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Optical and electronic properties of iron xanthate thin film

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The iron xanthate thin films (IXTF) were deposited by the chemical bath deposition method on various substrates, such as amorphous glass, *p* and *n*-silicon, indium tin oxide and poly(methyl methacrylate). The structure of the films was analyzed by far-infrared spectrum (FIR), mid-infrared (MIR) spectrum and scanning electron microscope (SEM) and their structural, optical and electrical properties were examined. Electrical properties were measured using the four-point method whereas optical properties were investigated via the UV-VIS spectroscopic technique. The transmittance was found to be 70-80% at optimum deposition time and temperature (4 h, 50°C). The optical band gap of the IXTF was graphically estimated to be 3.62-3.83 eV. The resistivity of the films was calculated to be between 23.5-38.5 Ω·cm on commercial glass depending on the film thickness and between 23.8-42.0 Ω·cm on the other substrates. It was found that resistivity changed with film thickness. The MIR and FIR spectra of the films were in line with the literature analogues.

Keywords: Thin films, Chemical synthesis, Electrical conductivity, Optical properties

1 Introduction

Iron xanthates are similar to hybrid materials, because they contain an organic sulphide and an inorganic metallic part. These organometallic compounds have a wide range of properties in terms of optical, electrical and magnetic characteristics[1-4]. It has been shown that these thin films have various features, such as an anti-bacterial agent, a magnetic and semi-conductor material. Therefore, these are used for data storage, solar cell production, water purification etc.[4-8].

In particular, metal xanthates have very interesting features as the organometallic compounds. One of the most important reasons for producing the thin films of such compounds is their property of semiconductivity. These semi-conductors have a wide range of utilization areas such as organometallic materials. Until now, metal xanthates have mostly been used as the main reactant in the production of metal sulphides and their thin films because it is a simple and cheap method[9].

Metals react with xanthates very easily, thus mixing their liquid solutions results in to the precipitation of a metal-complex (Fig. 1).

R is an element from the aromatic or aliphatic group, whereas M is a metal. In some studies, the reactants were not mixed in accordance to their stoichiometric ratio of metal ion valence (Fig. 1). Then, the metal xanthates were decomposed into metal sulphides with temperature. Metal xanthates can replace metal sulphides but we do not have sufficient information about their optical and electrical properties.

Neither iron isopropyl xanthate thin film production, nor its optical and electrical properties have been examined yet. Our preliminary tests showed that both the production of iron xanthate thin film via chemical bath deposition and its analysis are quite difficult because in water iron xanthate complexes are more soluble than other metal-xanthates.

The aim of this study was to produce iron xanthate thin film by chemical bath deposition and to examine its structural, optical and electrical properties.

2 Experimental Details

First, isopropyl xanthate was synthesized as described in the literature[10-14], and the stock solution of 0.1 M was prepared. High purity reagents were used for the preparation of all solutions and the stock solution was diluted each time when required. The other stock solution of iron nitrate salt was prepared

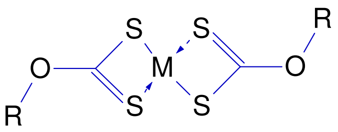

Fig. 1 — Metal-xanthate complex

from high purity compound (99.9%, *E. Merck*, Darmstadt, Sigma Aldrich). All laboratory glassware and substrates were cleaned by soaking in diluted nitric acid and rinsing with alcohol and deionized water prior to use.

Isopropyl xanthate was synthesized by dissolving 3.74 g of KOH (0.067 mol) in a mixture of 4.5 ml CS_2, 6 ml isopropyl alcohol and 9 ml benzene and heated under a reflux condenser. The mixture was mixed for 20 min at 35°C and for 45 min at 45°C. Then, it was mixed for 1 h at 60°C. Approximately 9 g of the reaction product was then purified by rinsing with acetone and drying in the oven[10-14] at 30°C for 48 h.

Ten milliliters mL of 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$ and 10 ml of 0.1 M isopropyl xanthate were mixed in a beaker. The substrates were dipped into this chemical bath; IXTF was formed as a result of the ion-ion mechanism and deposited on the substrates. The films were deposited at different temperatures, namely 30, 40 and 50°C, and the *p*H of the bath was kept between 5.00-5.50. In addition, different deposition times were tested, such as 4 to 7 h at 40 and 50°C, and 16-19 h at 30°C. The produced thin films were cleaned in purified water and dried prior to further examinations.

The infrared spectrum of IXTF was recorded by a Perkin Elmer Spectrum 400 spectrometer with a resolution of 4 cm^{-1} using a DTGS detector and 10 scans for each spectrum. The ^{1}H-NMR spectra were measured by a Bruker (400 MHz) spectrometer with 16 scans in each measurement. The surface properties of all films were examined using an EVO40-LEO computer controlled digital scanning electron microscope (SEM) with a secondary electron detector. Electrical properties were measured using the four-point measurement technique and the resistivity was calculated accordingly. The optical measurements were conducted by a Hach Lange DR 5000 UV-Vis spectrophotometer at room temperature by placing an uncoated identical glass substrate in the reference beam. The optical spectra of the thin films were recorded in the wavelength range 300-1100 nm. The film thicknesses were measured with a Veeco Multi Mode AFM (Controller = Nano Scope 3D). Thicknesses were measured in a 10×10 μm area with tapping mode.

3 Results and Discussion

The vibrational spectra (FIR & MIR) shown in Figs 2 and 3, display the structural properties of the iron xanthate thin films which formed on glass. Some characteristic bands shown in Fig. 2 are listed below:

The asymmetric stretching vibrations of the aliphatic groups ($-CH_3$) were observed at 2984 and 2920 cm^{-1}, and the symmetrical C–H stretching vibration was observed at 2885 cm^{-1} and the bending vibration of $-CH_3$ was seen at 1460-1370-1348 cm^{-1}, Fig. 1 also shows the asymmetric stretching vibration of C–O–C at 1253-1184-1144 cm^{-1}, the symmetrical stretching vibration of –C–O at 1085 cm^{-1}, the stretching vibration of –C=S at 1025 cm^{-1}, the rocking vibration of $-CH_3$ at 896 cm^{-1}, the symmetric stretching vibration of C–C–C at 793 cm^{-1} and the symmetric stretching vibration of S–C–S at 700 cm^{-1}.

The stretching vibration of the Fe-S bond observed at 330 cm^{-1} in the FIR spectrum is shown in Fig. 3. In addition to the other functional groups of the iron xanthate [15-21], characteristic bands of the xanthate group can also be observed for the stretching vibration of –C–S at 690-647-564 cm^{-1}, the bending vibration of C–O–C at 466-443 cm^{-1}, the bending vibration of C–C–O at 398-388 cm^{-1}, the bending vibration of O–C–S at 302 cm^{-1}, the bending vibration of S-C-S at 258 cm^{-1} and the torsion vibration of $-CH_3$ at 202 cm^{-1}.

The transmittance (T) and absorbance (A) for IXTF can be used to calculate the reflectance (R) using the following expression[22]:

$$T=(1-R)^2 e^{-A} \qquad \ldots(1)$$

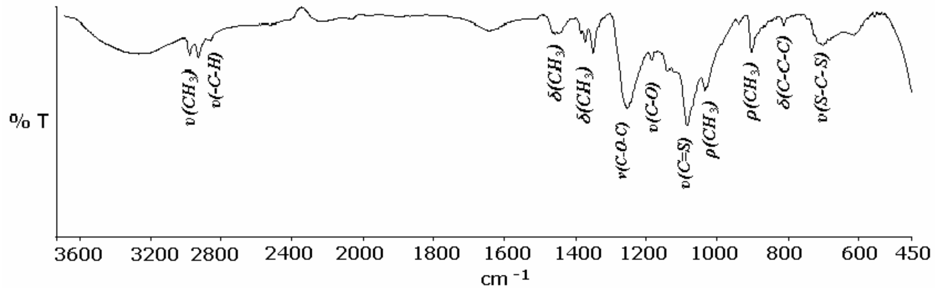

Fig. 2 — Iron xanthate thin film on glass substrate M-IR spectrum

Transmittance and absorbance measurements were performed at room temperature in the range 300-1100 nm. The films were deposited at different deposition temperatures and deposition times as shown in Figs 4-6. The change in the transmittance according to deposition time and deposition temperature can be seen from the curves. The optimum values for deposition time and temperature were selected as 4 h at 50°C, respectively to obtain maximum transmittance and minimum reflection (~70% transmittance).

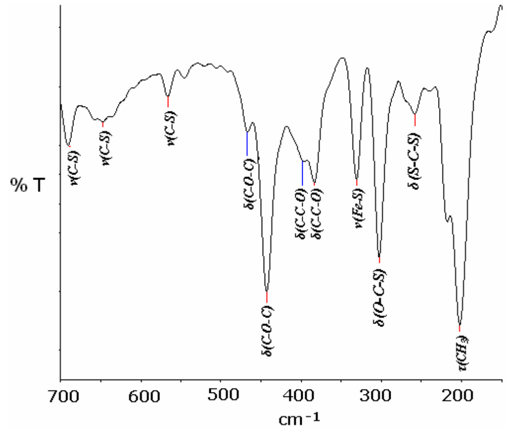

Fig. 3 — Iron xanthate thin film on glass substrate F-IR spectrum

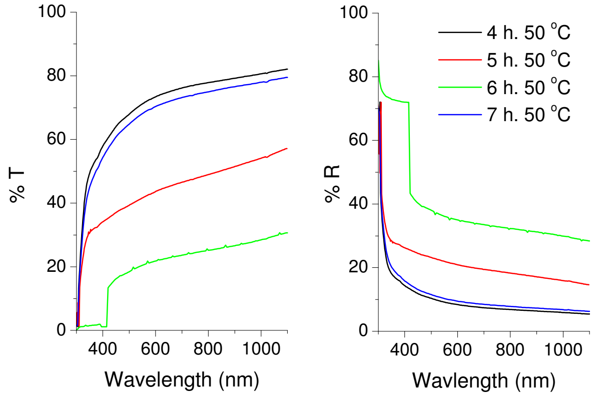

Fig. 4 — Change of % T and % R with wavelength at various deposition time (t=50°C)

The highest deposition temperature was 50°C and the longest deposition time was 19 h (at 30°C). The optimum deposition and temperature was found to be 4 h at 40°C. However, in order to save time and obtain maximum transmission and minimum reflection, 4 h and 50°C were selected as the optimum parameters. Metal xanthates are known to decompose beyond these limits[23]. Similarly, iron xanthate was decomposed into iron oxide, oxide chloride or sulphide (at 60°C and after 21 h of deposition time).

The refractive index and extinction coefficient for the films are given by the following equations[22]:

$$n=\frac{(1+R)}{(1-R)}+\sqrt{\frac{4R}{(1-R)^2}-k^2} \qquad \ldots(2)$$

$$k=\frac{\alpha\lambda}{e\Pi} \qquad \ldots(3)$$

It was found that the refractive indexes, calculated as 1.95, 2.13 and 1.94 (550 nm wavelength), were slightly affected by deposition temperatures (at 30°, 40°, and 50°C, respectively, Fig. 7). Similarly, the extinction coefficients were measured as 0.012, 0.015 and 0.012 at 30°, 40°, and 50°C. The optical band gap energy (E_g) was determined from the absorption spectra of the films using the following equation[24-28]:

$$(\alpha h\nu)=A(h\nu-E_g)^n \qquad \ldots(4)$$

where A is a constant, α is the absorption coefficient, $h\nu$ is the photon energy and n is a constant equal to ½

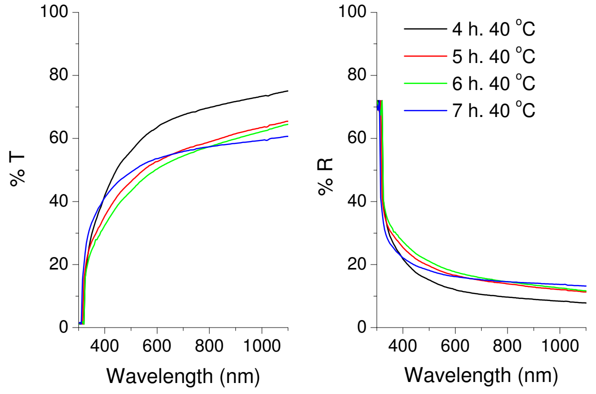

Fig. 5 — Change of % T and % R with wavelength at various deposition time (t=40°C)

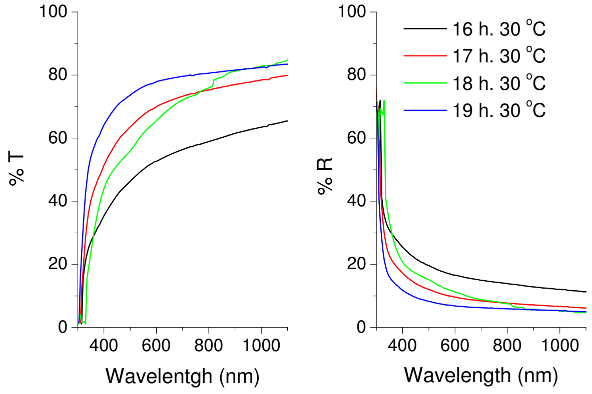

Fig. 6 — Change of % T and % R with wavelength at various deposition time (t=30°C)

of the direct band gap value for semiconductors. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 8.

From the plots of $(\alpha h\nu)^2$ versus $h\nu$, the band gaps (E_g) of the films were estimated as 3.70, 3.62 and 3.83 depending on film thicknesses obtained at different deposition temperatures (30°, 40°, and 50°C, respectively). Film thickness varied in the range 179.2-358.8 nm when deposition temperature was changed in the range 30°-50°C (Fig. 9).

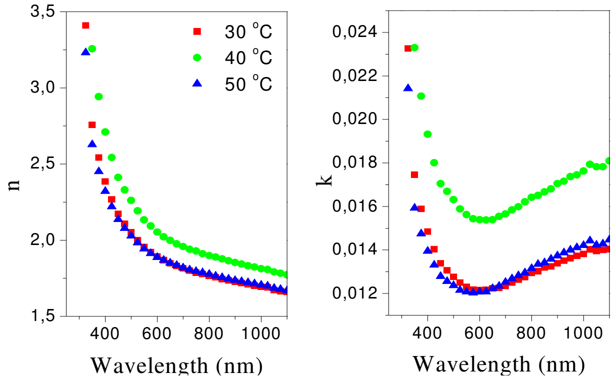

Fig. 7 — *n-k* graphic according to deposition temperature

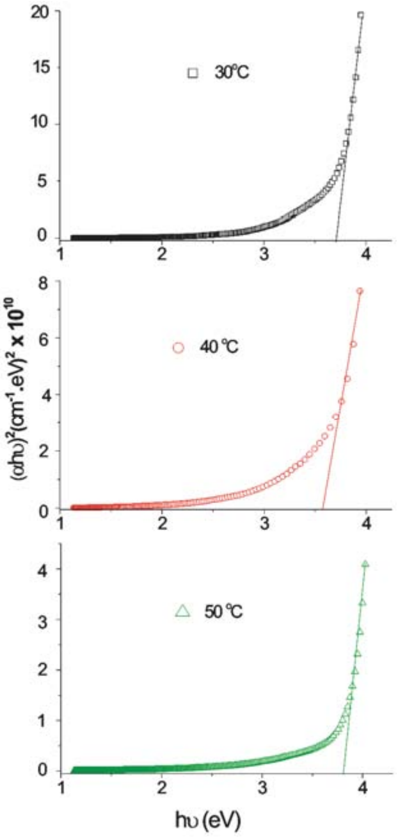

Fig. 8 — Plot of $(\alpha h\nu)^2$ versus $h\nu$ in different deposition temperatures

As expected, it was found that film thickness was – almost-linearly increased with deposition temperature whereas the band gap of the films was decreased with the increase in film thickness[28-32].

The resistivity of the films was determined by the four-point measurements of the films using the following relation [33-35]:

$$\rho = \frac{\Pi E}{\ln 2}\frac{V}{I} \quad (W \ll s) \qquad \ldots(5)$$

where W is the film thickness, V the voltage and I is the current. The resistivity was measured in the dark at room temperature. During the measurements, the distance between the probes (s) was a few millimeters whereas the film thickness was in nanometer scale. The resistivities of the films were measured as 23.51, 33.85 and 38.49 Ω·cm for the film thicknesses 179.2, 260.1, and 358.8 nm, respectively. Figure 10 shows that the resistivities of the deposited films were found to increase with film thickness. This finding is in line with the results given by Moualkia and Kasap[28-29], pointing out that film thicknesses in the range 250-900 nm slightly affected the resistivity of the film.

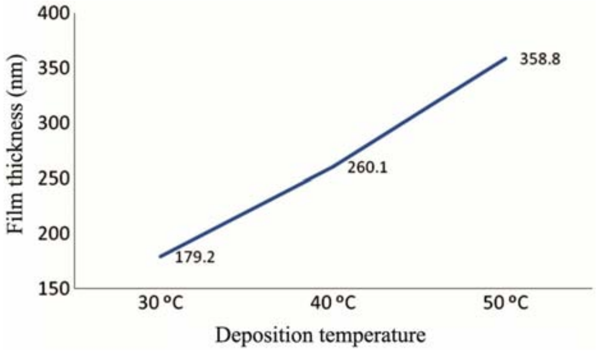

Fig. 9 — Film thickness-deposition temperature

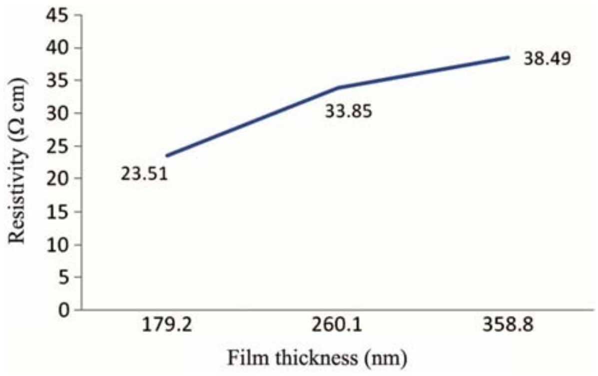

Fig. 10 — Resistivity-film thickness

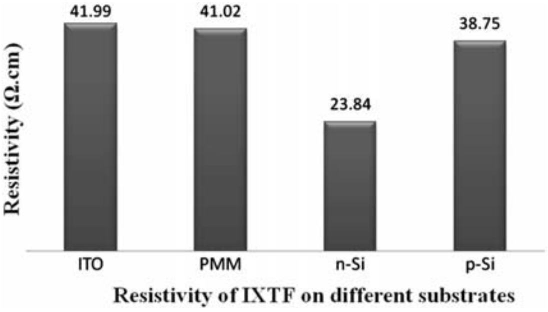

Fig. 11 — Resistivity of IXTF on different substrates

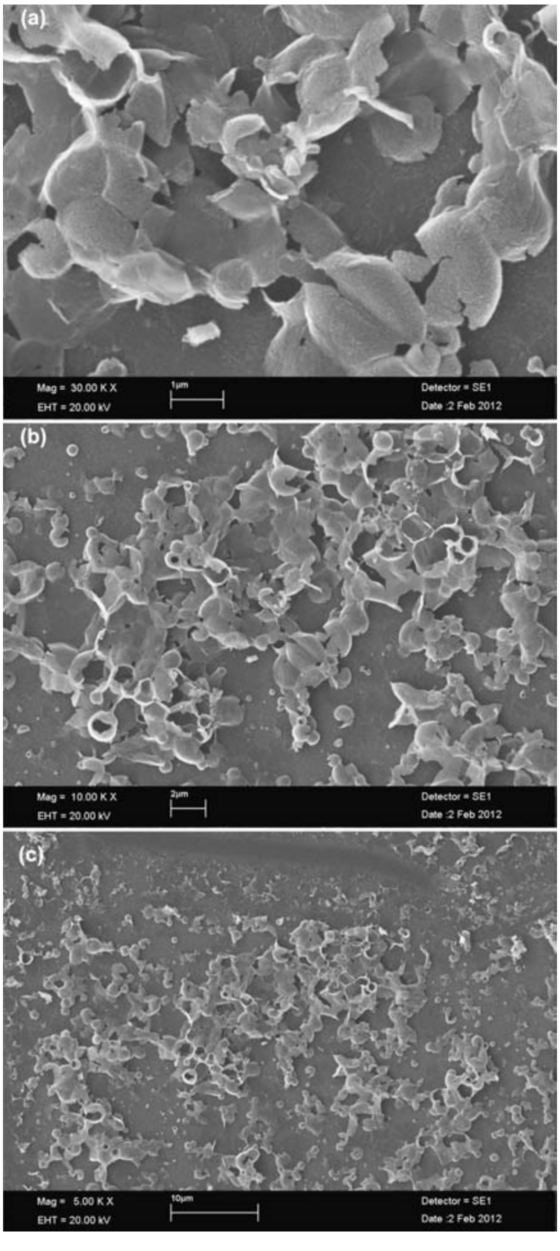

Fig. 12 — Iron xanthate thin film on glass substrate (a) (1 μm), (b) (2 μm) and (c) (10 μm)

Within the study, thin fims were also deposited on *n*-silicon (*n*-Si), *p*-silicon (*p*-Si), poly(methyl methacrylate) (PMM) and indium tin oxide (ITO). The resistivities of the films deposited on these substrates were found to be different from those on commerical glass. The resistivities of PMM, ITO, *n*-Si and *p*-Si substrates were measured as 41.02, 41.99, 23.84 and 38.75 Ω.cm, respectively, at the optimum deposition time and temperature (Fig. 11). IXTF had the highest resistivity when depositied on ITO and PMM substrates, whereas IXTF deposited on *n*-Si had the lowest resistivity[32-36].

In Figs 12(a,b,c), the SEM images of the thin films, magnified in 1, 2, and 10 μm scales, are shown. The SEM images in Figs 12(a and b) display broken shell-like structures whereas Fig. 12(c) clearly shows large spaces among the particles of the iron xanthate structure, which were not clearly visible in Figs 12(a and b). These large spaces and broken structures affect the homogenity of the thin films, which might be the reason for their high resistivity.

4 Conclusions

This is the first time that iron isopropyl xanthate thin film was deposited on glass, poly(methyl methacrylate), indium tin oxide, *n*-silicon and *p*-silicon substrate via the ion-ion mechanism. The optimum parameters were determined to be 4 h deposition time at 50°C. Some chemical and physical properties have been found to be changed at different deposition temperatures. At 30°, 40°, and 50°C, the refractive indexes were found to be 1.95, 2.13 and 1.94 (550 nm wavelength), the extinction coefficients were measured as 0.012, 0.015 and 0.012, and the band gaps (*E*g) of the films were found to be 3.70, 3.62 and 3.83 eV, respectively. The film thicknesses varied between 179.2-358.8 nm with the increase in the deposition temperature from 30° to 50°C. The resistivities of the films were measured as 2.35×10^1, 3.38×10^1 and 3.85×10^1 Ω·cm for the film thicknesses 179.2, 260.1, and 358.8 nm, respectively. The resistivities of the poly(methyl methacrylate) (PMM), indium tin oxide (ITO), *n*-silicon (*n*-Si) and *p*-silicon (*p*-Si) substrates were measured as 4.1×10^1, 4.2×10^1, 2.38×10^1 and 3.38×10^1 Ω.cm at the optimum deposition time and temperature. The SEM images of the thin films gave an idea about their resistivity and refractive index. The film deposited on *n*-Si had lower resistivity than the other substrates. It is concluded that further studies should be conducted for this new thin film, which was prepared and examined in order to see if this new material may be useful for solar cells, detectors or sensors.

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