

CHEMICAL DEPOSITION OF Cu_2O THIN FILMS

M. RISTOV AND GJ. SINADINOVSKI

Faculty of Physics, University "Kiril i Metodij", Skopje (Yugoslavia)

I. GROZDANOV

Faculty of Chemistry, University "Kiril i Metodij", Skopje (Yugoslavia)

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A simple method for the chemical deposition of Cu_2O thin films is described. The films obtained by this method are of high chemical purity and their thicknesses can easily be controlled during the deposition process. The physical properties of the films were examined and compared with the properties of Cu_2O obtained by other methods.

1. INTRODUCTION

Chemical deposition or electroless methods for the preparation of semiconductor thin films are very attractive because of their simplicity and economy. These methods seem to be very useful for the preparation of CdS, CdTe and PbS films because they offer an inexpensive way of producing solar cells¹.

A method for the production of Cu_2O thin films by chemical deposition is described in which the film can be deposited onto any type of substrate such as glass, mica, ceramics, copper and silver. There are several methods for the preparation of Cu_2O . The high temperature oxidation of copper in which a thin film of Cu_2O is grown on a copper substrate is the usual method²⁻⁴. Another method which yields a film on a copper substrate is the anodic oxidation of copper⁵. These methods are convenient for the production of rectifiers and solar cells. However, for the examination of the physical properties of the semiconductor Cu_2O these methods are inconvenient because of the metal (copper) substrate. For investigation of the physical properties such as the conductivity, thermopower and absorption spectra, the film should be grown on a transparent insulating substrate such as glass or mica. The usual methods for the deposition of Cu_2O onto a glass substrate are the reactive sputtering of copper⁶ and the vacuum evaporation of Cu_2O ⁷.

The method described here enables the deposition of thin films of Cu_2O onto any type of substrate that is chemically inactive with respect to the solutions. A film deposited onto a glass substrate shows a very high adhesion and persistence and can be wiped off only with chemical solvents such as NH_4OH , HCl and NH_4Cl solutions.

2. EXPERIMENTAL DETAILS OF THE FILM PREPARATION

For the examination of their absorption spectra, conductivity and thermopower, the films were deposited onto a glass substrate previously cleaned with a mixture of chromic and sulphuric acids. The deposition procedure comprises the successive immersion of the substrate in a cold complex solution A and a hot solution B. Solution A consists of 100 cm³ of a 1 M solution of CuSO₄ and 400 cm³ of a 1 M solution of Na₂S₂O₃ which is poured into the solution of CuSO₄ until it becomes colourless. In this way a complex solution of 3Cu₂S₂O₃·2Na₂S₂O₃ is formed. The complex solution is then diluted to 1000 cm³. Solution A decomposes easily, so the film preparation should be started with a freshly prepared solution. 200 cm³ of solution A is sufficient for the deposition of four films of thickness 1 μm onto a glass microscope slide.

Solution B is 2 M solution of NaOH maintained at 60–80 °C. A clean glass slide is immersed first in solution B, held for about 1–2 s and then immersed in solution A. After this, the procedure is repeated. After three to five successive immersions, a visible yellow film has been deposited onto both sides of the glass. As the successive immersion proceeds, the film becomes orange and then brown. The film thickness is proportional to the number of successive immersions, so that for the concentration given every ten immersions give an increase of 0.1 μm in the film thickness. The film thickness can be monitored visually during the growth procedure because of the appearance of an interference pattern; thus, after the fifth appearance of the red colour, the film thickness was found to increase by 0.6 μm. The film thickness was measured by the weighing of equally coloured parts of the film.

For the measurement of the absorption spectra, conductivity and thermopower, one face of the coated glass was cleaned with a solution of NH₄Cl. Acids were not used because their vapours are easily absorbed on the other surface of the glass and drastically modify the physical properties of the film.

3. RESULTS AND DISCUSSION OF THE PHYSICAL PROPERTIES OF THE FILM

As found previously, the film grown by this method with the given concentration of solution B at 70 °C shows an X-ray diffraction spectrum (Fig. 1) identical with that of a polycrystalline standard sample of Cu₂O⁶. From this it can be concluded that the as-prepared film is polycrystalline and chemically pure Cu₂O, the content of CuO or other compounds being below the detectable limits. The concentration of CuO can be increased, if necessary, by decreasing the concentration of NaOH in solution B.

The optical absorption spectrum of a film of thickness of 0.2 μm was taken with a Pye Unicam spectrophotometer. The absorption spectrum presented in Fig. 2 shows a fundamental absorption edge at 2.0 eV, which is in agreement with an earlier measurement performed on films obtained by other methods³.

The electrical conductivity of the films was measured on samples with silver paste electrodes painted on equally coloured surfaces 1 cm from each other. The resistance of the sample was measured for two current directions with a digital megaohmmeter, and the arithmetic mean was used. In this way all types of asymmetry were eliminated.

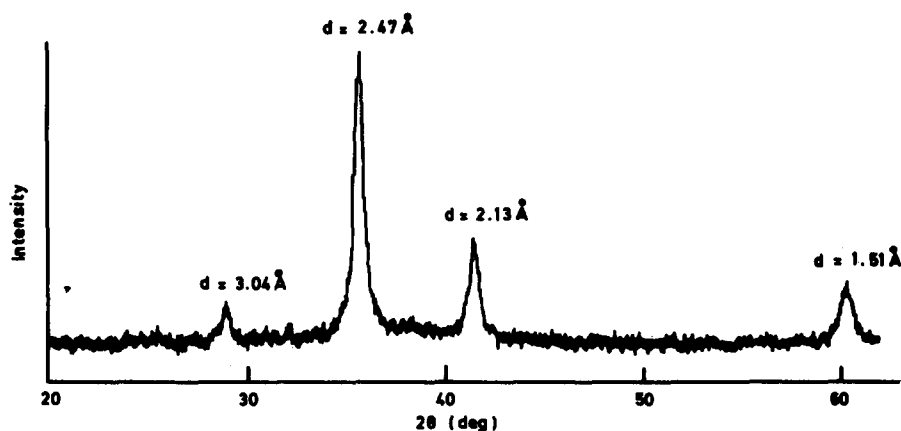


Fig. 1. X-ray diffraction spectrum of a Cu_2O film at $\lambda = 1.54050 \times 10^{-10}$ m (nickel-filtered $\text{Cu K}\alpha_1$ radiation).

The electrical conductivity shows similar characteristics to those for Cu_2O prepared by the high temperature oxidation of copper^{3,4,8}. The conductivity depends on the film thickness, a phenomenon that has also been observed for evaporated films⁵. The variation in conductivity with the film thickness for the films obtained by this method is presented in Fig. 3.

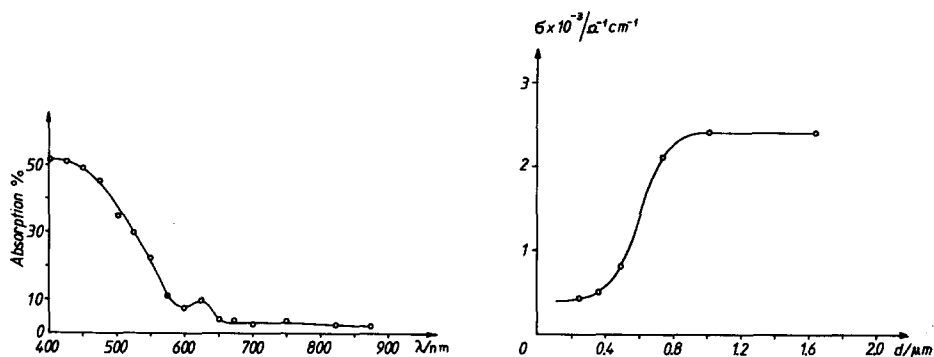


Fig. 2. Optical absorption spectrum of a Cu_2O film deposited onto a glass substrate.

Fig. 3. The dependence of the conductivity of Cu_2O on the thickness of the film.

A freshly prepared Cu_2O film shows photoconductivity with two components: a fast response component with a single relaxation time of 0.2 ms, and a slow response component with several relaxation times from 100 to 500 min⁹. In the case of illumination with a xenon flash lamp the light-to-dark conductivity ratio is 1.1:1.0 for the fast response component and 3:1 for the slow response component. During the photoconductivity experiments precautions were undertaken to prevent the heating of the sample under illumination. This was necessary when the slow component photoconductivity was being measured, since the relaxation times for this component are of the same order of magnitude as the time constant for cooling

of the sample. The changes in the conductivity of the film with temperature and time were examined by the measurement of the resistance of a sample inserted in a thermostat in which a temperature control of $0.1\text{ }^{\circ}\text{C}$ was possible.

Heat treatment of the film in air at a constant temperature of up to $200\text{ }^{\circ}\text{C}$ leads to a decrease in the conductivity. For example, a film maintained at $150\text{ }^{\circ}\text{C}$ shows an exponential decrease with time in the conductivity with a relaxation time of 73 min. After 24 h of heat treatment the conductivity has decreased by about two orders of magnitude, namely from 2.2×10^{-3} to $5.5 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$.

A freshly prepared thermally untreated film shows an irreversible exponential change in the conductivity with respect to T^{-1} (Fig. 4). This complex behaviour is probably due to the change in carrier concentration caused by the thermal excitation of acceptors and to the irreversible change in the impurity concentration with temperature. The temperature dependence of the conductivity of a film that was subject to a thermal treatment at $150\text{ }^{\circ}\text{C}$ is reversible exponential with respect to T^{-1} , with a single activation energy that varies from sample to sample but always falls in the range $0.26\text{--}0.56\text{ eV}$, values given by different researchers for samples obtained by the high temperature oxidation of copper^{3,4,7,8}.

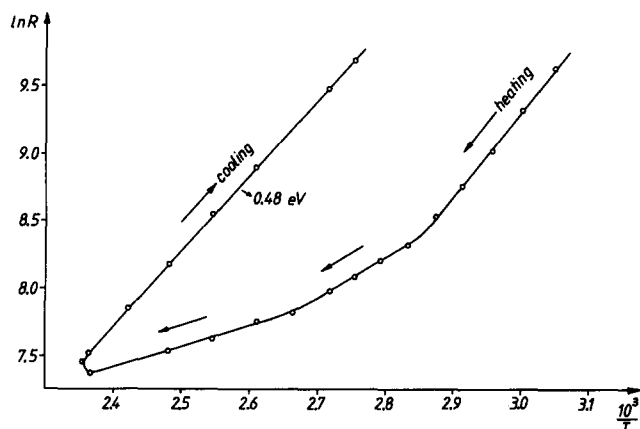


Fig. 4. The temperature dependence ($\ln R$ vs. $10^3/T$) of the resistivity of a freshly prepared Cu_2O film during heating and cooling.

The thermoelectric properties of the films were examined by the measurement of the thermovoltage developed under a temperature difference in the interval $16\text{--}250\text{ }^{\circ}\text{C}$. The thermovoltage was measured by the compensation method using a precise potentiometer and a high input impedance ($15\text{ M}\Omega$) digital microvoltmeter as a zero indicator. The temperatures of the hot and cold aluminium blocks, which served as heat sinks, were measured using Ni-(Cr-Ni) digital read-out thermometers with a precision of $0.1\text{ }^{\circ}\text{C}$. The constant temperature of the cold aluminium block was achieved by the circulation of water from a thermostat. The hot aluminium block was heated by means of a resistive heater inserted into the block. The thermovoltage was measured in a cooling cycle after the hot sink had been heated to $250\text{ }^{\circ}\text{C}$. In this way all spurious voltages were eliminated. The results of the measurements are represented on Fig. 5 by circles. The experimental values were

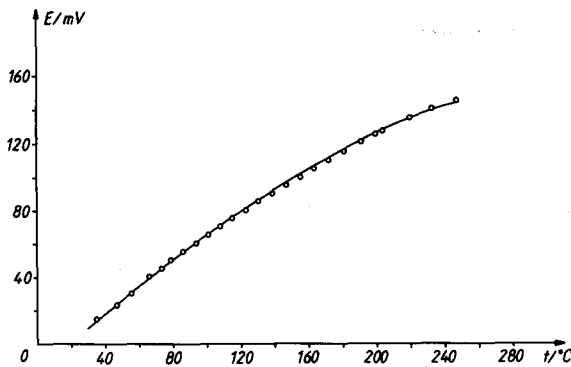


Fig. 5. The thermovoltage of a Cu_2O film as a function of the temperature of the hot end (cold end maintained at 16°C).

found to satisfy with an error of less than 1% the analytical expression

$$U = -0.071(T - T_0) + 285 \ln\left(\frac{T}{T_0}\right) \quad \text{mV}$$

where T and T_0 are the temperatures of the hot and the cold ends respectively. The thermopower of the Cu_2O film was found by differentiation of the expression:

$$S = -0.071 + 285/T \quad \text{mV K}^{-1}$$

For the samples prepared by chemical deposition the thermopower thus calculated is in agreement with the result obtained for a monocrystalline sample of Cu_2O ¹⁰. From this it follows that the thermoelectric behaviour of the Cu_2O film obtained by this method is typical for semiconductor materials with an activation energy of 0.285 eV that is temperature dependent^{10,11}. This discrepancy in the activation energies obtained by the conductivity and thermovoltage measurements shows that the carrier mobilities have a thermal activation character. Since the thermopower is positive, Cu_2O is a p-type semiconductor.

Efforts to prepare an n-type semiconducting Cu_2O film by doping with cadmium, indium, silver and mercury were unsuccessful.

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