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Fabrication of superconducting Mo/Cu bilayers using ion-beam-assisted e-beam evaporation

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Abstract

Superconducting/normal metal bilayers with tunable transition temperature are a critical ingredient to the fabrication of high performance transition edge-sensors (TES). Popular material choices include Mo/Au and Mo/Cu, which exhibit good environmental stability and provide low resistivity films to achieve adequate thermal conductivity. The deposition of high quality Mo films requires sufficient adatom mobility, which can be provided by energetic ions in sputter deposition, or by heating the substrate in an e-beam evaporation process. The bilayer T_c depends sensitively on the exact deposition conditions of the Mo layer and the superconducting/normal metal interface. Because the individual contributions (strain, crystalline structure, contamination) are difficult to disentangle and control, reproducibility remains a challenge.

Recently, we have demonstrated that low energy ion beam assist during e-beam evaporation offers an alternative route to reliably produce high quality Mo films without the use of substrate heating. The energy and momentum delivered by the ion beam provides an additional control knob to tune film properties such as resistivity and stress. In this report we describe modifications made to the commercial end-Hall ion-source to avoid iron contamination allowing us to produce superconducting Mo films. We show that the ion beam is effective at enhancing the bilayer interface transparency and that bilayers can be further tuned to reduced T_c and higher conductivity by vacuum annealing.

Keywords

transition edge sensors; ion-beam assisted deposition; Mo/Cu bilayers; proximity effect; contamination; stress

1 Introduction

Mo/Cu and Mo/Au bilayers are widely used to fabricate transition edge sensors with tunable T_c , particularly for high-energy resolution X-ray spectroscopy with state of the art-devices achieve energy resolutions of about 2 eV at 6 keV. Two techniques are in common use for the deposition of high quality bilayers: a) e-beam evaporation onto heated substrates for Mo/Au¹, and b) sputter deposition at room temperature for Mo/Cu^{2,3,4,5}. While in principle the bilayer fabrication should be straightforward, in practice reproducibility remains a significant challenge, partly because the interactions of various process and materials parameters are poorly understood. Film resistivity and stress, as well as the cleanliness of the bilayer interface all play important roles in determining T_c . More detailed studies of these correlations are hampered by the fact that it is nearly impossible to vary these quantities independently. For example, with heated e-beam evaporation, the film stress is always tensile due to the thermal expansion mismatch between the thin-film and Si substrate. In the sputter process, the energetic deposition leads to preferentially compressive stress, which is directly tied to the deposition rate via the sputter power/bias. We are studying an alternative approach to bilayer fabrication, which decouples the energy delivery for surface mobility from the deposition process: ion-beam assisted e-beam evaporation.

2 Ion-beam assisted deposition of Mo films

We have previously reported on Mo films fabricated using ion-beam assisted e-beam evaporation⁶. A commercial end-Hall ion source is used in a cryo-pumped e-beam evaporator to deliver sufficiently high ion doses at low energy. Ar, Kr, and Xe gas (99.999%) can be supplied through a gas purifier. Films are deposited on 300 μm Si wafers coated with 600 nm Si_3N_4 . The background vacuum in this shared-use equipment is about $2 \cdot 10^{-7}$ Torr, substantially worse than what is routinely achieved in dedicated UHV sputter systems. Nonetheless, the properties of the ion-assisted films are comparable to high-quality films fabricated using heated e-beam evaporation (GSFC) or sputtering (NIST). X-ray measurements showed polycrystalline films with the typical (110) fiber texture and bulk density ($\approx 10.2 \text{ g/cm}^3$). With sufficient ion-beam dose, low film resistivities ($\approx 11 \mu\Omega \cdot \text{cm}$ at room temperature) and residual resistivity ratios (RRR) of up to about 2 were achieved. Uniformity of across the 4" wafers is typically about 2–3%. Film stress showed a complex dependence on both ion energy and dose. Both tensile and compressive stresses can be produced, with higher ion energy and dose both leading to higher compressive stress⁶ due to the atomic peening effect of ion beam⁷.

Unfortunately, none of the films we reported on previously were superconducting in the as-grown state. We found that IBAD films were contaminated by about 2700 ppm (atomic) of Fe, sufficient to fully suppress superconductivity in Mo⁸. As the Fe was found to originate from erosion of ion-source components, we have since substituted (or, where necessary,

covered) all affected components (front-plate, anode, filament posts) with Mo equivalents. The modified ion source was tested over a wide range of discharge voltages and currents and operating parameters were found to closely trace those previously recorded for the stock ion-source.

Figure 1 shows a plot of superconducting transition temperature versus low-temperature resistivity for 21 samples deposited after the ion source was modified in the manner described above. In all cases, T_c is above the Mo bulk value of 0.92 K, which confirms that Fe contamination has been reduced to below ≈ 10 ppm. Over a wide range of deposition conditions, T_c appears to be closely correlated with resistivity, which in turn is believed to be dominated by grain-boundary scattering. The observed correlation agrees with that typically observed for sputtered films^{4,9} and can be understood by considering that disorder in the film smears the electronic density of states, thus, for Mo leading to an enhancement of the density of states at the Fermi level^{10,11}. Additionally, disorder could soften the phonon spectrum¹². Either effect would increase the electron-phonon coupling and result in increased T_c .

One open question is the impact of stress on T_c ; the literature on both sputtered and evaporated Mo films suggests that T_c increases with increasing compressive stress at a rate of about 250 mK/GPa¹³. This finding is at odds with the much smaller and opposite effect expected from the pressure dependence of T_c in bulk Mo. The inset in Fig. 1 shows T_c versus stress for a select set of samples of roughly identical resistivities (8.1 to 8.5 $\mu\Omega \cdot \text{cm}$) and thickness (51–63 nm). At present, no clear correlation between T_c and stress is observed, but further work is needed to confirm this and identify what other variable is causing the observed variation.

3 Mo/Cu bilayers

Aside from the T_c of the Mo layer, the quality of the superconducting/normal metal interface is known to be a decisive factor in determining T_c of the bilayer. This parameter has been notoriously difficult to control, see for example references^{1,13}. In our current setup, operational constraints require a minimum 10 minute interrupt before deposition of the Cu layer can commence after the deposition of the Mo layer is completed. With the relatively poor vacuum in our system, one expects a rapid degradation of the interface due to formation of oxides or other surface contamination. However, running the ion source during the growth interrupt should be effective at reducing or preventing this contamination¹⁴. Depending on ion energy, other surface modification effects, such as milling with associated roughening, smoothing, or ion implantation may be expected. In an attempt to distinguish between these effects we deposited three films, varying the ion beam delivery during the growth interrupt: a) the ion source was turned on during the 10 minute growth interrupt (film J4), b) the ion source was off during the growth interrupt (film J6), and c) the surface was exposed to the same ion beam as in a) for 10 minutes, but then turned off for another 10 minutes (film J5). To avoid ion milling of the surface, an average ion energy of about 35 eV (corresponding to 60 V discharge voltage) was chosen. This energy is just below the ≈ 40 eV threshold we observed for sputtering of Mo films off the crystal-mass monitor. X-ray reflectivity (XRR) measurements allowed us to accurately determine Mo and Cu thickness,

as well as interface roughness non-destructively. Superconducting transition temperatures for the bilayers and Mo layers were determined on unpatterned 1 mm x 10 mm strips diced side-by-side, where the Cu was removed from one strip with a selective wet etch (APS-100). The results from these measurements are summarized in Table 1.

The interface transmission obtained for the film with continuous ion-beam exposure during the growth interrupt is significantly higher compared to the films where the ion beam was turned off for 10 minutes before the Cu deposition was started. Since there is no clear indication that the ion-beam had a systematic impact on the interface roughness, we tentatively conclude that the increased transmission results from the continuous removal of surface contamination by the ion beam, rather than a milling or smoothing effect. Further experiments are needed to ascertain the reproducibility of these effects and to optimize the ion-beam conditions during the growth interrupt for best reproducibility.

Three additional bilayer films with reduced Mo and increased Cu thickness were produced using procedure a) to obtain lower T_c s more in-line with the requirements for practical sensors, see Table 2. Typical Cu resistivity is $2.1 \mu\Omega \cdot \text{cm}$ at room temperature (bulk: $1.7 \mu\Omega \cdot \text{cm}$) with a RRR of 5 for the 195 nm thick film.

4 Annealing

The mutual solid solubilities of Mo and Cu are very small below 900°C ¹⁶ and therefore the interface is expected to be stable at the temperatures typically encountered during thin-film processing. In contrast, one may hope that the conductivity of the Cu film may be improved by an annealing step. To that end, we subjected a ≈ 200 nm Cu film to 1 hour vacuum annealing cycles at temperatures between 200 and 600°C . No change in sample resistivity was observed at 200°C . Higher temperature annealing lead to a progressive reduction in room temperature resistivity and increased RRR, yielding a 30% improvement of low temperature conductivity. However, at 600°C films became discontinuous with a sharp increase in resistivity. Accordingly, a set of 2 cm x 2 cm bilayer samples from wafers J4, J5, J6 and J7 were subjected to anneals between 450 and 550°C . The annealed samples were characterized in the same fashion as described above. Sharp transitions with substantially lowered T_c s (Fig. 2) were obtained for the annealed samples compared to their as-deposited counter-parts. X-ray reflectivity data are well fit by a simple three layer (Si_3N_4 , Mo, Cu) model (Fig. 3). No significant changes of film density or interfacial roughness are observed, ruling out any substantial oxidation or diffusion beyond the interface. X-ray diffraction measurements show a narrowing of the Cu (111) reflection, indicative of grain growth. The crystallite size of the Mo appears to be unchanged at these annealing temperatures, but the overall peak shift indicates that Mo strain is reduced. We speculate that reduction in bilayer T_c results from recrystallization of amorphous Mo near the interface leading to increased interface transmission, or perhaps from migration of small amounts of Cu into the Mo film along grain boundaries. Further investigation of the film microstructure will be needed to clarify this effect.

5 Conclusions

We have demonstrated that superconducting Mo thin films can be reliably fabricated using ion-beam assisted e-beam evaporation onto room-temperature substrates. Iron contamination from the ion source was eliminated by replacing and covering parts with Mo equivalents. The IBAD technique opens a vast parameter space (evaporation rate, ion beam energy, dose, and ion species, substrate temperature) to tune Mo film properties (stress, grain size, resistivity). Initial experiments also indicate that the ion-beam can be used to reduce interface contamination. Using vacuum annealing, Cu conductivity can be improved and reduced bilayer T_c s are obtained. The ion-assisted evaporation process also presents some challenges: we have observed an increased tendency toward arcing, and for ion-energies above 50eV the Mo removal rate becomes non-negligible. Avenues to mitigate these effects (such as the use of Kr or Xe gas to enable cryopumping using LN_2) are currently being explored. Further work is underway to determine if this new deposition process offers advantages with respect to other parameters that affect TES device performance, such as the logarithmic temperature and current sensitivities (α and β).

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Fig. 1.

Left Superconducting transition temperature (T_c) for films deposited after modification of the ion-source. The inset shows T_c versus Mo film stress for a subset of samples (marked by the dashed oval) with nearly identical resistivity. *Right* Correlation of room-temperature resistivity and RRR, including wafers fabricated before ion-source modification.

Fig. 2.
Superconducting transitions of annealed films.

Fig. 3. X-ray diffraction (*left*) and X-ray reflectivity (*right*) ω - 2θ scans of as-grown and annealed films. The reflectivity scans have been offset by factors of 10 for clarity.

Table 1

Film thickness, transition temperatures, and interface transmission coefficient (calculated using equation (9) in Martinis et al.¹⁵) for three different Mo/Cu bilayers with different ion-beam exposure during the growth interrupt.

Wafer	t_{Mo}	t_{Cu}	$T_{\text{C}}^{\text{Mo}}/\text{K}$	$T_{\text{C}}^{\text{Bi}}/\text{K}$	Interface roughness	Interface trans.	Ion beam during deposition interrupt
J4	72 nm	95 nm	1.050	0.394	0.75 nm	11.4%	10 min @ 3A, 60V
J5	66 nm	94 nm	0.992	0.418	1.05 nm	7.8%	10 min @ 3A, 60V & 10 min @ no beam
J6	71 nm	93 nm	1.121	0.571	1.12 nm	7.2%	10 min @ no beam

Table 2

Film parameters for additional bilayers grown to demonstrate low- T_c capability.

Wafer	t_{Mo}	t_{Cu}	$T_{\text{C}}^{\text{Mo}}/\text{K}$	$T_{\text{C}}^{\text{Bi}}/\text{K}$	Interface roughness	Interface trans.	Ion beam during deposition interrupt
J7	45 nm	99 nm	0.983	0.195		8.7%	10 min @ 4A, 60V
J8	38 nm	130 nm	1.026	0.085	1.54 nm	9.1%	10 min @ 3A, 60V
J9	52 nm	195 nm	1.070	0.190	1.45 nm	7.5%	10 min @ 4A, 60V

Table 3

Table of transition temperatures for as-deposited and annealed bilayers.

Wafer	as-deposited	450°C	500°C	550°C
J4	0.394 K		0.237 K	
J5	0.418 K	0.198 K		0.165 K
J6	0.571 K	0.227 K		
J7	0.195K	0.073 K		< 0.050 K