Preparation and characterization of layered superconductors

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A chemical electrodeless deposition method has been applied to grow a layered superconducting films of K_xMoS_2. The growth rate of the films has been optimized. Hall-mobility and dc-conductivity measurements have been made in the temperature range 100 to 400 K. The films show a sharp drop in the absorption spectra at 4.5 μm and a superconducting transition between 8 and 12 K.

INTRODUCTION

Superconductivity in two-dimensional or layered structures was investigated several years ago[1–4] when the alkali metal intercalates of graphite were found to superconduct at very low temperatures. Reviewed interest in this type of system has been stimulated by the discovery of crystalline phases of La-Ba-Cu-O and Y-Ba-Cu-O.[5–9] In an attempt to investigate two-dimensional superconductors, we have developed a chemical method for deposition of potassium-molybdenum chalcogenide (K_xMoS_2).

Molybdenum disulfide is a superconductor consisting of sheets of molybdenum and sulfur atoms with the stacking set S-Mo-S-S-Mo-S (Ref. 10) (Fig. 1). Within each layer there exists trigonal prismatic coordination between the Mo and S atoms and the bonding in the layer is primarily covalent. Variations in the stacking sequence of the layers result in the formation of two polytypes.[11] These are the $2H$ (H denoting the hexagonal unit cell) and $3R$ (rhombohedral) polytypes. The layers are held together by weak van der Walls forces. The result of this weak binding is that the interlayer gap may easily be increased to accept alkali atoms or ions from an alkali atoms or ions from an alkali-metal—ammonia solution.[11] Our investigation indicates that a large number of layered chalcogenides will form complexes when treated with Lewis bases. We have concentrated on potassium molybdenum chalcogenide which is metallic for two reasons. First, we wanted to prepare a material in which conduction electrons are constrained to move in only two dimensions. A two-dimensional electron gas, and especially the fluctuations of long-range order which are thought to be characteristic of superconductivity in such systems, are a subject of theoretical interest.[12,4,13] Second, we are motivated by speculations that properties of superconductivity involving interactions between the conduction electrons and the molecular electrons might be found with materials prepared by different methods.[14]

EXPERIMENTAL

All chemicals were reagent grade. Corning 7059 glass substrates were prepared and cleaned by a method described elsewhere.[15] In a 100-ml beaker, 10 ml of 1 M molybdenum acetate [$Mo(OCOCH_3)_2$] solution was stirred with 0.5 ml of 1 M potassium acetate [$KCOOCCH_3$]. To this solution 10 ml of 12.8 M ammonia solution was added, followed by 10 ml of 1 M thioureau solution. The resulting mixture was diluted by adding 95 ml distilled water and stirred for 2–3 min.

The precleaned substrates were soaked in deionized (DI) water and suspended inside a beaker containing the K_xMoS_2 solution. The beaker was kept inside a constant temperature bath (± 0.5 °C). After 3–16 h of deposition, the K_xMoS_2 film appeared as a tan-colored coating on surfaces exposed to the bath. The substrates were removed from the bath, rinsed with distilled water, and heat treated for 15 min at 300 °C. Following heat treatment, which improves film adherence, the substrates were ready for measurements. The thicknesses of the films were measured with a Sloan-Dektak surface profile instrument.

The real χ' (T) and the imaginary χ'' (two parts of the ac magnetic susceptibility, χ_{ac}) were measured in the range 4.2–20 K for different values of ac field H (0.1–10 Oe rms) and frequency f (1 Hz to 20 KHz) by the ac mutual inductance technique. The essential part of the experiment involved two mutually coupled coils. The in-

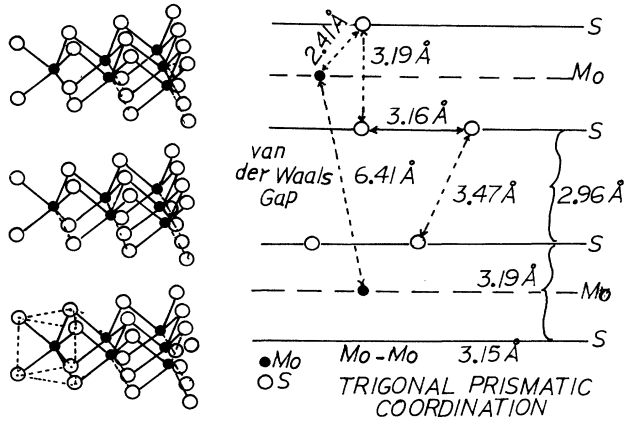

FIG. 1. Represents the structure of MoS_2 (after Ref. 4).

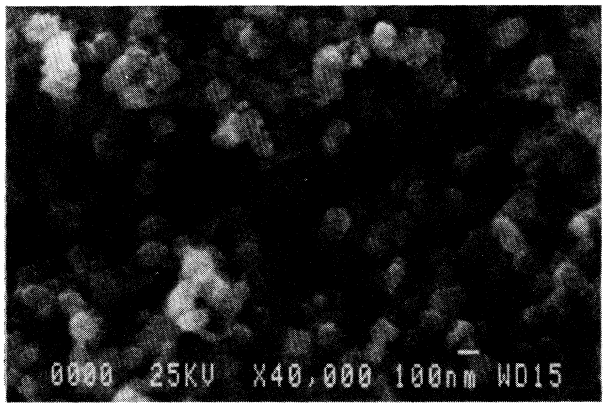

FIG. 2. Represents SEM micrograph of K_xMoS_2 film.

ductive voltages in the secondary coil with and without a specimen in place were measured and compared. The dc magnetic measurements were carried out from room temperature to 4 K in zero field. Then a 20-Oe magnetic field was applied along the long axis of the specimen. $\chi_{dc}(T)$ was always measured for a temperature cycle of 4-300-4 K.

Compositional analysis of K_xMoS_2 samples were conducted using a Nicolet 1211 series x-ray instrument. The instrument used a photomultiplier X3 amplifier and was interfaced with a Microvax computer for plotting the experimental data and for identifying the diffraction peaks of various constituent compounds.

RESULTS AND DISCUSSION

The scanning electron micrograph in Fig. 2 illustrates the morphology of the K_xMoS_2 film deposited by the present method. The average grain size is approximately 100 nm and the microstructure is noncolumnar. Close inspection reveals a high density of dislocations.

Figure 3 illustrates the kinetics of film growth at 30 and 60 °C. Growth rates of the films are seen to increase steadily after 4 h. However, it is observed that, after 12 h, film thickness reaches a saturation level. It may be argued that, after sufficiently long times, the release rate of Mo^{2+} and S^- ions become higher than the rate of formation of MoS_2 at the surface nucleation centers and the rate of formation of MoS_2 reaches saturation value.

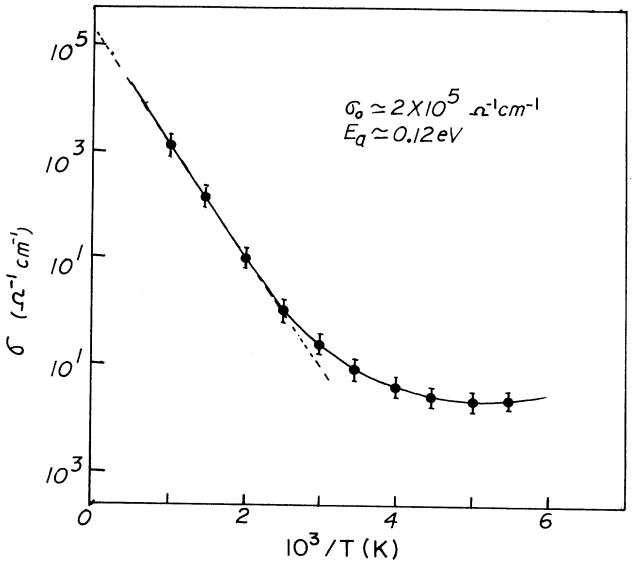

FIG. 4. Shows the electrical conductivity of the film as a function of temperature.

The temperature dependence of dc electrical conductivity of the K_xMoS_2 is shown in Fig. 4. Above room temperature, conductivity is seen to increase rapidly with increasing temperature. However, below 275 K, the rate of change of conductivity with temperature is slow. A similar finding was made by Lagrenaudie[16] and Evans

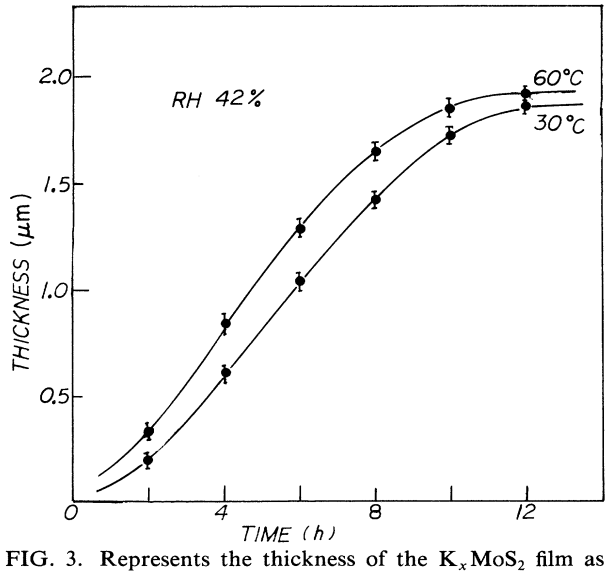

FIG. 3. Represents the thickness of the K_xMoS_2 film as a function of deposition time. Measured by Sloan-Dektak surface profile instrument at a relative humidity of 42%.

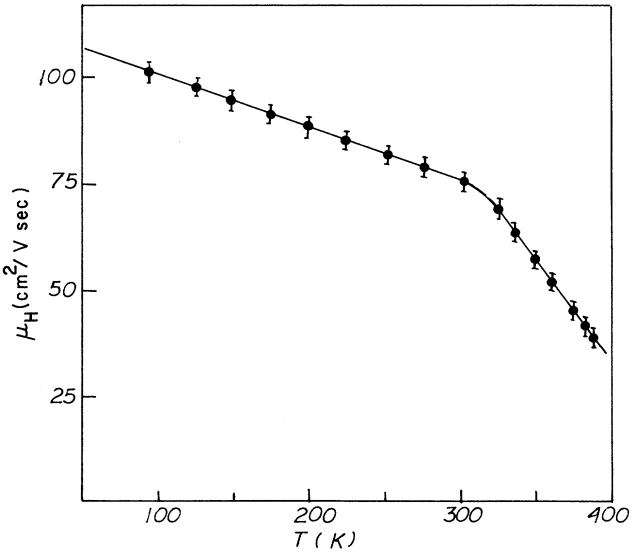

FIG. 5. Hall mobility-temperature dependence for K_xMoS_2 film.

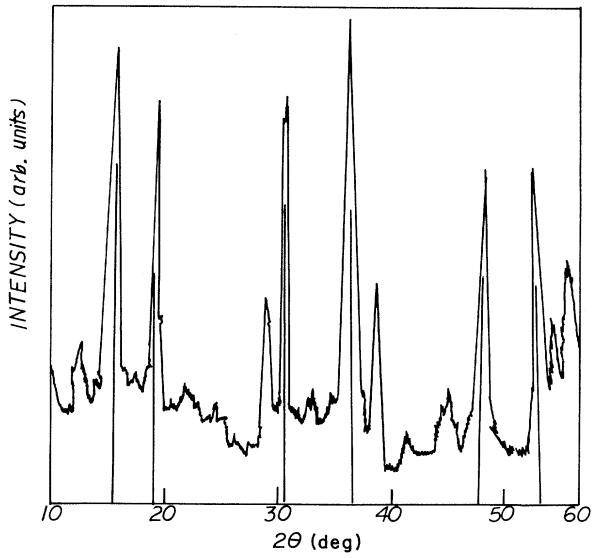

FIG.6. Shows relation between 2θ and the intensity of x-ray for K_xMoS_2 film.

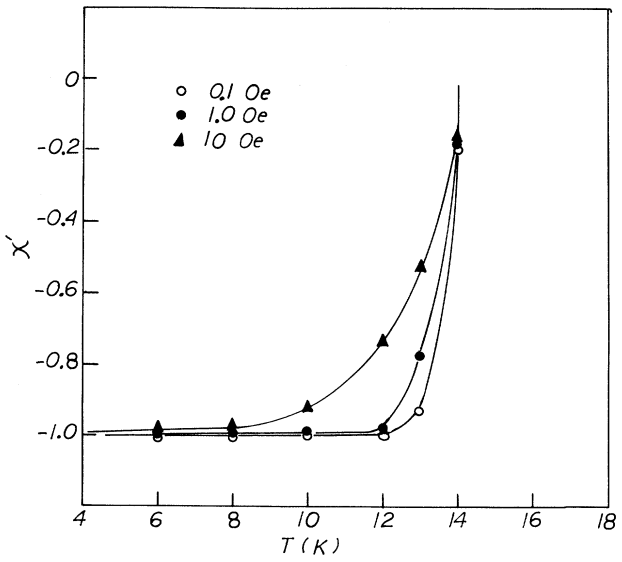

FIG. 8. Represents the onset of the superconducting transition in K_xMoS_2 film.

and Young.[10] The extrapolated low-temperature conductivity of the film measured in the present investigation is $\sim 2\times 10^5\ \Omega^{-1}\,\mathrm{cm}^{-1}$ (σ_0), with an activation energy of 0.12 eV (E_a).

Figure 5 represents the temperature dependence of Hall mobility (μ_H) for K_xMoS_2 film. In this figure μ_H and T are linearly related, and can be expressed mathematically

$$\mu_H \sim a_0 + b_0 T\ , \tag{1}$$

where a_0 and b_0 are different above and below 300 K. At 300 K μ_H is $\sim 75\ \mathrm{cm}^2/\mathrm{V\text{-}sec}$. Below 300 K Hall mobility increases slowly, but above 300 K carrier mobility falls rapidly. Such a phenomenon might be attributed to phonon scattering. If such a decrease in μ_H when temperature is raised were to be associated with a single free-carrier type via equations $\sigma = ne\mu$ and $R_H = 1/ne$, one would then interpret the carrier mobility as falling rapidly. Fivaz's[17,18] interpretation of the experimental data is questionable concerning this point.

The Hall voltage is positive for all measurements, which confirms the majority carriers in each film to be

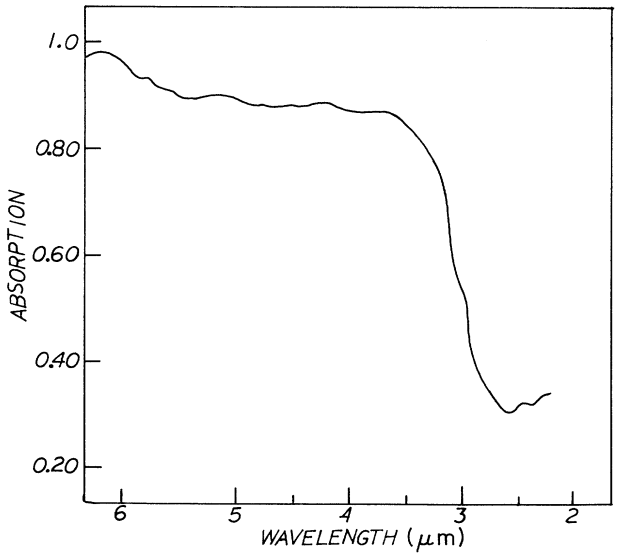

FIG. 7. Shows the optical absorption spectra at different wavelengths.

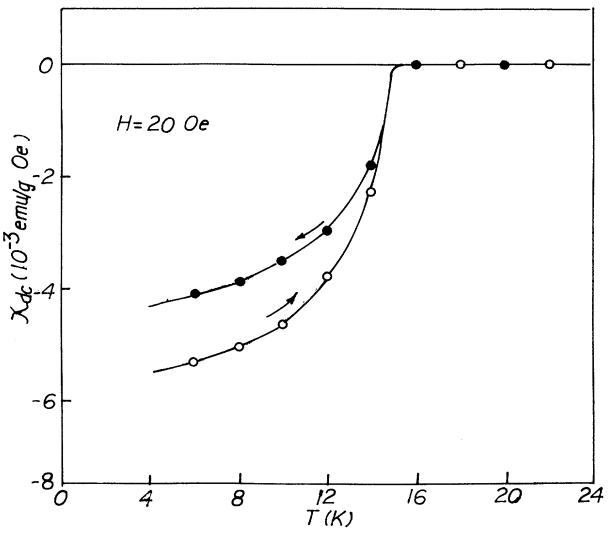

FIG. 9. Represents dc susceptibility of K_xMoS_2 sample.

holes.

The relative intensity of the reflected radiation from the K_xMoS_2 sample is presented as Fig. 6 for 2θ values ranging from 20° to 60°. Table I lists the characteristic lines (I/I_{max}) versus 2θ of the compounds suspected to be present in the sample. The marked lines indicate the relative intensity peaks of the spectrum for K_xMoS_2. The compounds thought to be responsible for five diffraction peaks not directly associated with K_xMoS_2 and their corresponding 2θ values are also tabulated. The highest peak indicates K_xMoS_2 compound and clearly indicates significant quantities of the compounds.

The chemical reaction might be as follows:

TABLE I. X-ray diffraction measurements of 2θ values for different peaks (Ref. 19).

Peak	I/I_{max}	2θ value Ours	Standard	Probable material
I	100	15.72	17.56	K_xMoS_4
II	80	19.33	19.29	K_xMoS_2
III	20	28.3	27.272	$K_2S_2O_3$
IV	80	31.45	32.43	K_xMoS_2
V	100	37.1	36.2	K_xMoS_2
VI	18	38.57	38.78	$(NH_4)_2So_4$
VII	60	47.8	47.085	K_xMoS_4
VIII	60	53.5	53.728	K_xMoS_2

$$[Mo(OCOCH_3)_2][KCOOCCH_3]+[NH_4OH]+[H_2NCSNH_2]=K_xMoS_2+(NH_4)_2SO_4+(NH_4)_2S_2O_3 + K_2SO_4+(NH_2)_2CO_2 .$$

The results for the optical absorption spectra at 77 K are given in Fig. 7. The band gap is obtained from the curve by extrapolating the absorption edges to zero absorbance. The band gap calculated for K_xMoS_2 film is found to be 0.39 eV.

Atomic absorption and chemical analysis show that films are partially intercalated and the composition of the films can be represented by K_xMoS_2 where the value of x is between 0.15 and 0.25 ($0.15<x<0.25$). The amount of potassium is less than in the specimens reported by Rudoff.[11]

Figure 8 shows the dispersive component χ' of ac susceptibility versus temperature plot. The $\chi'(T)$ curves exhibit abrupt onsets of diamagnetism around 12 K at all fields. For $h=0.2$ Oe, a very sharp transition width ΔT (10–90 % χ' signal) of about 1 K. The susceptibility reaches the ideal diamagnetic value of -1 at about 12.5 K for $h=0.2-1$ Oe and about 9 K for $h=10$ Oe. The dc measurements provide confirmation for the bulk nature of superconductivity. The $\chi_{dc}(T)$ data is shown in Fig. 9. The upper curve is cooling in a field, and the lower curve is for heating in a field after cooling in zero field.

These intercalacted K_xMoS_2 films are seen to exhibit superconducting transition between 8–12 K, which is higher than the superconducting transition temperature reported earlier.[5] Superconductivity in these intercalates of MoS_2 is believed to be caused by the electrons from the metal going into the unfilled d-band of MoS_2. The higher transition temperature in the present films might be due to an increase in free electron charge density. However, work is presently underway to determine the mechanism of this observed high-temperature superconductivity, the effects of the dopant alkali metal, and the structural effect of the thin film.

ACKNOWLEDGMENTS

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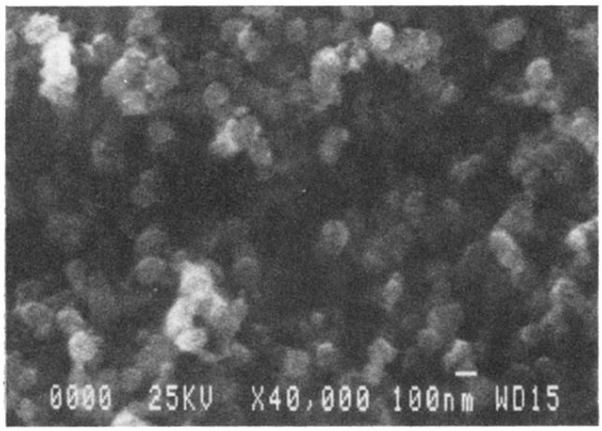

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