The deposition of cobalt molybdate (CoMoO₄) thin film by spray pyrolysis (SP) process, using its ammoniacal solution as precursor, has been presented. The growth of the film takes place by pyrolytic decomposition of the spraying precursor solution onto the preheated glass substrates. X-ray diffraction (XRD) studies confirm the microcrystalline, single-phase nature of the sintered thin films. Scanning electron microscope (SEM) images clearly show the aggregate of crystallites of dimensions 1-5 μm. The optical absorption studies of the sintered thin films in the wavelength range 350 - 850 nm show direct as well as indirect optical transitions in the material. The direct and indirect band gap values found to be 1.75 and 1.40 eV, respectively. The films are semiconducting in nature and highly resistive at room temperature as evident from their dc electrical conductivity measurements obtained by the two point probe method in the temperature range 300 - 500 K. Plot of log(σ) versus 1/T clearly indicates a break in the curve corresponding to the temperature 345 K. The thin films of CoMoO₄ deposited on FTO coated conducting glass substrate were sintered in hydrogen atmosphere to be used as photoanode in photovoltaic electrochemical (PVEC) cell. The PVEC cell configuration is: CoMoO₄ | Ce⁴⁺, Ce³⁺ | Pt; 0.1 M in 0.1 N H₂SO₄. The PVEC characterization reveals the fill factor and power conversion efficiency to be 0.431 and 1.20%, respectively. The flat band potential has been found to be – 0.32 V versus Standard calomel electrode (SCE).

Keywords: Cobalt molybdate thin films, Spray pyrolysis, Optical absorption, dc electrical conductivity

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1 Introduction
Cobalt molybdate (CoMoO₄) belongs to an interesting group of compounds because of its structural, electronic and catalytic properties⁴⁻⁶. At atmospheric pressure, two phases⁷,⁸, usually designated α and β, are known for CoMoO₄. The phase transition of the low temperature phase α–CoMoO₄ to high temperature β–CoMoO₄ has been studied using a large number of physical methods⁹. CoMoO₄ is an important component of industrial catalysts used for many organic reaction processes¹⁰,¹¹. Due to an optical band gap of 1.82 eV for CoMoO₄, it has been used as a photo anode in the polycrystalline pellet form for photovoltaic electrochemical (PVEC) cell by Kichambare et al.¹².

However, these materials in the polycrystalline pellet form showed very low (<1.0%) conversion efficiency¹² and the literature survey reveals that better solar to electrical conversion efficiency is obtained with photoelectrodes in the form of single crystals and thin films¹³⁻¹⁵. To the author’s knowledge no report has been found so far on the thin film deposition of CoMoO₄ by spray pyrolysis (SP) process. Hence, the structural, optical, electrical and photoelectrochemical (PEC) properties of the CoMoO₄ thin films deposited by SP process on the glass substrates have been investigated in the present paper.

2 Experimental Details
2.1 Thin film preparation
CoMoO₄ thin films were deposited on glass substrate obtained from Blue-Star, India by SP process using an apparatus described in detail elsewhere¹⁶. The precursor solution for CoMoO₄ thin film was the ammoniacal solution of the powdered material synthesized by the precipitation method¹²,¹⁷. The substrates used for thin film deposition were ultrasonically cleaned, acetone treated glass slides. 25 ml of the precursor solution of concentration 0.05 - 0.125 M were sprayed through a specially designed glass nozzle onto the preheated glass substrates held at various temperatures ranging from 300 to 450 °C. Compressed air was used as a carrier gas and the flow rate, deposition time, nozzle to substrate distance and frequency of the to and fro motion of the nozzle were kept constant at 5 ml/min, 5 min, 40 cm and 0.29 Hz, respectively, throughout the deposition process. After the deposition, the thin films were allowed to cool at
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2.2 Material characterization

The deposited films were first examined under an optical microscope (Leitz Orthoplan Microscope, Switzerland) to confirm the film deposition and adherence to the substrate. The thin films obtained were then sintered in air atmosphere at various temperatures from 350 to 450°C for crystallization, since the deposited films prepared at room temperature onto preheated substrates are always amorphous. These sintered thin films were then subjected to XRD studies (Philips PW-1710 X-Ray Diffractometer) using Cu-Kα (radiation source) anode, for structural characterization and phase identification. The surface morphology of the thin films was studied with scanning electron microscope (SEM), model JXA–840A from JEOL, Japan with acceleration voltage 20 kV at magnifications of 1000 and 5000×. A gold coating was deposited on the samples to avoid charging of the surface. The optical absorption spectra was carried out using Hitachi Spectrophotometer (UV-Vis., NIR model 330, Japan) in the wavelength range 350-850 nm. To study the electrical properties of the thin films, dark resistivity measurements were taken using the Two Point Probe method in the temperature range 300-600 K. Silver paste was applied to provide ohmic contact with the film. After complete optical and electrical characterizations, the material was found to be suitable for PEC studies.

2.3 PVEC cell construction and characterization

For the PVEC studies the films of CoMoO₄ were deposited on fluorine doped tin oxide (FTO) coated glass microslides under the optimised parameters. The resistivity of the CoMoO₄ film deposited on FTO glass slides was brought down from 10⁷ to 10² Ω·cm by sintering the film under hydrogen atmosphere for 10 h at 400 °C. With these sintered thin films of CoMoO₄ as photoanode and platinum plate as counter electrode, following PVEC cell (shown in Fig. 1) was constructed:

CoMoO₄ | Ce(SO₄)₂, Ce₂(SO₄)₃ | Pt
0.1 M in 0.1 M H₂SO₄

The distance between the photoanode and the counter electrode was 0.5 cm. The water lens was interposed between the lamp and the cell to avoid the heating of the cell. Current-Voltage characteristic of PVEC cell so constructed was measured using 150 W tungsten-halogen lamp. All the voltages were measured with respect to standard calomel electrode (SCE). The capacitance-voltage characteristic of the cell has been studied; measurement procedures are described elsewhere.

3 Results and Discussion

3.1 Deposition parameters

The films deposited below 350°C at all the concentrations are found to be non-uniform and not adherent to the substrate whereas no film deposition is observed above 350°C as revealed from the optical microscopic studies carried out for the films at a magnification of 200×. Therefore, the substrate temperature for the film deposition is set to be 350°C. Also the optical microscopic studies of films deposited at 350°C with varying precursor solution concentrations reveals that the films prepared at concentration above 0.10 M were porous, non-uniform and not adherent to the glass substrate. The film formation was not observed at concentration below 0.025 M. This may be due to unsuitable substrate temperature. At higher concentration the complete thermal decomposition of solution does not take place. Transparent films are obtained...
corresponding to the concentrations 0.075 M and 0.1 M of the precursor solution. Further, it was revealed from the optical microscopic studies that the films obtained from 0.1 M precursor solution concentration were uniform without any agglomeration. Therefore, the preparative parameter is set to held the substrate at 350°C and the precursor solution to be of 0.1 M concentration.

3.2 XRD and SEM studies

Figure 2 shows the XRD patterns of the as-deposited thin films of CoMoO₄ on the glass substrate at 350°C and also of the films annealed at 450°C for 10 h. Fig. 2(a) indicates that the as-deposited film at 350°C is amorphous in nature. After annealing at 450°C, the CoMoO₄ film exhibited an XRD pattern, shown in Fig. 2(b) is of the microcrystalline nature consistent with the monoclinic structure of CoMoO₄. Close inspection of the XRD pattern (by considering peak count and background count) indicates the presence of (111), (111), (110) planes of CoMoO₄ material. The d values of the planes are indexed on the basis of JCPDS data card. Observed d values are in good agreement with the standard d values. Therefore, the formation and single-phase nature of the CoMoO₄ are confirmed.

SEM images of the sintered CoMoO₄ films, taken at 1000× and 5000× magnifications are shown in Fig. 3. It can be viewed from the image that the deposition of material (nucleation) starts around scattered centres and deposits nearly spherical features with crystallite size of approximately 1-2 μm but at latter stage the film grows in ring form with some spherical features in the centre of the ring. From these patterns it can be inferred that initially grain type growth starts which continues till the whole surface is almost covered. After this, ring formation starts and the material is deposited on these rings and in the centre, leading to non-uniformity of the surface, above observations are typical features of the spray deposition process.

3.3 Optical properties

The absorption coefficient, α, for the film is obtained using the relation given below,

$$\alpha(\lambda) = \frac{104}{t} \log_{10} \left( \frac{1 - R(\lambda)}{T(\lambda)} \right)$$ ...

where, t is the thickness of the film in μm, R(λ) and T(λ) are, respectively, the reflectance and transmission of the film at wavelength λ. 

Fig. 2—XRD patterns of the CoMoO₄ thin films (a) as-deposited (b) sintered at 450 °C
transmittance at specific wavelength $\lambda$. The absorption coefficient is found to be of the order of $10^{10}$ cm$^{-1}$. To resolve the nature of the optical transmissions in the film, the absorption spectrum data are further analyzed as per the theory of Bardeen et al.$^{28}$ The optical band gaps for the deposited CoMoO$_4$ thin film are calculated on the basis of the optical spectral absorption using the following well-known relation$^{29}$

$$
\alpha = k (h\nu)^{1/2} (h\nu - E_g)^{n/2}
$$

where $k$ is the constant, $E_g$ the energy band gap, $h\nu$ is the photon energy and $n$ is equal to 1 for direct band gap and 4 for indirect band gap. Figure 4 shows the plot of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ for the CoMoO$_4$ thin film. The plots are linear, indicating direct and indirect type of optical transitions. The values obtained by extrapolating the straight-line portion to energy axis at zero absorption coefficients give the direct and indirect optical band gaps as 1.75 and 1.4 eV, respectively. The direct transition is attributed to spin orbit valence band to conduction band while indirect transition is due to transition from virtual state in valence band to conduction band minimum.

3.4 Electrical properties

Ohmic contacts to the CoMoO$_4$ thin film are made with silver paste. The electrical resistance is measured in the temperature range 300-600 K. At room
temperature the film possesses resistivity of the order of $10^{10}$ Ω cm. The electrical conductivity of the film increases with increase in temperature that indicates semiconducting nature of the thin film material. The plot of $(1/T)$ versus log($\sigma$) has been shown in Fig. 5 which clearly indicates a break in the curves corresponding to the temperature 345 K. The variation of log($\sigma$) with $1/T$ is linear in the two regions of the temperature showing the well known exponential law,

$$\sigma = \sigma_0 \exp \left( -\frac{E_a}{2kT} \right)$$

where the symbols have their usual meaning, is obeyed in the two temperature ranges covered for the CoMoO$_4$ thin film. The activation energy values have been calculated and are found to be 0.02 and 0.49 eV, respectively, for low and high temperature ranges. The activation energy for conduction is found to be lesser in the low temperature region. This low temperature conductivity can be considered to be extrinsic (impurity dominated), whereas, conduction in the higher temperature region may be regarded as intrinsic$^{30, 31}$. One of the major reasons for extrinsic conductivity for these compounds may be due to the presence of other metal impurities. Even very small amount of impurity can drastically modify the electrical properties of a semiconductor. At higher temperature these impurity atoms generally are ionized and do not show their effect$^{32}$. The difference in the values of optical band gap and activation energy, determined from the transmission spectra and electrical conductivity measurements respectively, is attributed to different experimental conditions and the source of electron excitation$^{17}$.

### 3.5 Effect of illumination intensity on photoresponse of photoanode in PVEC cell

In order to select proper light intensity for illumination of photoanode, it was decided to study the photoresponse of PVEC cell. The photoresponse of PVEC cell is studied by measuring short-circuit current ($I_{SC}$) and open circuit voltage ($V_{OC}$) as a function of light intensity ($I_L$). The variation of $V_{OC}$ and $I_{SC}$ of PVEC cell with varying light intensities of light source on CoMoO$_4$ thin film photoanode is shown in Fig. 6.

It is evident from the graph that $V_{OC}$ depends upon band bending and change in the photo-fermi level of photoanode, when exposed to light$^{33}$. The intensity dependence of $V_{OC}$ is attributed to changes in surface charge related to oxidation of redox couple on the CoMoO$_4$ thin film photoanode resulting in band edge movement. It is further revealed from the graph that above 20 mW/cm$^2$ light intensity, the surface state acts as recombination centres$^{33}$. The dominance of the recombination near the open circuit potential results in saturation in $V_{OC}$.

The non linear dependence of $I_{SC}$ on light intensity (beyond 15 mW/cm$^2$) indicates that the transport of
photo-generated carriers to the semiconductor-electrolyte interface is limiting the rate of overall charge transfer reaction over the range of light intensity employed. According to Kline et al., the observed deviation from linearity of short circuit current with respect to incident light intensity could mainly be attributed to the existence of numerous recombination centres. The flattening of conduction and valence as a result of high illumination intensity would reduce the space charge layer field and efficiency of charge carrier separation and thus, reduces the photocurrent. Hence, it was decided to use 10 mW/cm² light intensity for PEC characterizations of the PVEC cell.

3.6 Current-voltage (I-V) characteristics of PVEC cell

Current-Voltage (I-V) output characteristics for the PVEC cell is shown in Fig. 7. The maximum power output of the cell is given by the largest rectangle that can be drawn inside the curve. The \( I_{SC} \) and \( V_{OC} \) are found to be 0.381 mA and 0.734 V, respectively. The calculations lead to the fill factor (\( ff \)) and power conversion efficiency (\( \eta \)) of 0.431 and 1.20%, respectively. The low efficiency in this investigation might be due to high resistance of the cell, low thickness of the film and interface states, which are responsible for interactive recombination. But this efficiency is higher than that obtained by Kichambare et al. using the photoelectrode of CoMoO₄ in the polycrystalline pellet form. The higher efficiency in the present case may be due to high absorption coefficient and large surface area of the thin film photoelectrode.

Mott–Schottky plot

The semiconductor/electrolyte interface capacitance has been measured as a function of applied voltage at frequency of 1 kHz, assuming that the major contribution of the capacitance \( I \) arises from the space charge layer. The data is plotted based on Mott-Schottky relation as given below:

\[
C^{-2} = \frac{2(\varepsilon \varepsilon_0 N_e)}{q} (V - V_{fb} - kT/q) \quad \cdots (6)
\]

where, \( q \) is the charge, \( T \), the temperature, \( \varepsilon \), the dielectric constant of the space charge layer, \( \varepsilon_0 \), the permittivity of vacuum, \( N_e \), the charge density, \( V_{fb} \), the flat band potential and \( V \) is the applied electrode potential. A linear curve between \( (1/C^2) \) and applied potential, shown in Fig. 8 gave, upon extrapolation, a value for the flat band potential of – 0.32 V versus SCE.
4 Conclusions

It is concluded that spray pyrolysis is one of the good methods for the thin film deposition of CoMoO$_4$. The films are found to be microcrystalline and single phase in nature after sintering in air atmosphere at 450 °C, as revealed from their XRD spectra. The polycrystalline thin film obtained is of variable crystallite size between 1-2 μm as evident from its SEM images. The optical study depicts the presence of direct and indirect type of optical transitions in the CoMoO$_4$ thin film. The $dc$ electrical conductivity measurement reveals the semiconducting nature of the thin film material within the temperature range 300 - 600 K. The film is found to be highly resistive at room temperature. Thin films deposited on FTO coated glass slides are first sintered in hydrogen atmosphere to lower down its resistivity and then are used as photoanode in the PVEC cell. Finally, PEC characteristics such as $J_{SC}$, $V_{OC}$, $ff$, η% and $V_{fb}$ for the thin film photoanode have been determined and the power conversion efficiency is found to be higher than that obtained by the PVEC cell using CoMoO$_4$ as photoanode in the polycrystalline pellet form.

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