

## Deposition of cobalt sulphide thin films by successive ionic layer adsorption and reaction (SILAR) method and their characterization

S D Sartale & C D Lokhande

Thin Film Physics Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004

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Successive ionic layer adsorption and reaction (SILAR) method was used to deposit cobalt sulphide (CoS) thin films on amorphous glass and Si (111) wafer substrates in aqueous medium using cobalt sulphate ( $\text{CoSO}_4$ ) solution as the cationic precursor and sodium sulphide ( $\text{Na}_2\text{S}$ ) solution as the anionic precursor. The conditions for the formation of good quality films such as concentration, pH, and temperature of anionic and cationic precursor solutions, immersion and rinsing times and number of immersions were optimised. The structural, optical and electrical properties of the films are reported.

### 1 Introduction

Cobalt sulphide is a semiconductor with bandgap energy equal to 0.9 eV and has potential applications in solar selective coatings, IR detectors and as a storage electrode in photoelectrochemical storage devices<sup>1,2</sup>.

Chemical deposition of cobalt sulphide (CoS) thin films from an alkaline medium bath using thioacetamide as the sulphide ion source has been reported by Basu and Pramanik<sup>3</sup>. For this, 0.25 M cobalt (II) chloride solution was mixed with 16 N TEA and 14 M  $\text{NH}_4\text{OH}$  solution with constant stirring and 0.2 M thioacetamide solution was added to it. After 6 to 7 hr, the slides were covered with thin black deposits. The films were polycrystalline. The band gap energy was estimated to be 0.62 eV and electrical resistivity was of the order of  $10^6 \Omega\text{-cm}$ . Thermoelectric power measurement showed that CoS films is a p-type semiconductor. Lokhande has prepared CoS films from acidic medium using sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) as the sulphide ion source<sup>4</sup>. For this, 25 ml 0.1 M cobalt sulphate and 25 ml 0.74 M sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solutions were mixed together with constant stirring and to this, 10 ml 0.1 M EDTA solution was added. The solution was kept at 80 °C. After one hour the slides were covered with dark-grey shining deposit. The films were found polycrystalline in nature and showed p-type electrical conductivity. The optical band gap was found to be 0.94 eV and electrical resistivity was of the order of  $10^3$  to  $10^4 \Omega\text{-cm}$ . Eze and Okeke have deposited CoS films using cobalt chloride and thiourea as  $\text{Co}^{2+}$  and  $\text{S}^{2-}$  ion sources, respectively through chemical bath deposition technique<sup>5</sup>. Mane et

al.<sup>6</sup> have prepared the CoS films by spray pyrolysis method using thiourea as a sulphide ion source and cobalt sulphate as a cobalt ion source<sup>6</sup>. The films were microcrystalline. It was found that the optical band gap is 0.97 eV and electrical resistivity is of the order of  $10^4 \Omega\text{-cm}$ . Thermoelectric power measurements revealed that CoS is a p-type semiconductor.

The successive ionic layer adsorption and reaction (SILAR) is a new, simple and convenient chemical method for large area deposition of thin films of metal chalcogenides. The successive ionic layer adsorption and reaction (SILAR) method is based on immersion of substrate alternately into different cationic and anionic precursor solutions (adsorption and reaction) and rinsing in between with ion exchanged solution to avoid homogeneous precipitation. The time durations for adsorption, reaction and rinsing can be experimentally determined. In principle, it is possible to deposit metal chalcogenide thin films using this method onto variety of substrates<sup>8,9</sup>. The detailed mechanism of CdS thin film formation by successive ionic layer adsorption and reaction (SILAR) method has been discussed earlier<sup>7</sup>. The method has been applied for the preparation of thin films of CdS, ZnS, CdZnS, PbS,  $\text{Cu}_x\text{S}$ ,  $\text{Sb}_2\text{S}_3$  etc. [Ref. 9-12]. As far as authors are aware of, there are no attempts made to prepare CoS thin films using successive ionic layer adsorption and reaction (SILAR) method.

In the present investigation, we report the first successful deposition of cobalt sulphide thin films by successive ionic layer adsorption and reaction (SILAR)

method. Conditions for the formation of CoS thin film are optimized. X-ray diffraction (XRD), optical absorption, electrical resistivity and thermoemf measurements are carried out to study the properties of the CoS films.

The cationic precursor for CoS thin film formation was 0.02 M cobalt sulphide (CoSO<sub>4</sub>) solution. The pH was adjusted to ~ 8 by adding liquid ammonia. The cationic precursor was 0.05 M sodium sulphide (Na<sub>2</sub>S) solution with pH ~12. For rinsing purpose double distilled water (resistivity ~18 M Ω-cm) was used. Microslide glass of the dimensions of 26 mm × 76mm × 2 mm and single crystal Si (111) wafer of dimensions 20 mm × 20 mm × 0.5 mm (*n*-type, electrical resistivity 0.005 to 0.015 Ω-cm) was used as substrates. The glass substrate was cleaned ultrasonically for 10 min, first in acetone and then in distilled water ethanol (1:1) solution. The single crystalline Si (111) wafer substrate was etched in 10% NH<sub>4</sub>F solution at 10°C for 10s to make it hydrogen terminated and then rinsed with double distilled water deposition was carried out at room temperature (27 °C).

The adsorption, reaction and rinsing time durations for CoS thin film deposition were optimised by conducting several trials, so that the homogeneous thin film formation takes place. One SILAR growth cycle involves following four steps. 1) The substrate was immersed into cationic precursor (0.02 M CoSO<sub>4</sub> solution) for 50 s, so the Co<sup>2+</sup> ions were adsorbed onto the substrate surface. 2) Then the substrate was rinsed with double distilled water for 75s to remove loosely bounded Co<sup>2+</sup> ions from the substrate. 3) Further, the substrate was immersed into anionic precursor (0.05M Na<sub>2</sub>S solution) for 50s, so S<sup>2-</sup> ions were adsorbed and reacted with Co<sup>2+</sup> ions to form thin film of CoS. 4) Again the substrate was rinsed with double distilled water for 75s to remove the unadsorbed and unreacted S<sup>2-</sup> ions from the substrate. Thus one SILAR cycle consisted of 50s adsorption of cations, 75s rinsing, 50s adsorption and reaction of anions and 75s rinsing. In order to study the versatility of the method, large area films of CoS up to ~ 50 cm<sup>2</sup> were deposited on the amorphous glass substrate.

Film thickness was determined by the method of weight difference in which area and weight of the film were measured. The thickness was obtained by assuming bulk density of CoS (5.45 g/cm<sup>3</sup>). The crystal structure and crystalline orientation of the films were determined with a Philips PW-1710 X-ray diffractome-

ter using CuKα radiations (λ = 1.5405 Å). Scanning was made between 10 to 100°C. Optical absorption spectra of the films were recorded on the UV-VIS-NIR spectrophotometer (Hitachi model, 330, Japan). The electrical resistivity was measured using dc two probe method with silver contracts.

The CoS films deposited up to 25 SILAR growth cycles were uniform and well adherent to the substrate. The films were black in colour. Film thickness was found to be about 0.3 μm for 25 SILAR growth cycles. After 25 SILAR growth cycles, film started peeling off the substrates, probably due to formation of powdery film over a compact film adherent to the substrate.

Fig. 1 shows the XRD patterns of cobalt sulphide thin films on a) amorphous glass and b) single crystalline Si (111) wafer substrate. The film onto amorphous glass substrate is amorphous or consists of very fine grains, whereas film onto Si (111) wafer substrate is polycrystalline. Such type of improvements in crystallinity in case of ZnS thin films by using single crystal Si (100) substrate has been reported earlier<sup>14</sup>. The comparison of the observed *d* values with standard *d* values<sup>15</sup> for CoS thin film is shown in Table 1. These values are in good agreement confirming that the deposited material is CoS.

The optical absorption spectra of CoS films deposited on amorphous glass substrates were recorded in the wavelength range 1000-2000 nm with amorphous glass as a reference at room temperature (27 °C). Fig. 2 shows the plot of adsorption coefficient against wavelength for CoS thin film. The optical data were analysed from the following classical relation.

$$\alpha = \frac{A (h\nu - E_g)^{n/2}}{h\nu} \quad \dots(1)$$

where α is absorption coefficient, E<sub>g</sub> is the semiconductor band gap and A is a constant which is related to the

Table 1 — Comparison of observed *d* values with standard *d* values [Ref. 13] of CoS thin film onto glass and Si (111) wafer substrates.

Substrates	Observed <i>d</i> values (Å)	Standard <i>d</i> values (Å)	Reflection planes (hkl)	Remark
Amorphous glass	1.46	1.46	200	amorphous
	1.08	1.08	211	
Si(111) wafer	1.54	1.5	103	polycrystalline
	1.04	1.03	114	

effective masses associated with the valence and conduction bands. For allowed direct transitions,  $n$  equal to 1 and for indirect transitions equal to 4. Fig. 3 shows plot of  $(\alpha h\nu)^2$  against  $h\nu$  of CoS film. Since the variation of  $(\alpha h\nu)^2$  with  $h\nu$  for CoS film is a straight line indicating

that the involved transitions is direct one. Bandgap energy,  $E_g$  was determined by extrapolating the straight line portion to the energy axis for zero absorption coefficient ( $\alpha$ ). The bandgap was found to be 0.94 eV, which is comparable to the values reported earlier<sup>4</sup>.

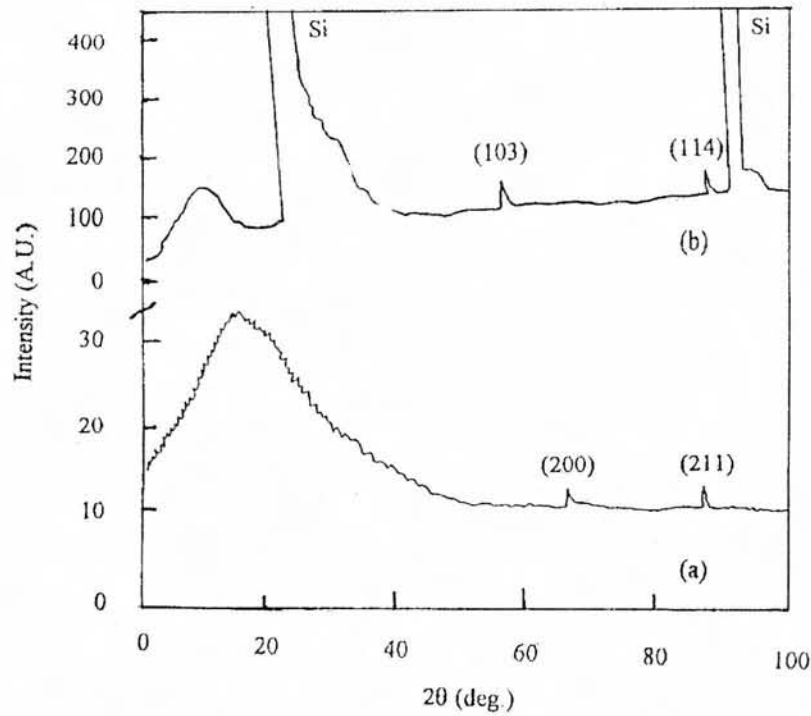


Fig. 1 — X-ray diffraction patterns of CoS films on a) amorphous glass and b) Si (111) wafer substrates.

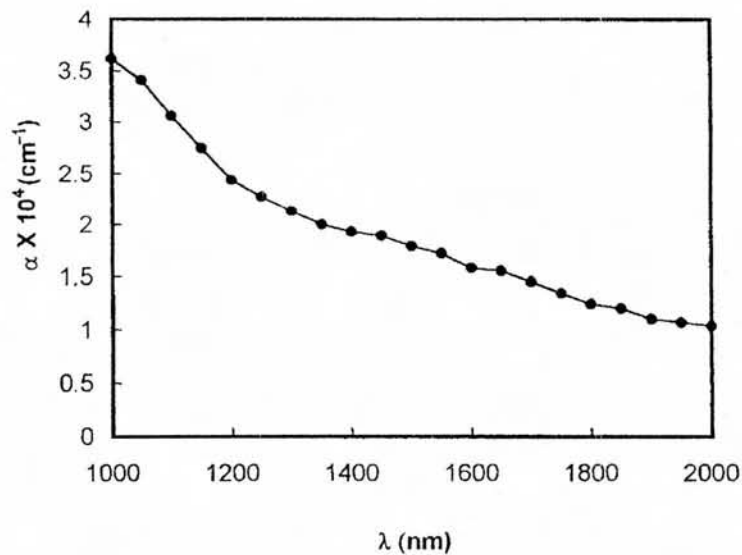


Fig. 2 — Plot of optical absorption coefficient ( $\alpha$ ) against wavelength ( $\lambda$ ) for CoS films

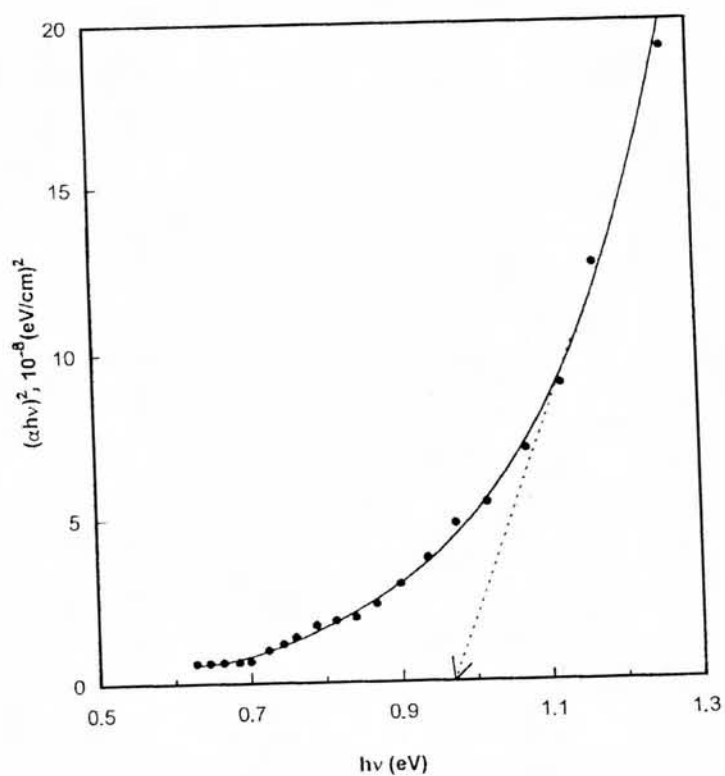


Fig. 3 — Plot of  $(\sigma h\nu)^2$  against  $h\nu$  for CoS films

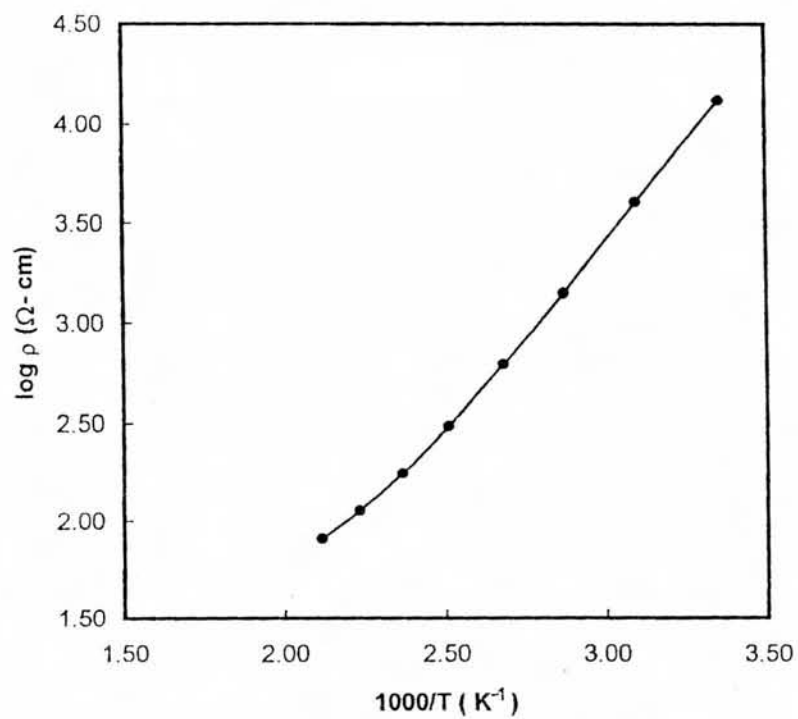


Fig. 4 — Variation of  $\log \rho$  with  $1000/T$  of CoS films

Variation of electrical resistivity ( $\rho$ ) with temperature was studied in the temperature range 300-500 K. Plot of  $\log \rho$  against  $1000/T$  (Fig. 4) shows linear nature. Resistivity decreases with increasing temperature showing that CoS film is a semiconductor. The dark electrical resistivity at room temperature (27 °C) was found to be of the order of  $10^4 \Omega\text{-cm}$  which is comparable to the values reported earlier<sup>4,6</sup>. From the thermoemf measurement, it was found that CoS film is a *p*-type semiconductor, similar to previous reports<sup>4,6</sup>.

Relatively new and simple successive ionic layer adsorption and reaction (SILAR) method is employed to deposit CoS films on amorphous glass and Si (111) wafer substrates. The crystallinity of the films depends upon the substrate. Using this method large area deposition up to 50 cm<sup>2</sup> have been obtained on amorphous glass substrate. The optical transition involved in CoS is of direct and its bandgap was found to be 0.94 eV. From electrical resistivity measurements, it is clear that the CoS films are semiconductor with dark electrical resistivity at room temperature of the order of  $10^4 \Omega\text{-cm}$ . From thermoemf study the CoS is *p*-type semiconductor.

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