used to ascertain that no residual contamination remained after cleaning, and a typical trace of a clean Te surface showed no contaminants, to the limits of instrument sensitivity.

The PbTe crystals which were used as substrates were cleaned by ion bombardment. Prior to being put in the vacuum system, slices of PbTe single crystals were cut and mechanically polished to expose a (100) plane, then electrolytically etched to remove mechanical damage due to the polishing procedure. A commercial ion gun was used for sputter cleaning. Because of the low sticking coefficient for most gases on PbTe,[11] AES showed that bombarded surfaces remained relatively clean for several days at pressure of 1×10^{-9} Torr or lower. An AES trace of PbTe cleaned and annealed in this manner has previously been published.[7] Heating the PbTe to about 200°C annealed sputter-produced damage, and sharp diffraction patterns characteristic of an unreconstructed (100) PbTe plane were easily obtained.[7,9] The combination of LEED and AES therefore indicated that both the PbTe and Te substrates were prepared with atomically clean and ordered surfaces having atomic symmetries characteristic of the bulk arrangement, as desired.

Metal films were deposited on the prepared substrates by evaporation from resistively heated sources. The metals deposited were Pb, In, Tl, and Sn, all of which are soft superconductors with moderately low melting points and fairly high vapor pressures at easily attainable temperatures, around 800°C. After a short amount of initial outgassing, oven-type sources could easily provide controlled, uniform metal arrival rates at the substrate in excess of 1 Å/sec without raising the pressure in the vacuum chamber by more than 4×10^{-10} Torr. Two sources were always in place during any one pumpdown, so that two different metals could be deposited without breaking vacuum.

Film epitaxy, growth, and purity were monitored by LEED and AES after each deposition. No impurities were detected by AES in any of the deposited films, as was expected from the deposition rate, background pressure, and metal purity (at least 99.99% in all cases). Epitaxial growth was achieved with Pb, In, and Tl on PbTe, while Sn on PbTe, and Pb and In on Te grew with no crystal structure detectable by LEED.

The thickness of the films was determined with a commercial quartz-crystal-oscillator-rate monitor, calibrated interferometrically at film thicknesses near 500 Å. LEED also gave some indication of the film coverage at very small thicknesses. Another indication of the thickness of an overlayer was obtained by monitoring the strength of an AES signal originating from the substrate as metal was deposited over it.[8,12] From analysis of this data it appears that uniform films of Pb form on PbTe at very small thicknesses, as low as 5 Å, apparently without noticeable changes in sticking coefficient or agglomeration between subsequent depositions. For In deposited on PbTe, the film behavior is not as ideal, with possible slight agglomeration or nonuniform deposition occurring.

Other factors in addition to the AES data also tend to indicate a fairly uniform overlayer. For amorphous or polycrystalline films of In and Pb deposited on Te, and for one sample of Pb deposited on PbTe and measured *in situ*, sample conductance was measured as a function of thickness. These data are plotted in Fig. 1. The linearly increasing conductance as a function of thickness above about 20 Å for In films is to be expected from a uniform film, whereas gross departures from uniformity, such as the formation of discrete islands which eventually coalesce to form a continuous film, would show up as a definite change in the resistivity at some thickness, as seen previously.[13] The curves for the Pb films deposited on Te do indicate that these Pb films may have a type of granular or island

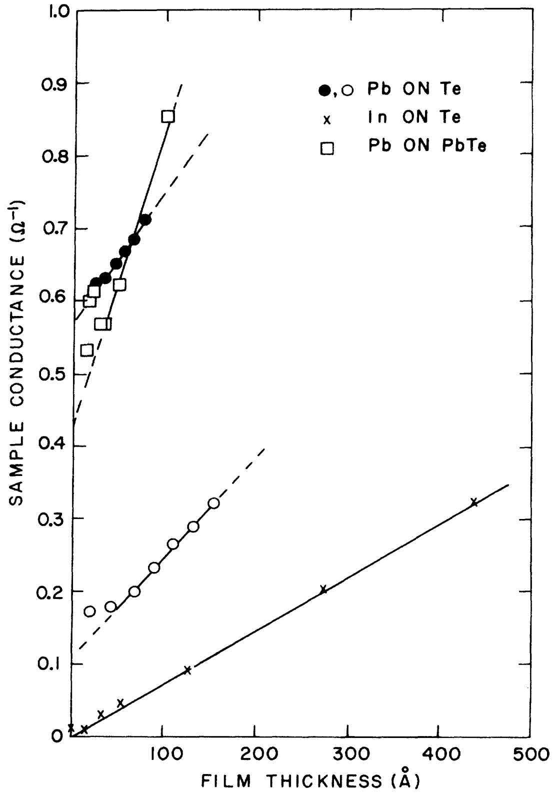

FIG. 1. Sample conductance as a function of metal-film thickness for samples consisting of Pb deposited on PbTe, Pb deposited on Te, and In deposited on Te. Film resistivity was obtained from the approximately linear regions of the data.

structure below about 40-Å thickness. The same effect may also be present in the In films below 20-Å thickness. The dip in conductance for the Pb on PbTe data at about 25 Å was due to an unintentional anneal to 115 K between metal evaporations. The rapid increase in conductance below this point, however, indicates that continuity is achieved for very thin films.

Since the region 5–10 Å on either side of the metal-substrate interface is critical for excitonic superconductivity, there was concern that one or more layers of an interfacial compound or alloy may have formed at the boundary between the substrate and film, even at the relatively low substrate temperatures maintained throughout the measurement of samples *in situ*. One indication that this did not happen, at least for Pb on PbTe, is given by the epitaxial overgrowth of the Pb films. It would seem highly unlikely that an ordered crystalline metal film could grow over a disordered interfacial layer and still retain a high degree of preference for orientation along lines of symmetry of the substrate (epitaxy). Epitaxial growth over an intermediate pseudoepitaxial interfacial compound would be possible, but no indication of such an intermediate compound was observed by LEED.[8] Even in the case of Pb on Te, where no epitaxy was observed, there are indications that an interfacial layer of a compound different from the substrate or metal overlayer does not grow to any appreciable thickness. Electron-energy-loss measurements were made with the retarding-grid LEED-AES system for the Te and PbTe substrates and for a series of Pb overlayers made at about 5 K.[8] Identification of the structure in these curves provides a clear means of identifying the three materials, particularly by observing the varying position and width of the bulk-plasmon loss peak. In the series of Pb depositions on a Te substrate, the loss pattern appeared to change smoothly from that of Te, to a superposition of Pb and Te, to that of Pb, without the appearance of the narrow peak at about 17 eV which characterizes PbTe. Although the sensitivity of this type of line-shape identification was unfortunately somewhat limited by the resolution of the instrument, it still can be concluded at least that no large areas with thickness of more than 10 Å or so of PbTe are formed during the deposition process of Pb on Te.

A LEED spot pattern was obtained of each substrate prior to film deposition and of each film immediately after deposition. In this way a record was made of the crystal structure of the films during the experiment. As has been mentioned already, no epitaxy was obtained for films deposited on Te substrates.

Epitaxy did occur for Pb, In, and Tl (but not for Sn or Al) deposited on the PbTe (100) substrates, but not for Pb on PbTe (111) nor for Pb or In deposited on Te $(10\bar{1}0)$. The epitaxy of Pb, In, and Tl on PbTe occurred with the close-packed metal plane equivalent to the Pb (111) plane parallel to the substrate plane (100). All three of these metals have fairly similar crystal structures with similar lattice parameters and physical characteristics, so it is not surprising that epitaxy occurs in the same way.

Since the details of the epitaxy obtained for these materials is discussed elsewhere,[7,8] we only mention that for Pb, In, and Tl deposited on PbTe, the metal-overlayer LEED spot pattern could be produced at a substrate temperature of 77 K with less than 10 Å of metal deposited. As with all thickness measurements in this range, there is about a factor of 2 uncertainty in the thickness, but it appears that a few atomic layers are sufficient to establish the crystallinity of the overlayer. Below this amount, the atomic positions of the overlayer appear random, leading to no additional spots on the LEED pattern, but giving increased background. This was checked in more detail by taking an intensity-vs-energy trace for one of the spots both before and after the deposition of about 4 Å of Pb—the intensity maxima remained unchanged in position but decreased in magnitude. It seems likely that at low coverage, the atoms arrange themselves in a random manner or in crystallites only a few atoms across. With the addition of more metal, it then becomes favorable for the atoms to order themselves into a crystal structure completely covering the surface. The interaction between the substrate and the metal atoms must provide the impetus for epitaxial growth rather than a disordered or random overgrowth. It seems unlikely that such epitaxy would occur over an intervening disordered layer, although the possibility cannot be eliminated.[14]

To summarize, the combination of LEED and AES with other measurements such as sample resistivity and energy loss have provided a reasonably complete picture of the samples produced in this experiment. On Te, the metal films were microcrystalline (crystallite size <500 Å, the coherence width of the LEED beam) or amorphous, and for at least the In films, appeared to be uniform with little clumping. The Pb films on Te may have been somewhat less uniform as indicated by the sample resistivity. The data are more complete for films on PbTe. For Pb, In, and Tl, epitaxy occurred on the unreconstructed PbTe (100) surface. It is possible that a disordered intervening layer less than one or two atomic layers thick between the crystalline overgrowth and the substrate could have existed, but this is considered unlikely exactly because epitaxy was achieved. The films gave LEED spot patterns indistinguishable from those expected from the bulk metal, except for strain-induced broadening of the spots. For Pb and In, at least, the AES and LEED data indicate that the film was not composed of discrete islands although a certain amount of lumpiness or thickness variation from point to point may not have been detectable. AES also suggests that the rate-monitor indication of thickness was accurate to within a factor of 2. It appears, therefore, that a reasonably close approach to the ideal configuration desired for excitonic superconductivity was achieved with the Pb on PbTe samples.

IV. SUPERCONDUCTIVITY

A. Introduction

Although these experiments were designed to look for an excitonic mechanism of superconductivity, much general information was also obtained about thin-film superconductivity which is strongly influenced by substrate effects. A general discussion is given below which includes a reassessment of old data on ultrathin layers in terms of what has been learned here. It is remarkable that films prepared under such varying conditions as were encountered in these several experiments can have depressions in transition temperatures which are so similar, and it is suggested that a similar mechanism accounts for the depression in T_c in various cases to be discussed.

In the data discussed here there are essentially two cases: (i) initial experiments where the films were made in ultrahigh vacuum, sometimes overcoated with a thin protective layer of Ge, and then removed from the vacuum system for measurement; (ii) later experiments where the films were measured *in situ*. The films that were removed from the vacuum chamber for measurement were found to have agglomerated to a certain degree, yet they remained superconducting. The effects of agglomeration in these thin layers led to unusual behavior in a magnetic field, which is discussed later on, and which is thought to be due to the weak coupling of the metal grains through the substrate.

B. General results on agglomerated and *in situ* films

The superconducting transition temperatures for all Pb and In films measured in this experiment are shown in Fig. 2, as a function of thickness of metal indicated by the quartz-crystal-oscillator deposition monitor. It is seen that the transition temperature for either Pb or In on PbTe or Te substrates increases with increasing thickness, approaching either the bulk T_c for Pb, or some higher value at large thicknesses for In. The implications of this behavior will be discussed later.

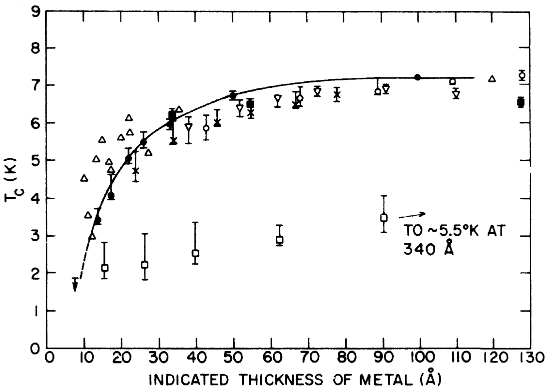

FIG. 2. Superconducting transition temperature, measured resistively, as a function of the thickness of metal deposited, indicated by a calibrated quartz-crystal-oscillator-rate monitor. ●—Pb deposited on PbTe at 77 K, measured *in situ*; ○, ×, ∇—Pb deposited on Te at about 7 K, measured *in situ*; ∇—Pb deposited on PbTe at 77 K, warmed to room temperature and exposed to air before measurement; ■—In deposited on Te at about 7 K, measured *in situ*; □—In deposited on PbTe at about 7 K, measured *in situ*.

The scatter in the earliest data in Fig. 2 for various metals on PbTe is felt to be due to differences in agglomeration as the sample was warmed and removed from the vacuum for measurement. Additionally, each data point in this curve was obtained from a separate substrate preparation and film-deposition sequence, so that variations in substrate cleanliness or metal-deposition-source calibration also would have affected the results. The effect of agglomeration on the transitions can be estimated from Fig. 3, which shows transitions from two different films of In on PbTe, before and after annealing overnight at room temperature in a vacuum of better than 10^{-9} Torr. These data suggest that changes in T_c and in transition width of a few tenths of a degree can be expected from annealing and agglomeration of In films. The Pb films appeared to agglomerate even more readily than In when warmed above about 90 K.

The transition-temperature data for metals on Te, and Pb and In on PbTe measured *in situ* were obtained from a series of depositions done sequentially, building up the films by small increments after each T_c measurement. For Pb on PbTe, the substrate temperature was kept below 80 K, and for both Pb and In on Te, and In on

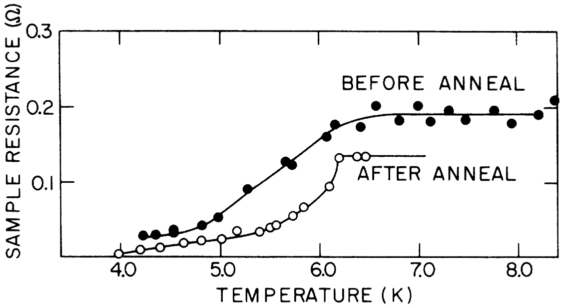

FIG. 3. Resistance as a function of temperature for a sample consisting of In deposited on PbTe at about 7 K, before and after annealing to room temperature by allowing the cryostat to warm overnight.

PbTe, the substrate temperature was below 10 K. For all samples measured *in situ*, a vacuum of less than 2×10^{-9} Torr was always maintained. Therefore, for these samples not only has the effect of annealing-induced agglomeration been largely eliminated, but also the conditions of substrate preparation and metal-source behavior are identical for each point of a given curve.

C. Sample and substrate resistance

Figure 4 shows a family of plots of sample resistance as a function of temperature for one of the runs made *in situ*. The initial resistance of this particular PbTe substrate was about 2 Ω, which was larger than the typical PbTe substrate resistance measured *in situ*. The width of the resistive transitions shown are typical, being larger for small thicknesses and low T_c's than for higher thicknesses and higher T_c's. This is probably due to a nonuniformity of deposition thickness across the sample. Since the data indicate that T_c decreases with film thickness faster at small thicknesses than at large, a constant amount of thickness nonuniformity would lead to a broader transition at small thicknesses that at large thicknesses; a 5-Å thickness nonuniformity at 10-Å average thickness would be a much larger fractional deviation than at 50-Å average thickness. In Sec. III, it was concluded that this amount of thickness nonuniformity may have not been detectable with the techniques employed. One would also expect fluctuations to broaden the resistive transition as the thickness is decreased and $R_\square$, the sheet resistance, becomes large. However it will be seen below that $R_\square$ for these films is of the order of 100 Ω, which implies a half-width due to fluctuations of about 1 mK, which is much less than the observed width.

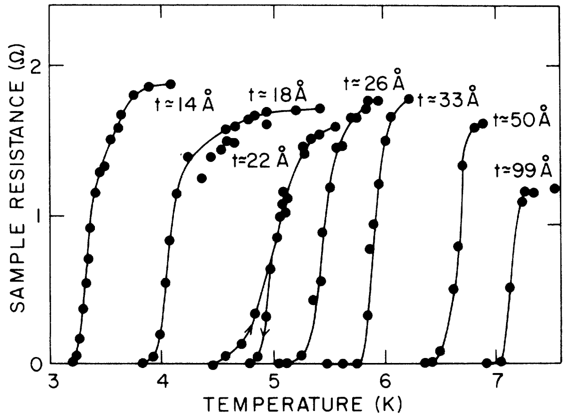

FIG. 4. Resistance of a sample consisting of Pb deposited on PbTe at about 77 K, as a function of temperature, for several thicknesses of deposited Pb films. The measurements were made *in situ*, without warming about 80 K (except for an accidental warming to about 115 K between $t = 22$ Å and $t = 26$ Å).

For In and Pb films deposited on Te, and one Pb film deposited on PbTe and measured *in situ*, the higher resistivity of the substrate made film-resistivity measurements possible, as discussed in Sec. III, and shown in Fig. 1. These resistivities, obtained from the slope of the conductance-vs-thickness plot, indicate that the In on Te had a resistivity of approximately 1.4×10^{-5} Ω cm. The Pb films deposited on Te, which exhibited two resistivity regions, had an average resistivity of 6.3×10^{-6} Ω cm for $t > 40$ Å. For Pb on PbTe, for $t > 25$ Å, the resistivity was about 2.4×10^{-6} Ω cm. It should be kept in mind that these numbers depend linearly on the thickness calibration which, in this case, was probably accurate to only within a factor of 2, although the reproducibility was much better. These values of resistivity are much smaller than those usually associated with such thin films. For example, data in Ref. 13, Fig. 8, indicate resistivities of about 5×10^{-5} to 5×10^{-4} Ω cm for Pb about 40 Å thick deposited on SiO_x at $T < 7$ K. Resistivities of our Pb films were 10^{-1} to 10^{-2} times the resistivities of Ref. 13, and the In films reported here had resistivities a factor of 5 to 50 lower than Ref. 13. This indicates that either the conducting Te and PbTe substrates had an influence in reducing the interfacial barriers between small grains of metal, or that these films were much more uniform, with fewer barriers to conduction along the film. Clearly, however, the film structure for Pb on Te must have undergone some change at 40 Å, since the slope of the conductivity curve changes sharply at that point.

If a free-electron calculation of the normal electron mean free path l is made, we obtain $l \sim 60$ Å for In on Te, $l \sim 160$ Å for Pb on Te with $t > 40$ Å, and $l \sim 410$ Å for Pb on PbTe with $t > 25$ Å.

An empirical relation, $\rho l \cong 1.5\times10^{-11}\ \Omega\ \mathrm{cm}^2$ has been given for Pb films in the range from 400 to 16 000 Å thick deposited on glass slides at room temperature.[15] If this relation is used, we obtain values of $l\sim240$ Å for Pb on Te and $l\sim630$ Å for Pb on PbTe, in reasonable agreement with the free-electron values. These values of the film mean free path are from one to two orders of magnitude larger than previously obtained for films in this thickness range, and the fact that the mean free path is much larger than the film thicknesses would imply specular reflection at the boundaries. It seems unlikely to us that films in the 25-Å range, even though grown under the best conditions, can have such ideal properties. While the data in Fig. 1 look convincing there is still the possibility of some systematic errors in the measurement, which will be investigated in future work. Nevertheless, we still feel that it is unlikely that such large values of l are due to an error in the measurement. It is also possible that the combination of film and semiconductor surface form a system with a high conductivity, since electrons "donated" from the metal would encounter a relatively high mobility in the semiconductor (bulk PbTe electron mobilities of up to 10^7 $\mathrm{cm}^2/\mathrm{V\,sec}$ have been reported[16] at 4 K; our bulk samples were measured at $1.3\times10^3/\mathrm{cm}^2/\mathrm{V\,sec}$ at 77 K). This type of interaction between substrate and metal is also discussed below to account for the large depressions in the superconducting T_c.

D. Analysis of Pb data using proximity-effect model

Explanations of the cause of the observed decrease in T_c as films were made thinner can generally be separated into two catagories: (a) effects associated with the nature of the substrate and interface region, and (b) effects associated with the nature of the film. For this experiment, some of the more probable effects under category (a) would be a proximity effect to states in the substrate or interface region, and also possible alloying of substrate Pb with (in particular) an In overlayer. Effects from category (b) also were felt to be present in some of the experiments, such as the formation of barriers or weak links between grains or small metal particles on the surface, particularly for films which were annealed to room temperature and agglomerated, and also the possibility of the formation of metastable high-T_c phases to explain the T_c's above bulk values.

Our proximity-effect explanation for the decrease in T_c has the virtue of simplicity. If we use a simple Cooper-limit argument for the case where the thicknesses of the different regions are less than their coherence lengths, we can write $T_c\sim\Theta_D e^{-1/\rho}$, where ρ is given by $N_s V_s[N_s d_s/(N_s d_s+N_n d_n)]$, assuming that $N_n V_n\sim0$. N_n and N_s are the densities of states in the substrate and superconductor, V_n and V_s are the interactions in the substrate and superconductor, d_s is the thickness of the superconductor, and d_n is the effective thickness of the normal surface region on the semiconducting substrate. One can then easily show that

$$\ln\left(\frac{T_{c0}}{T_c(d_s)}\right)=\frac{N_n d_n}{N_s^2 V_s d_s}\ , \tag{1}$$

where T_{c0} is the bulk T_c, and $T_c(d_s)$ is the film transition temperature. The data for Pb on Te and PbTe, and In on PbTe are shown in Fig. 5. The data for Pb on Te and PbTe appear to agree with this very simple treatment, whereas for In on PbTe, the agreement is poor. Figure 5(a) shows a fairly straight-line behavior for Pb on both substrates. If one accepts the slope of such a fit to be meaningful, this implies that $N_n d_n/N_s$ is about 5 Å for Pb on Te and 2.2 Å for Pb on PbTe. This means that there are about 5×10^{15} electrons/cm^2 associated with the Te substrate giving rise to the proximity effect, and about half that number for the PbTe substrates. These could occur in a 5-Å-thick layer with a metallic density of states, or in a thicker layer of lesser density. This is a rather large number of electrons to be contained either in surface states or a charged region of the semiconductor obtained by bending the bands. For example, if one forms a Schottky barrier on PbTe by depositing Pb, the resulting band bending would form an inversion layer on p-type material containing about 1.3×10^{14} electrons/cm^2. A factor of 2 error in the density obtained from the proximity-effect calculation might easily arise from uncertainty in film-thickness calibration, but that still leaves an order of magnitude unaccounted for. It may be that the model is too oversimplified to be expected to give quantitative results, or that some unknown mechanism is involved and the straight-line behavior in Fig. 5(a) is only fortuitous. However, the anomalously high mean free path discussed previously gives a definite indication of a strong film-substrate interaction, and adds strength to the proximity-effect model.

E. Indium-film data

Data for In deposited on PbTe are shown in Fig. 5(b). There are two interesting points raised by the In data. First, although measurements made with LEED and AES indicate a fairly crystalline, epitaxial overlayer, the proximity-effect

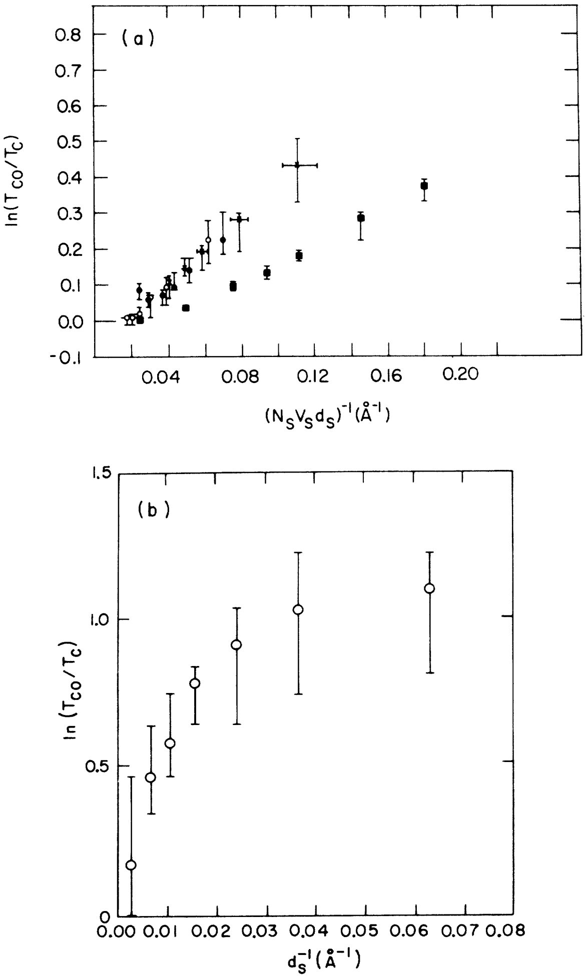

FIG 5. (a) A plot of ln (T_{c0}/T_c) as a function of $(N_sV_sd_s)^{-1}$ for Pb deposited on Te at about 7 K and measured *in situ*, and Pb deposited on PbTe at about 77 K and measured *in situ*. T_{c0} is the thick-film T_c, N_s (N_n) is the electron density of states in the superconductor (normal region), d_s (d_n) is the thickness of the superconductor (normal region), and V_s is the effective interaction in the superconductor. The slope of the linear regions of the plot gives a value of N_nd_n/N_s of about 5 Å for Pb on Te and about 2.2 Å for Pb on PbTe. ●, ○, ×—Pb on Te; ■—Pb on PbTe. Bars indicate transition widths and estimated uncertainty in film thickness. (b) A plot of $\ln(T_{c0}/T_c)$ as a function of d_s^{-1} for In deposited on PbTe at about 7 K, measured *in situ*. Bars indicate the width of the resistive transitions.

argument which appears to hold for Pb on PbTe breaks down here. Second, the maximum transition temperature measured was near 6 K, for a film more than 300 Å thick. It is likely that these two points are related. For example, it has recently been found that In films may be prepared with T_c up to 5.7 K by stabilization of some nonequilibrium phase by the addition on 10–15 at.% of Sb.[17] The behavior of T_c with thickness in our case may be the result of a combination of the proximity effect, which lowers T_c for the thinner films, and a nonequilibrium phase, which raises the T_c of the deposited material. Some doubt, however, is cast on this explanation by the fact that LEED indicates a crystalline, epitaxial film of In growing on the PbTe, although there is more disorder than for the case of Pb, as indicated by the fuzziness of the LEED diffraction spots. If more of some high-T_c phase were growing as the films became thicker, a change in the LEED spot pattern symmetry would be expected as metal was added, or an increase in the ratio of background intensity to spot intensity would be expected. Neither of these was seen. Also, one would expect annealing to room temperature to greatly lower the T_c, if the high-T_c phase is not stabilized by impurities. Auger analysis detected no impurities, and for the 300-Å film with a T_c of near 6 K, an anneal at room temperature slightly changed the shape of the transition but did not materially affect T_c, as seen in Fig. 3. If the metal crystal structure growing initially on the PbTe surface was the high-T_c phase [it, however, appears to be the (111) plane of the bulk In lattice, with some strain, as with the Pb layers], one would expect a proximity-effect calculation to work with a T_{c0} of about 6 K. This clearly does not apply either.

Another possibility is that there was some free Pb metal remaining on the surface of the PbTe after the sputter-cleaning procedure. However, one sample of In deposited on Te was made, also with a maximum T_c of over 6 K. Since no Pb was available for alloying in this case and high T_c was still obtained, it is not necessary to hypothesize alloying with Pb in the In-on-PbTe samples to explain high T_c's. Alloying of In with Te from both the PbTe and Te substrates would be possible, but InTe is a semiconductor which has a doping-dependent T_c of 2–3 K. No other superconducting In-Te compounds have been reported.[18] The T_c data for In on PbTe remains unexplained.

F. Critical fields

Finally, some mention should be made of the effects of agglomeration on the earlier films of metals deposited on PbTe but not measured *in situ*. Critical fields both parallel and perpendicular to the plane of the film were measured for these agglomerated films,[7] and the results are plotted in Fig. 6. The large uncertainty in H_c values arose from extrapolation to zero temperature. This has been discussed in more detail in Ref. 7. The reason for including the data is to point out

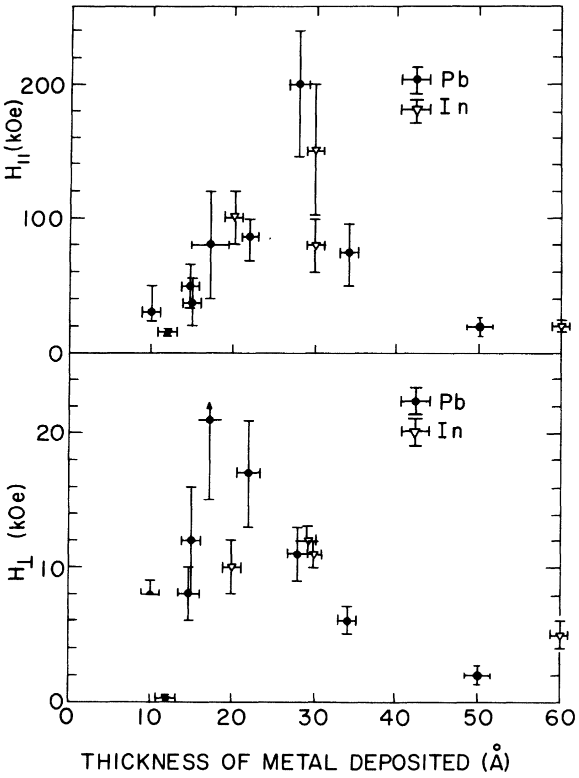

FIG. 6. Critical fields parallel ($H_{c\parallel}$) and perpendicular ($H_{c\perp}$) to the plane of the substrate surface, for Pb and In films deposited on PbTe at 77 K, as a function of the thickness of metal deposited. The films were warmed to room temperature and exposed to air in being transferred to a Dewar for measurement. Neither $H_{c\parallel}$ nor $H_{c\perp}$ increases with decreasing thickness below about 20–30 Å, as expected for a continuous film.

that as the films were made thinner, neither $H_{c\parallel}$ nor $H_{c\perp}$ increased as expected, below about 20–30 Å, and in fact decreased. Above that thickness, the behavior became more characteristic of an ideal thin film, where one would expect $H_c = \sqrt{24}(\lambda/d)H_{cB}$, where the field grows larger as d is made thinner. Despite the apparently large agglomeration effects, these films were superconducting, and would also sustain critical current densities on the order of 5×10^5 A/cm^2, calculated assuming all current flowed through the metal. Actually it seems unlikely that the current flows through the metal without significant flow through the region between the particles. Probably a superconducting gap is induced in the region between the metallic particles and a supercurrent can be supported. More important, this type of picture can explain why the critical field starts decreasing for the thinnest films instead of reaching very high values. For example, if the distances between the areas of agglomerated metal are on the order of a coherence length in the normal material ξ_N, one might expect that $\Delta_n \sim \Delta_s(N_n/N_s)T_j e^{-x/\xi_N}$ and hence $\Delta_n \sim 0.1\Delta_s$ to $0.01\Delta_s$. Here we have taken the transmission coefficient T_j to be about 0.5, and $N_n/N_s \cong 0.5$ to 0.05, which would correspond, in our proximity-effect model, to an interacting normal region 10–100 Å thick. Because the regions between globs are weakly superconducting it might be expected that a relatively small field would destroy the superconducting link. With this type of model one would expect H_c to rise as the distance between grains becomes smaller and the gap gets bigger, and finally when a coherent film is obtained H_c will start decreasing in the usual manner expected for a film.

V. DISCUSSION

Although the present results have not yielded any evidence for an excitonic mechanism, they do indicate a strong participation of the substrate in both the normal and superconducting properties. Furthermore we consider the fact that the superconducting behavior of the films measured *in situ* did not deviate significantly from the results of earlier work, to indicate the importance of normal electron states associated with the substrate as a general mechanism for the depression of T_c in the cases considered so far. Other interpretations may of course be possible, since presently unknown effects may be inherent to very thin films *per se*. Our view is, however, that down to about 30 Å such effects are small, as indicated by work on epitaxially grown Al films on clean Si substrates[6] and also work on small metallic particles,[19] which show that T_c's close to the bulk can be obtained under special conditions. However, we emphasize that the bulk T_c is usually not found in thin films. For example, in the thinnest disordered films of almost all "soft" metals T_c has been found to decrease from its value in thicker films. This decrease of T_c has been studied for Pb on SiO and Ge,[13] and also for other materials.[13,20,21]

In a recent consideration of this problem, Grandquist and Claeson have fit their data to a proximity-effect model which considers a dead region on the film surface.[21] While we essentially agree with this interpretation, particularly with the phenomenology of their approach, there still seems to be a question as to whether it is necessary to postulate an actual dead region of the order 5 Å in the metal itself. Leakage of the electron wave function out of the metal may be sufficient to account for the observed T_c decreases, both on semiconductors and nominal insulators such as glass. This could be viewed as a kind of generalized proximity effect. Although one would expect the penetration distance of the electron wave function from the metal into vacuum to be significantly shorter than 5 Å, the substrate and especially regions of substrate material between the metallic grains of granular films probably serve to make this penetration distance effectively greater. Such an effect could result from an increase of the surface area as the film becomes granular, some increase in penetration of the wave function into the dielectric substrate as compared to penetration into the vacuum, and also real electron states at the interfaces. This view is somewhat similar to one proposed by Halbritter, in which electrons are scattered into "pair-weakening" states at the interface.[22,23]

Despite the complications presented by the higher-T_c In films and by granularity and agglomeration, a large portion of the data on normal-state resistivity, critical fields, critical currents, and T_c for this experiment is consistent with the involvement of a relatively low density-of-states region of the PbTe or Te substrate of thickness 10–100 Å. Perhaps this substrate region lowers T_c by providing a region with a small superconducting interaction for some of the metal electrons to explore, leads to a large normal-state mean free path by providing a thick region of relatively high mobility for conduction, gives low critical fields in thin agglomerated films because of weakly superconducting regions between globs, yet retains higher critical currents than expected for a granular film due to the coupling of grains by the weakly superconducting yet relatively thick substrate region between. Although taken individually each of these points might equally well be explained by other mechanisms, taken together they are difficult to explain otherwise. Furthermore, it is possible that the substrate has an even more important influence on the superconducting properties due to the electron-phonon interaction in the semiconductor near the interface with the metal film. PbTe, for example, has been investigated for superconductivity at carrier concentrations up to $5\times10^{20}/\mathrm{cm}^3$, and although no superconductivity has been found, the material has been considered a candidate for a large electron-phonon interaction on theoretical grounds.[24] Although inclusion of a nonzero interaction in the substrate would require some modification to our proximity-effect analysis, it might help explain some of our results; especially the anomalous results for In films. If deep, narrow inversion layers exist in these samples due to band bending to accommodate work-function differences between metal and semiconductor, near-metallic carrier concentrations may be realized, leading to superconductivity in a narrow region of semiconductor at the interface. This, in proximity with the superconductivity of the metal film (or agglomerated metal islands) would lead to a thicker region of superconductivity and enhanced normal-state conductivity as indicated by our measurements.

VI. SUMMARY AND CONCLUSIONS

There are several important implications for further work on finding an excitonic superconductor. The first is that one cannot expect that producing the theoretically correct spatial arrangement of materials is sufficient for a definitive test of the theory. Epitaxial, crystalline 15-Å-thick Pb films deposited on clean, crystalline, unreconstructed PbTe and measured *in situ* closely approach the ideal structure proposed by ABB, yet there is no evidence at all in these experiments for an excitonic enhancement of superconductivity. All transition temperatures increase with increasing film thickness, rather than showing a maximum at some small thickness such as 10–15 Å, as predicted by theory. The enhanced T_c of In and Tl films occurred at such large film thicknesses that it is highly unlikely that this was the result of the excitonic mechanism proposed by ABB.

This does not imply that the theory has been given a rigorous experimental test and found to be lacking. A materials configuration which satisfies the requirements for the spatial arrangement of the atoms of metal and substrate separately does not automatically lead to the appropriate electronic configuration at the interface when the system is combined. The theory of ABB requires an appropriate dielectric response from the substrate within 5–10 Å of the interface. Indeed, it appears from the superconducting behavior that the necessary conditions are not attained at the interface and deviations from bulk densities of states at the interface region actually cause a depression of T_c for the thinnest films. To seriously undertake further experiments, methods of characterization must be used which are sensitive to the configuration of electronic states at the surface and interface region.

Serious questions have also arisen as to the possibility of ever achieving an appropriate electronic structure for an appreciable enhancement of T_c. For example, Phillips[25] has suggested that the maximum transition-temperature enhancement available for an excitonic mechanism will be limited to a few degrees by instabilities at the interface which lead to a high density of localized interface states. However, until more experiments are done to see whether the proper interface conditions can be attained these theoretical questions must remain open.

ACKNOWLEDGMENTS

We are grateful for the advice and encouragement of Professor J. Bardeen in this work. We would also like to thank T. Arns and G. Hrabak for their help in the design of the apparatus, and D. Myers for growing some of the PbTe crystals used as substrates.

---

*Work performed under the auspices of ERDA.

†Partially supported by Joint Services Electronics Program (U. S. Army, U. S. Navy, U. S. Air Force) under Contract No. DAAB-07-72-C-0259.

[1] J. R. Gavaler, Appl. Phys. Lett. 23, 480 (1973); J. R. Gavaler, M. A. Janocko, and C. K. Jones, J. Appl. Phys. 45, 3009 (1974); L. R. Testardi, J. H. Wernick, and W. A. Royer, Solid State Commun. 15, 1 (1974).

[2] W. A. Little, Phys. Rev. 134, A1416 (1964).

[3] V. L. Ginzburg, Phys. Lett. 13, 101 (1964).

[4] David Allender, James Bray, and John Bardeen, Phys. Rev. B 7, 1020 (1973).

[5] Myron Strongin, J. M. Dickey, H. H. Farrell, T. F. Arns, and G. Hrabak, Rev. Sci, Instrum. 42, 311 (1971); H. H. Farrell, Myron Strongin, and J. M. Dickey, Phys. Rev. B 6, 4703 (1972).

[6] Myron Strongin, O. F. Kammerer, H. H. Farrell, and David L. Miller, Phys. Rev. Lett. 30, 129 (1973).

[7] D. L. Miller, thesis (University of Illinois, Urbana, 1973) (unpublished).

[8] D. L. Miller (unpublished).

[9] D. L. Miller, Myron Strongin, O. F. Kammerer, and B. G. Streetman, Phys. Rev. B 8, 4416 (1973).

[10] D. L. Miller, T. Arns, and G. Hrabak, Rev. Sci. Instrum. 46, 1642 (1975).

[11] M. Green and M. Lee, J. Phys. Chem. Solids 27, 797 (1966).

[12] P. W. Palmberg and T. N. Rhodin, J. Appl. Phys. 39, 2425 (1968).

[13] Myron Strongin, R. S. Thompson, O. F. Kammerer, and J. E. Crow, Phys. Rev. B 1, 1078 (1970).

[14] F. Jona and J. A. Strozier, Jr., in *Epitaxial Growth, Part A,* edited by J. W. Matthews (Academic, New York, 1975), p. 309.

[15] G. D. Cody and R. E. Miller, Phys. Rev. 173, 481 (1968).

[16] J. F. Miller *et al*., AIME Metal Soc. Trans. 239, 342 (1967).

[17] A. Comberg, S. Ewert, and G. Bergmann, Z. Phys. 271, 317 (1974).

[18] B. W. Roberts, Natl. Bur. Stand. Technical Note No. 724 (U. S. Dept. of Commerce, Washington, D. C., 1972).

[19] A. Saxena, J. E. Crow, and Myron Strongin, Bull. Am. Phys. Soc. 17, 333 (1972); R. A. Buhrman, W. P. Halpern, and W. W. Webb, *Proceedings of Thirteenth International Conference on Low Temperature Physics,* Boulder, Colo., edited by W. J. O'Sullivan, K. D. Timmerhaus, and E. F. Hammel (Plenum, New York, 1974).

[20] D. G. Naugle and R. E. Glover, Phys. Lett. 28, 611 (1969).

[21] C. G. Grandquist and T. Claeson, J. Phys. (Paris) 35, C4-301 (1974); C. G. Grandquist and T. Claeson, Phys. Kondens. Mater. 18, 79 (1974).

[22] J. Halbritter, Phys. Lett. A 53, 377 (1975).

[23] J. Halbritter, *Proceedings of the Fourteenth International Conference on Low Temperature Physics, Otaniemi, Finland, 1975,* edited by M. Krusius and M. Vuorio (American Elsevier, New York, 1975), Vol. 2, p. 227.

[24] J. K. Hulm, M. Ashkin, D. W. Deis, and C. K. Jones, *Progress in Low Temperature Physics,* edited by C. J. Gorter (North-Holland, Amsterdam, 1970), Vol. VI.

[25] J. C. Phillips, Phys. Rev. Lett. 29, 1551 (1972)