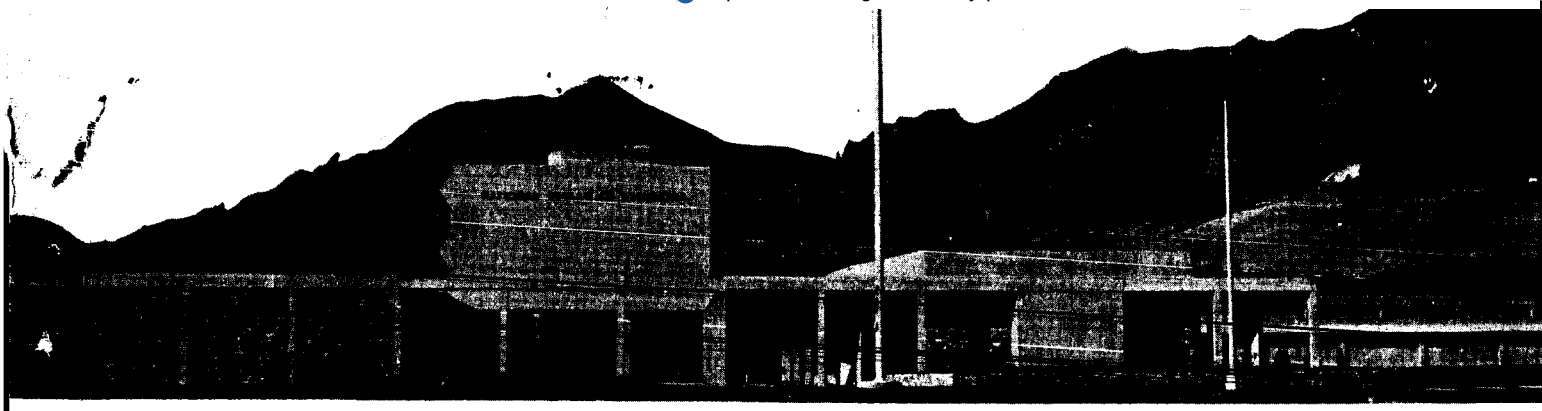

NBS REPORT

9269

FINAL REPORT

On Research and Development of Superconducting Thin Films

by

R. S. Collier, R. A. Kamper, L. O. Mullen, and R. J. Duffy

December 15, 1965 to December 15, 1966

for

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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ABSTRACT

The effort on superconducting thin films for the past year has been primarily concerned with the production of good quality Niobium films. Deposition parameters were varied, resulting in different values for the critical temperatures. The highest value was 8.8°K (as compared with 9.0°K for the high purity starting material).

We have made preliminary tunneling measurements on Pb films in a magnetic field; for magnetic field and critical temperature measurements, a cryostat was built which is stable (in a changing magnetic field) to .001°K in the range 5-10°K.

We have also done some high vacuum annealing of large Niobium single crystals.

Deliveries were made to the contractor of

(1) One sample of vacuum annealed Niobium crystal

(2) Several Lead films

(3) High purity Niobium films

INTRODUCTION

Our point of view in making good Niobium films has been to deposit Niobium at a comparatively slow rate while keeping the background pressure very low. By doing this we control the recrystallization of the Niobium as it condenses on the substrate and at the same time have a slow gettering rate of the background gases. The film quality is determined by the impurities in the film and the mode of recrystallization on the substrate. The film purity is usually improved by increasing the evaporation rate while the recrystallization is usually improved (depending on the substrate temperature) by decreasing the evaporation rate. Therefore, we expect to find an optimum rate relying on the low background pressure (10^{-9} - 10^{-10} torr) to reduce impurities. We have selected three tests to measure the film quality: 1) The electron microscope to give a qualitative picture of the mode of recrystallization and the surface morphology. 2) The measurement of the critical temperature T_c is a very sensitive test of chemical purity particularly for Nb, V, Ta. 3) The measurement of the Ginzburg-Landau parameter, κ, indicates the electrical purity (which includes impurity, grain boundary, and surface scattering). We have used a stable temperature cryostat to measure T_c, κ, and the field dependence of the energy gap.

The sensing device of this cryostat is a helium gas bulb thermometer which controls the balance between a thermal leak from the sample to the liquid helium bath and a heater connected to the sample. The absolute temperature is measured by a Germanium resistance thermometer in zero magnetic field at the same time that the gas thermometer is locked into the system. This system maintains the temperature stable to better than 0.001°K with a 3 second time constant.

FILM DEPOSITION

We have been able to evaporate Nb, Ta, and Pb films at background pressures approximately 10^{-9} torr. For Nb and Ta this requires a 48-hour degassing of source and surrounding shields which heat up by radiation. The source is high purity triple zone refined material supplied by MRC. The degassing is accomplished by heating the source to approx. 2000°C. (If necessary we can reduce the background pressure even further by filling a built-in liquid He dewar.) At 10^{-9} torr the rate of gas accumulation on the substrate is approximately .001 Å/sec (assuming a sticking coefficient of unity). Therefore, to safely achieve better than 1% impurity the evaporation rate must be at least .1 Å/sec. With the existing equipment this rate has been easily accomplished except for Nb, where there is excessive heat loss to the copper when the Niobium melts. This is because of an increase in heat conduction between the Niobium and its water cooled crucible as the molten Niobium increases in temperature. So our main effort has been concentrated in improving the crucible design and increasing the efficiency of the electron beam power source.

For our best films (T_c = 8.8 °K) we have used a water cooled Tungsten pedestal which has been designed for an optimum conduction heat loss. We also decreased the source to substrate distance from 10" to 4" (this increases the deposition rate by a factor of 10). With these modifications, deposition rates in the range 1 Å/sec to 10 Å/sec were achieved. The substrate temperature ranges from 350°C to 500°C. The vacuum system is shown in figure 1.

As a by-product of our work on water cooled pedestals we have developed a stainless steel crucible for evaporating Aluminum (Al is normally the reference film in tunneling measurements). This has greatly enhanced the speed and reliability of Al deposition which, heretofore, had been plagued by Al dissolving Tungsten and Carbon crucibles.

As the evaporation rate for Niobium has improved we have noticed that the oscillating quartz crystal normally used to monitor the deposition rate becomes less accurate, probably due to an increase in the concentration of free Niobium ions. A similar behavior of the oscillating quartz crystal is observed during a glow discharge. We have used an optical pyrometer for monitoring the temperature of the evaporating material. Corrections for the energy loss to the optical detector are referenced to an operating filament in the vacuum system, using the melting point of Niobium as a fixed point. The corrected monitored temperature is used to determine the vapor pressure from the data of Honig[1] from which the deposition rate is calculated as a function of temperature, the diameter of the source, and the distance from the source to the substrate.

From kinetic theory, the deposition rate n is

$$n = \frac{r^2 NP}{d^2\sqrt{2\pi RMT}} \quad \text{molecules per unit area}$$

where N is Avagadro's number, P the vapor pressure of the source, R the gas constant, M the molecular weight and T the vapor temperature, which we take to be the same as the source temperature. The radius of the ball or molten material is r and its distance from the substrate is d. Table 1 shows the calculated relationship between temperature, vapor pressure and evaporation rate in molecules per unit area.

TABLE 1

CALCULATED EVAPORATION RATES

Temperature °K	Pressure torr	Evaporation rate $\frac{NP}{\sqrt{2\pi RMT}}$ molecules/cm^2
1765	10^{-11}	8.69×10^{8}
1845	10^{-10}	8.52×10^{9}
1935	10^{-9}	8.27×10^{10}
2035	10^{-8}	8.09×10^{11}
2140	10^{-7}	7.88×10^{12}
2260	10^{-6}	7.67×10^{13}
2400	10^{-5}	7.46×10^{14}
2550	10^{-4}	7.22×10^{15}
2720	10^{-3}	7.00×10^{16}
2770 melting point		
2930	10^{-2}	6.76×10^{17}
3170	10^{-1}	6.48×10^{18}
3450	1	6.23×10^{19}

The precision of this method is limited by temperature variations of up to 150°C observed over the surface of the evaporating Niobium source. Despite this, however, the calculated deposition rate agreed with the observed rate within a factor 2.

VACUUM ANNEALING

A technique was developed for heating a 3/8" diam. Nb rod to a temperature of 2200°C by electron beam bombardment. Near this annealing temperature the sample temperature had a tendency to rise catastrophically to its melting point. This was corrected by building in a feedback loop to limit the total input power to the sample. NASA sample B-3572 was then annealed at 2200°C. The base pressure of the system at this temperature was 1×10^{-10} torr. The sample was annealed for 5 hrs. at this pressure and then oxygen was leaked into the system at 3×10^{-6} torr for 2 hrs. and then pumped back down to base pressure for another five hours. The resistance ratio $RR = \rho_{273°K}/\rho_{9°K}$ was determined by measuring the time constant τ of eddy current decay in a pulsed magnetic field. $\tau_{9°K}$ as received was 2.65 millisecond; after anneal, $\tau_{9°K}$ = 27-30 millisecond. $\tau_{273°K}$ = 22.5 microsecond was calculated from the expression

$$\tau = k \frac{2.17 \mu r^2 \times 10^{-9}}{\rho} \text{ sec;}$$

μ = permeability, r = radius in cm., ρ = resistivity in ohm-cm., and k is a 7% adjustment for the short length. Therefore RR = 120 in the sample as received and RR = 1330 after anneal with estimated accuracy for these figures as ±5%. The sample was immersed in liquid nitrogen to chemically de-activate it and was delivered to Mr. J. Simmons at NASA, Lewis Research Center.

TUNNELING MEASUREMENTS ON Pb FILMS

Preliminary tunneling experiments on lead films have extended the work which was done on tin films. The K values for lead are greater than 0.5 and have taken us into new regions of the theoretical K vs. 2d phase diagram which was recently published.[2] Here, the one dimensional G. L. equations predict an assymetric solution for the energy gap. This is the type of solution we expect for almost all Niobium films. Numerical solutions of the G. L. equations are being studied to determine the nature of the field transition from the symetric to the assymetric form. Hopefully, this will give an interpretation of tunneling experiments on high K materials.

CONCLUSIONS AND RECOMMENDATIONS

We have acquired the technique of making Niobium films with good chemical purity and well defined crystal structure (as demonstrated by the high critical temperature). The next step in our program must be to develop a controllable insulating barrier for tunneling junctions which is compatible with the high substrate temperature during the deposition of the Niobium films. Probably Niobium oxide can be used for such a barrier.

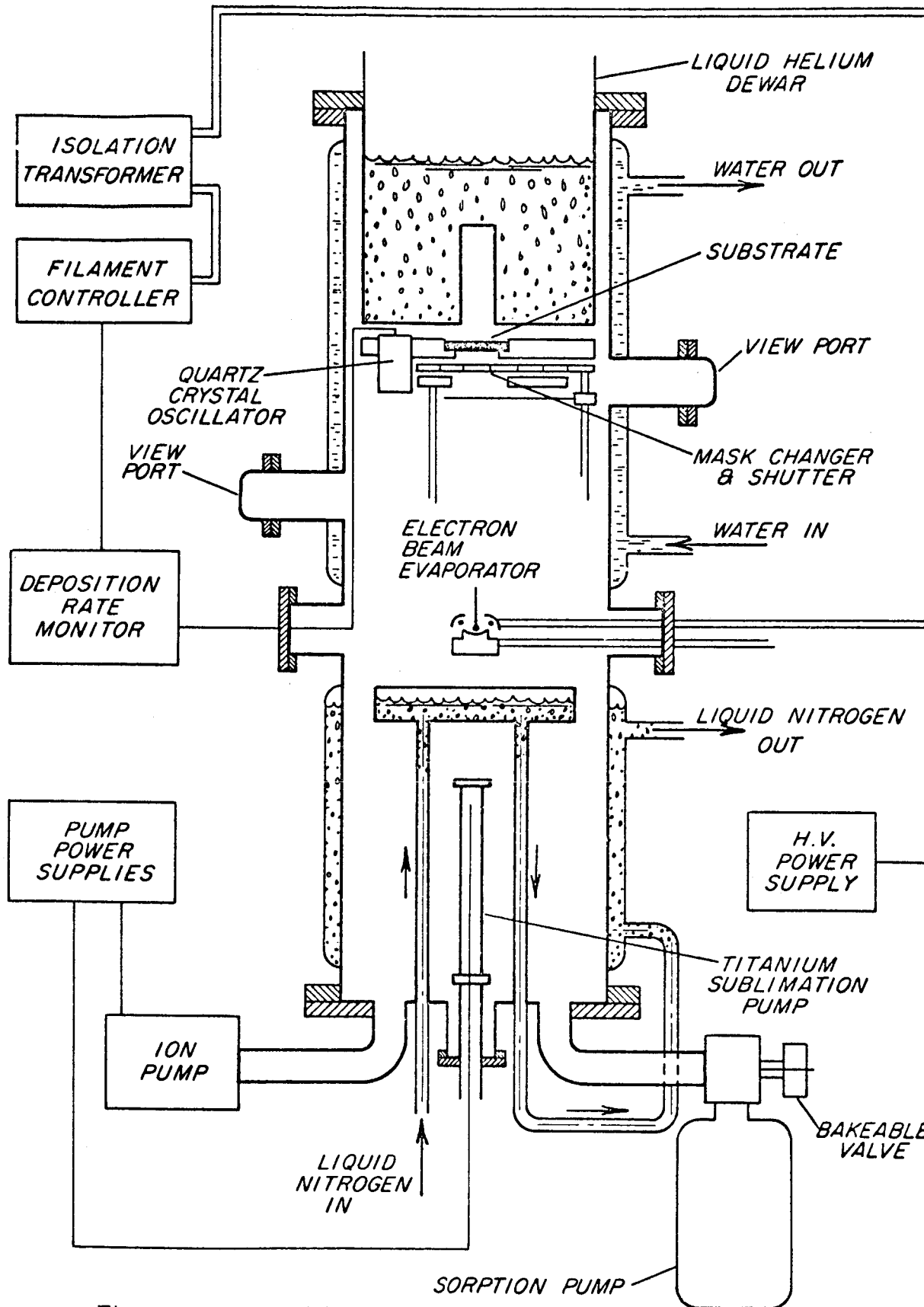

Figure 1. Ultra-high vacuum deposition system.

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