

MO-RE FILMS FOR SRF APPLICATIONS

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Abstract

Single (sintered composite Mo₃:Re₁) and dual (separate Mo and Re) targets were used to grow superconducting films of Mo:Re, using cathodic arc plasmas. Sharp, superconducting transitions (at up to 13K) were observed in ~1 μ m thick films deposited on a-sapphire and MgO crystals. XRD (Bragg-Brentano spectra) revealed a single sharp peak of Mo-Re (611) plane, from the composite Mo₃:Re₁ film. SIMS measurements revealed the role of impurity concentrations on superconducting properties. The XRD spectra in this case showed the (330) plane of Mo-Re. The transition temperature of the Mo-Re films depends upon the stoichiometry of the film. The dual-target approach allows control of stoichiometry by varying only the current to each target (cathode). This demonstration of stoichiometric control in dual-target arcs enables other compound films (e.g. Nb₃Sn, MgB₂ etc.) to be grown in a single-step. The measured RRR (defined as the ratio of residual resistivity at 300K to that at 14K) in the best films was 6, which is higher than measured by others at higher annealing temperatures. However, for SRF cavity applications, the RRR should be increased to >100, which is our next goal.

INTRODUCTION

All of today's industrial accelerators use normal conducting RF cavities to accelerate the particle beam. Normal conducting RF cavities are selected based on technology cost and maturity, the latter being an overriding factor as commercial use of RF accelerators demands turn-key and reliable systems, as evidenced by years of demonstrated use. The application of superconducting RF (SRF) technology to accelerators has been confined primarily to the scientific research and development arena. Superconducting RF cavities have been incorporated only in a small number of research oriented accelerators and most of these use bulk niobium cavity RF structures. SRF cavities consume less power than conventional cavities to produce a given accelerating gradient, even when the additional energy cost of the cryogenics system is taken into account [1]. However the cryogenics system costs do represent a significant portion of the operating expense of SRF accelerators. Operation at higher temperature would naturally reduce those costs. Niobium, the only presently accepted superconductor for SRF accelerators, has a transition temperature T_c of 9.3K, but a practical operating temperature of 2K at the typically used 1.3–1.5 GHz RF frequencies. Operation below T_c is required to minimize surface resistance and

maximize critical magnetic field. Increasing the operating temperature of the accelerator from 2K to 4.5K could cut the cryogenics system costs in half [1], but would require use of an alternative superconductor with an operating temperature of 10K or higher, such as Mo₃Re, NbN, Nb₃Sn or MgB₂. Since the RF (London) penetration depth on the cavity surface is only ~50nm, it is of interest to develop thin film coatings on the nano-scale (~100nm) for particle accelerators. There is also strong motivation to understand and develop higher temperature superconductors, including the A-15 candidates [2-3]. In an article in Nature [4], Eric Hand states that the superconducting cavities that drive most of the world's particle accelerators are running out of room for improvement. But new theoretical work suggests that overlooked superconducting materials could be used to make cavities that accelerate particles to higher energies over shorter distances - thereby doing the job more cheaply. For decades, researchers have worked to improve the performance of superconducting cavities.

A higher temperature superconductor has not yet been qualified. Several A-15 compounds (such as Nb₃Sn, NbN, Mo₃Re and others), as well as MgB₂ are potential replacements to expensive niobium. However, A-15 coating development requires innovation to demonstrate the necessary properties to replace Niobium. An increase in operating temperature makes SRF technology more attractive for commercial applications in industry as well.

Alameda Applied Sciences Corporation (AASC), mostly with DOE SBIR Grant support, has been developing superconducting thin-films for over four years. We began with Nb films, progressed to MgB₂ films and are presently working on Mo₃Re films and on Nb₃Sn films (an ongoing PhII SBIR). Our approach uses a patented process that we have dubbed Coaxial Energetic Deposition (CEDTM) to grow the films. Recently we have brought into operation a different version of such an energetic condensation apparatus that we have dubbed Cathodic Arc Deposition (CAD).

EXPERIMENTAL ARRANGEMENT

The CAD apparatus (Figure1) is a vacuum planar arc between the front face of a cathode bar and a Mo mesh. An alumina insulator surrounds the cathode bar, to force emission only from the cathode face. The main arc plasma is initiated by a short duration secondary trigger arc plasma that provides enough metallic plasma between the electrodes to trigger the main arc/s.

No external magnetic field is applied so the movement of the arc spot is random across the cathode face.

Parameters such as distance (source, sample, mesh), angle of the ion beam, deposition rate, flux density and magnetic field, can be varied to scan parameters and define the optimum configuration.

The CAD apparatus is a multi-cathode source. Compounds such as Mo_3Re , Nb_3Sn , MgB_2 , etc., can be produced using dual-target discharges, where the stoichiometry of the films is controlled by the individual currents that in turn control the mass eroded from each arc.

Figure 1 shows a photograph of the electrode configuration. Looking down from the top, the anode mesh is seen and 10mm below this lies the cathode. The substrate is located 87mm from the anode.

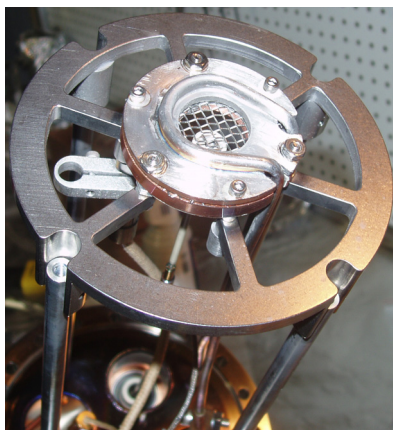


Figure 1: CAD apparatus.

The arc discharge is driven by a pulse forming network (PFN) that is shown in Figure 2a. The inset in this figure shows an electrical equivalent circuit for the PFN, consisting of ten stages, each of 500 μF capacitance and 4.8 μH inductance. The Thevenin equivalent source impedance is $\approx 100\text{m}\Omega$ and the pulse width is $\approx 1\text{ms}$.

Figure 2b shows a typical discharge current pulse. For a -170V bank charge voltage, a 1kA flat-topped current is driven into the arc in a 1ms wide pulse. This is a charge of one Coulomb. For a typical cathode erosion rate of $\sim 40\mu\text{g}/\text{C}$, this charge converts 40 μg of cathode metal into a hot, highly ionized plasma with $\sim 60\text{--}160\text{eV}$ ion kinetic energy [5]. If the discharge is fired repetitively at 10Hz (which it is designed to do) the rate of ionization would be 0.4mg/s. This is roughly 1g/hr of erosion. The CAD coating apparatus is capable of depositing very thick films or covering a large area, such as an RF cavity.

Figure 3 shows a photograph of the heated substrate holder. Up to three 10mm \times 10mm substrates are clipped to the substrate, which may be heated to 900 $^\circ\text{C}$.

To study the effect of substrate preparation on epitaxial growth of metallic ions, a 3 hour pre-anneal of the substrates in the 100 $^\circ\text{C}$ – 900 $^\circ\text{C}$ range was performed on a-, c-plane sapphire and $\text{MgO}(100)$ samples. Prior to the thermal treatment of the samples, the CAD apparatus is baked out for 18 hours at 120 $^\circ\text{C}$. A turbomolecular pump in series with a mechanical pump, allows the chamber to reach a background pressure of 2×10^{-8} torr. The samples are supported on a 50 mm diameter Alumina-heater,

allowing several samples (10 mm \times 20 mm) to be placed on the heater. The frequency of the discharge is 0.25 Hz, low enough to permit pump-out of molecules that have been desorbed from the wall by energetic ion bombardment from the previous pulse.

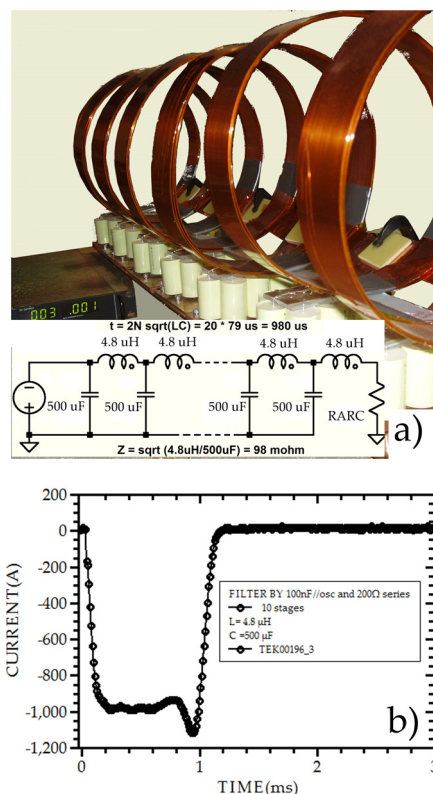


Figure 2a: Pulse Forming Network(PFN) of 10 stages, inset shows the electrical diagram. Figure 2b: PFN current trace.



Figure 3: Front view of 50 mm alumina heater on the CAD. Three samples can be placed at the same time.

SUPERCONDUCTING TRANSITION VS SUBSTRATE TYPE AND TEMPERATURE

Most of the samples prepared by the CAD apparatus present superconducting properties. Transition temperature (T_c) in the range of 7 – 13K was measured using a standard four probe DC resistivity measurement apparatus available at Jefferson Lab.

Figure 4 shows T_c /RRR measurements from two samples, CAD-40 and CAD-41 that were coated on a-plane sapphire and MgO crystals respectively. The RRR for both films was at best ≈ 1.5 . These films were grown using the dual-cathode assembly at 900/900. EDX allowed quantification of the amount of Molybdenum and Rhenium. The T_c transitions shown in figure 4 correspond to films that had 10 atoms of Molybdenum per each atom of Rhenium, i.e. $\text{Mo}_{10}\text{Re}_1$. The stoichiometry was very different (10:1) from the $\approx 3:1$ measured for the synthetic target (CAD-61), grown at 700/800.

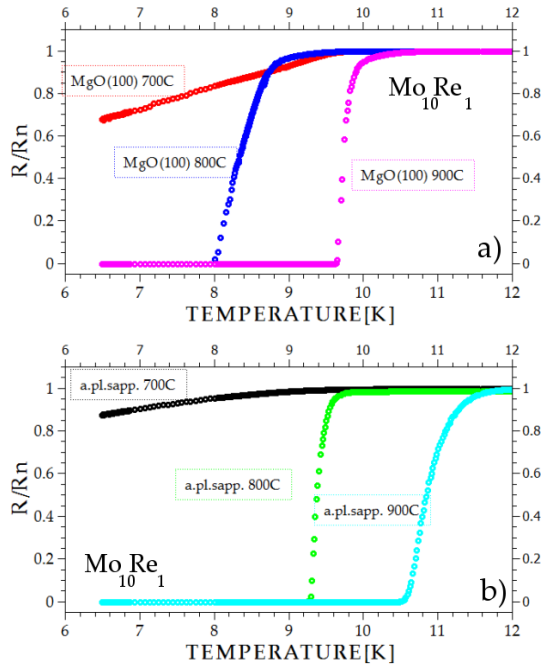


Figure 4: T_c evolution as function of deposition temperature for $\text{Mo}_{10}\text{Re}_1$ films prepared on: a) MgO(100) and b) a-plane sapphire substrates.

The curves in Figure 4 demonstrate the dramatic effect of substrate temperature on T_c for Mo-Re samples deposited on MgO(100) and a-plane sapphire substrates. T_c is observed to shift to higher values as the temperature of pre-annealing and deposition were increased. Figure 4b shows the T_c shifting to higher temperatures on a-plane sapphire substrates as the temperature of pre-annealing and deposition were increased.

For samples prepared on MgO(100) substrates (Figure 4a) T_c reached 10K at 900°C, but for samples prepared on a-plane sapphire T_c reached 11K at 900°C. We speculate that the lower mismatch between the a-sapphire and Mo_3Re unit cells in the crystal lattice might favor a higher T_c that moves closer to the theoretical T_c of the A-15 phase.

All the samples prepared with a single composite cathode also presented superconducting properties. Figure 5 shows how the transition temperature increases from 8.3 K to 10.5 K for samples (both from composite and dual-target films) grown at room temperature.

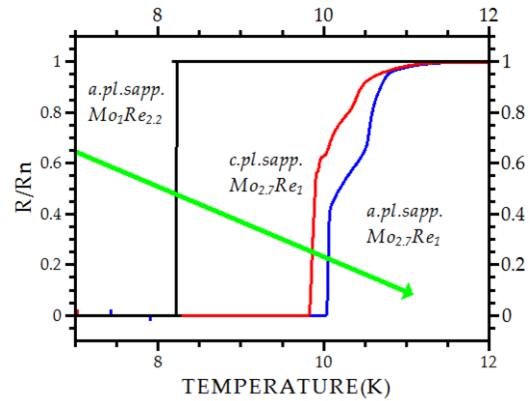


Figure 5: Transition temperature of samples prepared without heater. As the stoichiometry gets closer to Mo_3Re_1 , the T_c increases.

As the stoichiometry (controlled by the current of the arc in the case of the dual-target films), get closer Mo_3Re_1 , the T_c of the films shows a 2K increment; i.e. as the stoichiometry changes from $\text{Mo}_1\text{Re}_{2.2}$ to $\text{Mo}_{2.7}\text{Re}_1$. This special property of the A-15 compound has been reported before [6], Mo-Re is able to preserve a high T_c even when far from the ideal Mo_3Re_1 . However this is the first time (to our knowledge) that $T_c \sim 11\text{K}$ in thin films of Mo-Re prepared at room temperature has been reported. It is important to mention that the T_c of pure Molybdenum is 0.9K and that of Rhenium is 1.4K [7].

Figure 6 shows T_c /RRR measurements from two samples, CAD-61 and CAD-62, that were coated on a-plane and c-plane sapphire respectively.

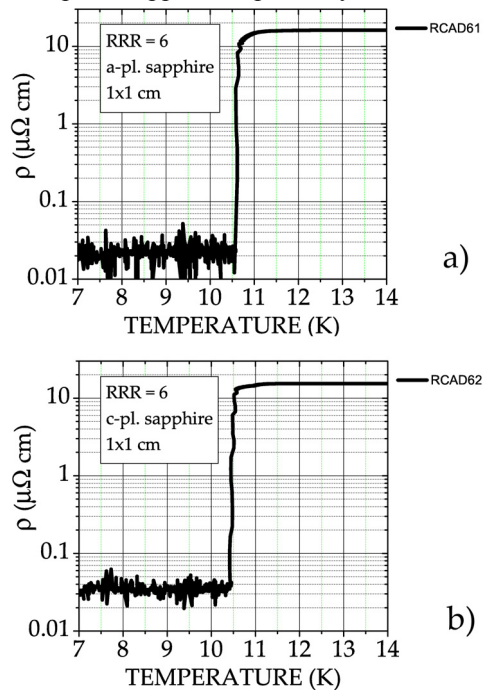


Figure 6: T_c /RRR measurement in a-plane sapphire a) and c-plane sapphire b).

Both samples were pre-annealed at 700°C for 3 hours and coated at 800°C, using 7100 pulses of 1040A peak and 1ms duration.

Both samples show a fairly sharp transition around 10.4K to 10.5K, with $RRR \approx 6$. RRR is a normal state measurement, traditionally defined as the ratio of resistivity at 300K to that at 10K [1]. For our Mo-Re films, since the transition temperature is higher than 10K, we have chosen to define the lower temperature in the ratio as 14K. To put these RRR values in perspective, we quote in Table 1 from earlier work published by S. Deambrosis of LNL/Padua, Italy, to compare with our results.

Table 1: Reproduction of Table 1 from Deambrosis et al. paper* and our results.

	$T_c(K)$	$\Delta T_c(K)$	RRR	$T_{\text{substrate}} (^\circ C)$	Annealing $T (^\circ C)$	Annealing $t(\text{min})$
Mo ₇₅ Re ₂₅	11.82	0.012	1.71	751	751-793†	30*
Mo ₃₈ Re ₆₂	9.47	0.029	1.11	750	750-785†	60*
Mo ₆₀ Re ₄₀	12.13	0.065	1.3	800	800-856†	60*
Mo ₇₅ Re ₂₅	10.4	0.090	6	800	700**	180
Mo ₇₅ Re ₂₅	10.6	0.050	6	800	700**	180
Mo ₇₃ Re ₂₇	10.2	9.8-11	1.6	20-88†	--	--
Mo ₇₃ Re ₂₇	9.9	10-11	1.5	20-88†	--	--
Mo ₃₁ Re ₆₉	8.2	0.002	1.0	20-88†	--	--
Mo ₇₃ Re ₂₇	12.8	12-14	2.5	900	900†	60
Mo ₇₃ Re ₂₇	12.6	11-14	2.6	900	900†	60

This earlier work used very similar annealing and coating temperatures, but reported RRR of <2 . While our value of 6 is still very low for high-Q cavity use, it is nevertheless higher than the best values quoted earlier, so we are encouraged by this result. Our T_c values fall right in the range of Deambrosis' values, which is reasonable given the strong variation of T_c with stoichiometry. However because the transition temperature is higher than in Nb, lower R_{BCS} resistance is expected [6,8].

X-RAY DIFFRACTION (XRD) DATA

X-ray diffraction (XRD) data ($\theta/2\theta$ scan) were obtained using a four-circle PANalytical X'Pert PRO-MRD diffractometer.

Figure 7a shows the Bragg-Brentano spectra from Mo₆Re₁, Mo₃Re₁ thin films and reference spectra obtained from the composite bar itself. The composite bar spectrum shows several Mo-Re crystal peaks, (330)Mo-Re, (422)Mo-Re, (530)Mo-Re and (611)Mo-Re, with the predominant orientation being (422). However the spectra from the thin films obtained by the dual target and the single target, present only one predominant peak: the (611)Mo-Re, for both Mo₆Re₁ and Mo₃Re₁. The lattice orientation of the substrate crystals is lost, a phenomenon also observed when we deposited Nb films [9-12] on similar substrates. The crystal growth is driven by the $\sim 100\text{eV}$ energy of the ions that drives adatom mobility and modifies the sub-surface layers of the film

sufficiently to promote epitaxial growth. Also important is the substrate preparation [9-13].

Figure 7b shows a higher resolution spectrum of the (611) peaks of Mo₆Re₁ and Mo₃Re₁. As the Re inclusion into the Mo lattice increases, the (200)Mo peak shifts to the right in 2θ .

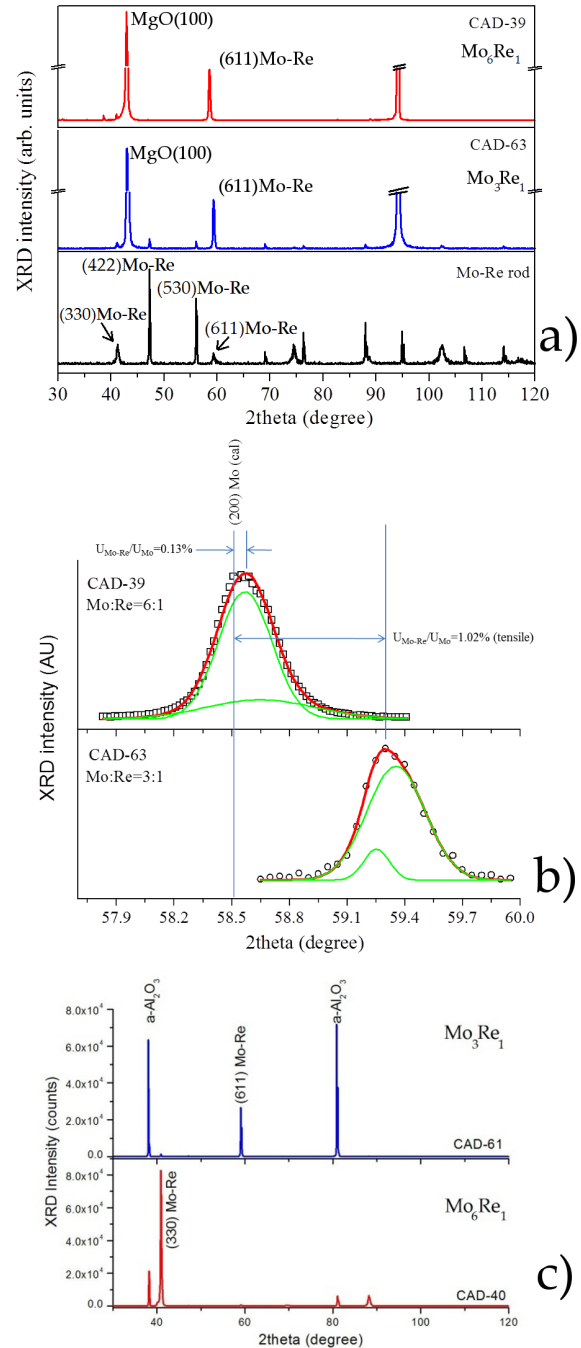


Figure 7a: Bragg-Brentano spectra of Mo-Re thin films on MgO(100) substrates and the reference spectrum from the composite bar.

Figure 7b: Mo-Re(611) peak shifts to the right as the content of Re increases.

Figure 7c: Bragg-Brentano spectra of Mo-Re thin films on a-plane sapphire: observe a switch of orientation from (330) for the Mo₆Re₁ films to (611) for the Mo₃Re₁.

* Data from Deambrosis et al paper

† Post-annealing

‡ The heater was off, but the ion bombardment heat the substrate to 88°C

** Pre-annealing

Figure 7c shows a complete switch of orientation from (330) for the Mo_6Re_1 films to (611) for the Mo_3Re_1 . More study is required to understand whether this has relevance to better SRF properties.

SIMS MEASUREMENTS

Figure 8a shows a SIMS depth profile from a Mo-Re sample with the highest RRR achieved, $\text{RRR}=6$, and Figure 8b shows the SIMS of a thinner sample with lower $\text{RRR}=1.5$. Both cases show how impurities from the substrates and surroundings are present across the entire film. The Aluminum stems from the a-sapphire substrate, but Mg also is observed in the sapphire grown film. This is most likely due to the presence of an MgO substrate that was placed on the same heater. Despite these impurities, the film reached a RRR of 6 with a T_c of $\sim 11\text{K}$. While the RRR 6 is not a laudable result, the SIMS profiles do suggest that if we were to minimize impurities such as Al and Mg from permeating the film, we might push to higher RRR.

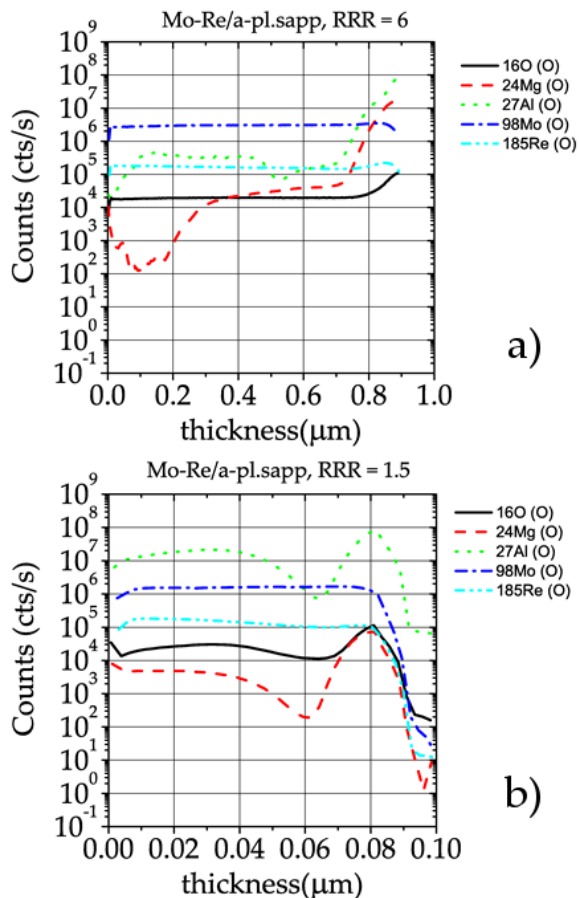


Figure 8: SIMS depth profiles for Mo-Re films.

DISCUSSION

This paper has presented preliminary data on Mo:Re thin films grown using energetic condensation [12]. The Mo:Re ions are generated in two different types of cathodic arc plasma sources. One source uses a single

composite bar of Mo_3Re_1 to generate the plasma while the other uses two separate targets, one pure Mo the other pure Re, to create separate plasmas that combine before reaching the substrate, to deposit Mo:Re films of variable stoichiometry. We have found that by varying the current to the two cathodes, we can vary the eroded mass and hence control the stoichiometry at the deposited film. This demonstration of stoichiometric control using an external circuit parameter such as current, enables growth of several other high temperature compound films such as Nb_3Sn , MgB_2 etc.

Mo_3Re is a good candidate for SRF cavities due to its imperviousness to Oxygen and high ($\sim 15\text{K}$) transition temperature. Our SIMS measurements confirm the low O contamination of the films, but the $\text{RRR}=6$ measured is worthy of considerable improvement, before we may attempt to coat a cavity with this material.

Our cathodic arc sources are particularly well suited to this compound because such arcs create very high temperature ($\sim 4\text{eV}$) plasmas that ionize the Mo:Re atoms and drive them into the substrate with $\sim 100\text{eV}$ energy that promotes crystal growth. Such energetic condensation when combined with substrate heating leads to high quality crystal growth. Our related work with Nb [9-14] has shown how the combination of thermal and energetic effects allow control of film properties. This work has shown similar trends in Mo:Re, but more work is required to optimize these compound films.

ACKNOWLEDGMENTS

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