Growth and Characterization of Superconducting In and Pb Films

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Abstract. Elemental In and Pb films ranging in thickness from 200 - 2000 nm have been grown on glass (SiO$_2$) and other substrates using vacuum vapor deposition. Film growth was monitored and controlled by in-situ four-point probe resistance measurements. Samples grown concurrently were analyzed using several techniques: X-ray transmission for thickness measurement and X-ray Diffraction for morphology, structure, and composition of the films. The In films exhibited a tendency to grow in the (101) direction, with slight variations caused by the deposition rate. Ambient temperature transport measurements and temperature scans down to below the superconducting transition temperature ($T_c$) were carried out, with transition temperatures consistent with bulk metals. The films exhibit high residual resistance and temperature coefficients of 0.003/K for Pb slightly lower than published bulk measurements and 0.0025/K for In. Using the Matthiessen’s rule for conduction in metals, the crystallite or grain size was inferred to be an order of magnitude lower as compared to that obtained from X-ray diffraction using the X-ray peaks’ full width at half maximum (FWHM), suggesting a preferred direction growth of the In crystallites on glass, but not for Pb. Some In sample films were annealed at 150 °C in N$_2$ to improve on their morphology.

1. Introduction
Recent work on superconductors has focused on either ceramics or ultra-thin films. Resistance measurements can detect superconducting transition of small, but macroscopic, diameter wires and nm to μm sized films if care is taken to adjust for the inherent low resistance of metallic samples. In the times since the original studies of elemental superconductors, the techniques to grow and characterize high quality metallic films have matured, allowing for the study of elemental films with thickness of nm to μm.

Superconductivity is dependent on electron-phonon-electron interaction, and the phonon or lattice spectrum is affected by both impurities and crystallite or grain size. Under the growth conditions in the present study, the impurities are relatively non existent. Therefore, as the thickness of metal film decreases, the electrons drifting through the film are mainly scattered by grain boundaries and phonons in the normal state. According to the Bardeen, Cooper and Schrieffer (BCS)[1] theory for elemental metals (e.g. In and Pb), the transition temperature is given by $k_BT_c \sim \hbar v e^{-1/N(0)V}$. Here $V$ is the weak coupling potential, which gets weaker with grain size and film thickness.

The purpose of this study is to investigate the effects of film thickness on both the normal and superconducting properties of films of In and Pb. Both elements have a transition temperature (3.4 K and 7.2 K, respectively) accessible with a $^4$He cryostat. In particular, In has a very
sharply defined transition between 1.5 and 4.2 K, a range that can be scanned in detail with a $^4$He bath through slow control of its saturated vapor pressure. The resistance of a thick film is much larger than that of small diameter wire, which makes the study of the transition temperature easier.

2. Experimental Details
Films were grown using vacuum vapor deposition under moderately high vacuum. Four point resistance measurements were used for both in-situ monitoring of film growth and for the resistance temperature dependence of resulting films, in the range $2 < T < 300K$. Post growth film characterization was done using X-ray absorption to determine and confirm the film thickness and X-ray diffraction for crystal structure and grain size.

Pure reagent-grade metals (99.99% for Pb, 99.998% for In) were evaporated from a tungsten boat in a chamber that was purged multiple times with dry $N_2$. The boat was heated by a current (100 A to 140 A, AC) and controlled for a steady growth rate. During the deposition, several substrates were used: ultrasonically cleaned glass ($SiO_2$) slides of ~0.5 mm thickness and commercial Si and Ge. For any one deposition, several substrates were held by an aluminum mask/holder supported by a stand at ~20 cm above the boat. All concurrently grown samples had a total area of 5 cm$^2$.

The deposition rate was monitored by the voltage across two separate four-point probes due to a DC current. Using the distance between the voltage leads on the substrate and the width of the film strip, growth rates of 5 to 60 nm/min were achieved. In all cases, the in-situ inferred thickness was consistent with later X-ray determination. A total of 7 In and 5 Pb films of thickness 200 nm to 2000 nm were grown.

The films were transferred to an X-ray Diffractometer for both absorption and diffraction scans. Scans around the attenuated direct beam through both bare glass and film-covered glass were obtained. From the intensity ratio and the mass absorption coefficient at the X-ray wavelength the metal film thicknesses were deduced, corroborating the in-situ results. With different geometry, wide angle diffraction scans $10^o < 2\theta < 120^o$ were carried out on samples from all 12 depositions.

Resistance measurements with temperature were done on 2 films and on an In wire ($d = 0.250$ mm, 99.998% pure) using four point contacts with a floating AC current source[2] and a lock-in-detector at low frequencies. To carry out the measurements on the wire, the current source was modified to provide 0.250A to compensate for the huge decrease (by ~1400) of the wire resistance. The current in the wire was at most $2.85 \times 10^8$A/cm$^2$, and 10× lower in the film to avoid self heating. This current generated a magnetic field at the surface of the wire 3× below $H_c$ [3]. The contacts were made using a 2 component silver epoxy that cures at ambient temperature and is designed for cryogenic use. The temperature scans are routine in our laboratory with LabView monitoring and data collection. A calibrated Si-diode was used to measure the samples’ temperature (2 at a time). All samples were in intimate thermal contact with a boron nitride holder and cooled overnight down to 4.2 K. Below 4.2 K the helium bath vapor pressure was monitored with capacitance gauges while pumping at a very slow rate.

3. Results and Discussion
We present the X-ray diffractions results, as shown in Fig. 1, where the intensity of the diffracted beam is plotted vs. $2\theta$. The peaks appearing in the XRD scans are those characteristic of polycrystalline In [4] or polycrystalline Pb [5]. The polycrystallinity is due to the formation of growth centers with random orientations early in the film growth. While not obvious in the graph, other peaks are present in the Pb diffraction scan, but the (111) peak dominates. For both films, each peak in the diffractogram can be attributed to pure metal In or Pb. Surface oxidation may have occurred after exposure to ambient atmosphere, but no XRD evidence of
crystalline oxide was noticed. Films were annealed in a \( N_2 \) environment exhibited an increase in resistance with no new peaks observed.

Figure 1. X-ray Diffractograms for \( In \) and \( Pb \) on glass films.

Detailed scans of the first 3 peaks of \( In \) films were taken and a summary of their analysis is shown Figs. 2 and 3. It can be seen from Fig. 2 that the film thickness has an effect on the relative sizes of the peaks. This suggests that the favored growth direction is for the (101) planes to be aligned parallel to the substrate surface. It can also be noticed that the growth rate appears to have an effect on the grain size. Faster growth rates, denoted by large circles in the graph consistently fall above the trend line, which denotes an average of all sample growth rates and thicknesses. The grain size was determined using the Scherrer relation. The grain sizes are related to the film thickness, but the individual crystal grains do not appear to have a preferred growth direction. The growth rates used in our experiments (5 to 60 nm/min) are much slower than those used in other studies[6] on \( In \) films (100 nm/s).

The resistance results are shown in Fig. 4 where \( R(T)/R(300K) \) vs. \( T \) is plotted in the range \( 4.2K < T < 300K \). This kind of graph is very useful, one can, by inspection, read off the residual resistance ratio (RRR) and the coefficient of temperature (\( \alpha \)). All data exhibit metallic behavior with different RRR and temperature coefficients, with excellent thermal cycling. The \( In \) film (red data points) and its thermal cycling have the highest RRR followed by the \( Pb \) film (blue and green data points), with \( RRR = R(T > T_c)/R(300K) \), of 0.73, 0.07, and \( \alpha \) of 0.0001 K\(^{-1}\), 0.003 K\(^{-1}\), respectively. The \( In \) wire has a room temperature resistance of 0.150 \( \Omega \) and

Figure 2. \( In \) XRD peak intensities by film thickness and growth rate.

Figure 3. \( In \) grain size by film thickness and growth rate.
**Figure 4.** $R(T)/R(300K)$ vs. $T$ for $In$ (higher RRR) and $Pb$ films on glass, and an $In$ wire ($d = 0.25$ mm).

**Figure 5.** $R(T)/R(4.2K)$ vs. $T$ for the $In$ film (1000 nm) (red) and wire (blue) around transition temperature ($T_c = 3.4$ K).

107 $\mu\Omega$ at 4.2 K and thus exhibits the smallest RRR (0.00071) due to its high purity and and $\alpha$ of 0.0025 K$^{-1}$. Although both the $In$ wire and the $In$ used to grow the film have same purity, $\alpha$ for the wire is 2.5× larger than for the film. However, the $Pb$ film showed no difference in $\alpha$ than the literature.

Using Matthiessen’s rule for a high purity sample(s), $\rho_T = \rho_b + \rho_i + \rho_L$, due to electron scattering off of grain boundaries, impurities, and lattice vibrations, respectively. In a pure specimen at low temperature but above the relevant $T_c$ the electron scatter mainly off of the grain boundaries and their mean free path is the grain size along the direction of the current. This leads to grain sizes, $l = \rho(300)/\rho(lowT) \cdot v_F\tau = R(300)/R(lowT) \cdot v_F\tau$, of 10 nm, 33 nm, and 10,000 nm, for the $In$ and $Pb$ films and the $In$ wire, respectively. Here, $v_F\tau$ is the electron mean free path at ambient temperature in the relevant metal.

Fig. 5 shows a graph of $R(T)/R(4.2K)$ vs. $T$ for the $In$ film (red data) and wire (blue data). It is readily seen that relative drop in resistance is the same for both, and the transition into the superconducting state occurs at 3.40K for the wire and is lowered by 50 - 60 mK for the film and the transition region is wider for the film.

4. Conclusions

A least one $In$ film exhibits a grain size inferred from XRD (100 nm) much bigger than from the RRR (10 nm) while the two results are the same (30 - 50 nm) for the $Pb$ film. The temperature coefficient, $\alpha$, for $In$ film is 2.5× smaller than for bulk but is similar for both $Pb$ bulk and film.

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