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Sputtered Films of Superconducting Ternary Molybdenum Sulfides*

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The preparation of superconducting ternary molybdenum sulfide films of the formula $M_xMo_3S_4$, where $M = $ Pb, Sn, Cu, and Ag, with the technique of RF sputtering from a composite target is described. The transition temperatures of these films are 13.3, 11.0, 10.7, and 8.8°K, respectively.

Introduction

Several members of the ternary molybdenum sulfide family $M_xMo_3S_4$ have been reported to be superconducting with transition temperatures (T_c) ranging up to 15.2°K (*1*, *2*). The critical fields of some of these compounds were recently found to be exceptionally high (*3*, *4*). Reported here are our successful attempts in preparing coherent films of the four ternary molybdenum sulfides with the highest known T_c's ($M = $ Cu, Ag, Sn, and Pb) by the technique of RF sputtering from a composite target. The structure of the superconducting phase in these films was positively identified and their T_c's were comparable to those of bulk samples.

Experimental

Ordinarily the ternary molybdenum sulfides are prepared by sintering powdered constituents in a sealed quartz tube at 1100°C (*5*). Because of the high volatility of sulfur, preparation of films by conventional evaporation techniques does not appear feasible, and for the same reason, sputtering from a homogeneous ternary sulfide target would likely result in sulfur deficiency in the film. Our approach was to use an RF sputtering target composed of a 5 in. disc of MoS_2, pressed from powder, overlayed with wedge-shaped pieces of Mo sheet. The third element was introduced in either wedges of the *M*-metal, in the case of Cu and Ag, or in a 2 in. disc of the metal sulfide, also pressed from powder, in the case of Sn and Pb. Elemental Sn and Pb could not be used as target materials because of their low melting points. By varying the relative sizes of the wedges and by masking portions of the 2 in. metal sulfide discs with Mo sheet, the composition of the film could be controlled.

The vacuum system consisted of an 18 in. diameter working chamber evacuated by a 6 in. diameter diffusion pump with a liquid nitrogen cold trap. The background pressure of the system was consistently below 2×10^{-7} Torr. The sputtering medium was ultra-high-purity argon, continuously bled into the working chamber, with the diffusion pump gate valve partially closed so as to maintain the pressure at 14 μm Hg. Substrates were in most cases Mo. Substrates when unheated were supported on a Cu table $1\frac{1}{2}$–$3\frac{1}{2}$ in. from the target. The heated substrate consisted of a strip of 0.005 in. Mo sheet suspended between two electrical feedthroughs and heated by a low-voltage ac current. Substrate temperature was measured by a thermocouple spot-welded to the substrate. The sputtering power was 200–400 W, and the time, 1–3 hr. The thickness of the films condensed under the prescribed conditions ranged from one to several micrometers.

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The material sputtered on an unheated substrate was amorphous, as indicated by X-ray diffraction, and nonsuperconducting above 2°K. The formation of the ternary molybdenum sulfide was accomplished by annealing at 1100°C for 3–8 hr, in a sealed quartz tube under reduced He atmosphere. In the cases $M = \mathrm{Ag}$, Sn, and Pb, better results were achieved by placing a small amount of the M-element ($10 \sim 20$ mg) in the quartz tube during the heat treatment.

Transition temperatures were measured by monitoring the mutual inductance of two coils containing the sample. The frequency used was 50 Hz. Temperature was determined through a calibrated Ge thermometer which was located in the vicinity of the specimen.

Composition of the films has not been measured. Composition, however, was varied to optimize transition temperature.

Results and Discussion

The onset temperature of the superconducting transition for better samples was 13.3, 11.0, 10.7, and 8.8°K, for Pb, Sn, Cu, and Ag, respectively. Typically, a signal tail of several degrees representing 5%–30% of the transition was observed. However, determined from the major part of the signal, transition widths are estimated to be 0.6–1.5°K.

X-ray diffraction patterns of annealed films were nearly identical to those of sintered samples. One main difference between the two was that MoS_2 was often present as a major second phase in the latter and was consistently absent in the former (*6*).

We attribute the absence of MoS_2 in the films to the present experimental arrangement. Clearly the Mo–S bond was broken by the sputtering process. Since, in addition to MoS_2, pure Mo was also used as part of the target, the ratio of Mo to S in the sputtered material would have to be greater than 1:2.

According to our results, Mo seems to be the best substrate material. Films deposited on sapphire and W substrates were also superconducting but at somewhat lower temperatures, and X-ray diffraction revealed that additional phase(s) existed in films deposited on W. The desired ternary compound was totally absent in films deposited on Ta and consequently no superconducting transition was detected above the T_c of Ta.

While the highest T_c's have resulted from annealing at 1100°C, it is possible to anneal at much lower temperatures. For example, we annealed a series of films with $M = \mathrm{Cu}$ at temperatures from 700 to 1100°C, with correspondingly longer annealing times for the lower temperatures. The T_c was reduced by only 0.4–0.6°K by annealing at 700°C rather than 1100°C, but transition widths were increased from 1.5°K to between 2.5 and 5°K.

For $M = \mathrm{Cu}$, we have also formed the superconducting molybdenum sulfide by direct sputtering onto a heated Mo substrate, with substrate temperature controlled in the range of 700–950°C. The best of these films have had T_c's 1.4°K below the best films deposited on unheated substrates and annealed at 1100°C. Films deposited on substrates heated above 950°C did not superconduct and X-ray diffraction indicated only metallic Mo. We consider this to be caused by reevaporation of sulfur. We were unable to form the desired ternary phase with $M = \mathrm{Pb}$ on heated substrates, presumably because the Pb reevaporated at temperatures lower than that required for the compound to form.

In the case of $M = \mathrm{Pb}$, Sn, and Ag, we have obtained our best T_c by placing a small amount of the M element in the sealed quartz tube along with the substrates during annealing. We have also been able to form the ternary molybdenum sulfides in these three cases by sputtering from a target consisting only of MoS_2 and Mo, and annealing in a quartz tube containing vapor of the third constituent. However, transition temperatures of films formed by this method were not as high.

The structure of $M_xMo_3S_4$, where $M = \mathrm{Pb}$, has been reported (*2*) to be a rhombohedral structure which may be viewed as a distorted primitive-cubic network of sulfur atoms with one-eighth of the cubes occupied by an octahedron of six molybdenum atoms, and with another one-eighth of the cubes occupied by Pb atoms. The distortion of the cubic structure is such that channels are formed in the structure, within which the Pb atoms are located.

We interpret our annealing experiments to indicate that the M atoms in the structure $M_xMo_3S_4$ are loosely bound and relatively free to move along these channels at annealing temperatures. Thus the partial pressure of M present during annealing will affect the composition of the annealed film. In the case of deposition on heated substrates we found that relatively more area of MoS_2 on the target was required than for deposition on unheated substrates. We believe this corresponded to a loss of sulfur to the vacuum system. When films were annealed in a sealed quartz tube, an equilibrium partial pressure of sulfur was presumably established, and no further loss of sulfur occurred.

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