Structural, optical and electrical properties of (\(\text{V}_2\text{O}_5\))\(1-x\)\(\text{MoO}_3\)_\(x\) thin films

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Thin films of \(\text{V}_2\text{O}_5\), \(\text{MoO}_3\) and \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) were deposited on to glass and \(p\)-\(\text{Si}\) \((1 0 0)\) substrates by flash evaporation technique at the substrate temperatures of \(300 \text{ K}\) and \(500 \text{ K}\) at a fixed oxygen partial pressure of \(5 \times 10^{-4} \text{ mbar}\). These deposited films were characterized by XRD, IR, UV VIS spectra. The structure of \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) films is found to be amorphous for \(x = 0.5\). The IR spectra confirm the formation of \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) mixed oxide films for \(0 < x < 1\). The energy gaps of the mixed oxide films are in between 2.1 to 2.56 eV. The width of localized states is 0.92 eV (for \(x = 0\)). The electrical conductivity of the \(\text{V}_2\text{O}_5\) films is \(2 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}\) and decreases with increasing the \(\text{MoO}_3\) concentration in \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) thin films.

**Keywords**: Mixed oxide thin films, Flash evaporation, Characterization

1 Introduction

Transition metal oxides are an important class of materials that find applications in various fields such as electrochemistry, microelectronics, optics, magnetism and environmental science. Among the transition metal oxide semi-conductors, vanadium pent oxide in thin film form, has wide range of applications i.e. multi-vacancy, layered structure, wide optical band gap, good chemical and thermal stability, excellent thermo electric property etc.

Another important material in the transition metal oxide group is molybdenum trioxide which finds applications in optical data storage of display schemes\(^1\). It also acts as an active selective catalyst for the oxidation of hydrocarbon and alcohols\(^2\). Moreover, \(\text{MoO}_3\) also shows photo chromic, thermo chromic and gaso-chromic properties which makes it suitable for preparing variable reflection mirrors, anti-dazzling mirrors in automobiles, and smart windows in energy efficient architecture\(^3\).

The individual practical applications of \(\text{V}_2\text{O}_5\) and \(\text{MoO}_3\) have encouraged the researchers to test their performance when they are mixed. The results obtained in case of molybdenum doped vanadium pent oxide thin film electrodes illustrated higher charge density, better cycling performance when used in solid state batteries and also exhibit improved electro-chromic property compared with pure \(\text{V}_2\text{O}_5\) thin films\(^5\). In the present investigation, \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) thin films were deposited by flash evaporation and studied their structure, optical, infrared and electrical properties.

2 Experimental Details

2.1 Film preparation

\((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) (with \(0 \leq x \leq 1\)) thin films were prepared by flash evaporation in a vacuum coating unit supplied by Vacutech Systems Pvt Ltd, Bangalore, India. Pure \(\text{V}_2\text{O}_5\) powder (purity of 99.96%) and \(\text{MoO}_3\) powder (purity of 99.99%) are used to prepare \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) mixture. The prepared \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) powder was thoroughly mixed in the mortar, sintered at 500 K and used as source material for deposition of films. The substrates used for the present investigation are glass substrates and mono crystalline \(p\)-type single side polished silicon wafers. The oxygen gas was introduced into the chamber and the flow was controlled by needle valve to maintain the partial pressure in the chamber about \(5 \times 10^{-4} \text{ mbar}\). The \((\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x\) powder was filled in a slant chute and vibrated manually by operating electromagnetic relay which was fixed to chute. The films were deposited at various substrate temperatures varying from 300 to 500 K at a fixed partial pressure of \(5 \times 10^{-4} \text{ mbar}\).

2.2 Characterization

The deposited films were characterized for their structure by X-ray diffraction using Philips X-ray diffractometer. The wavelength of the X-rays is...
λ = 1.54Å from CuKα with the scanning angle varied from 10° to 60°. The IR transmission spectra of the films were performed by FT-IR Spectrophotometer (JASCO FTIR-6300) in the wave number range 500-4000 cm\(^{-1}\). The optical transmittance of the films were recorded using JASCO Spectrophotometer (JASCO FLH-741). The electrical conductivity of the films at room temperature is measured by (Solid State Electrometer, Keithley make) standard two probe method.

3 Results and Discussion

3.1 XRD analysis

The X-ray diffraction spectra of the V\(_2\)O\(_5\), MoO\(_3\), V\(_2\)O\(_5\)-MoO\(_3\) films have been studied to understand crystallographic structure of the deposited films. The literature reveals that the X-ray diffraction spectra of V\(_2\)O\(_5\) thin films deposited at lower substrate temperatures were broad and diffused which indicates the amorphous phase. The amorphous films change to polycrystalline with orthorhombic structure with increasing substrate temperature above 473 K. The crystallographic orientations observed were (2 0 0), (0 0 1) and (1 1 0).

The MoO\(_3\) thin films deposited at lower substrate temperature (< 303 K) were also amorphous and polycrystalline when deposited at 500 K with predominant (0 2 0), (0 4 0) orientations which indicate orthorhombic α-phase. The further increase in substrate temperature changes the films structure to β-phase\(^7\).

In the present investigation, we have deposited (V\(_2\)O\(_5\))\(_{1-x}\)-(MoO\(_3\))\(_x\) films at a substrate temperature of 300 K and 500 K. The value of \(x\) is varied from 0 to 1. It was observed that the films deposited at 300 K were amorphous. The X-ray diffraction spectrum of the films deposited at 5×10\(^{-4}\) mbar and 500 K is shown in Fig. 1. The spectra was recorded for various compositions of V\(_2\)O\(_5\), MoO\(_3\) in (V\(_2\)O\(_5\))\(_{1-x}\)-(MoO\(_3\))\(_x\) mixer. It was observed that only a single crystallographic orientation (0 0 2) at 2\(θ\) = 35° was observed for (V\(_2\)O\(_5\))\(_{0.75}\)-(MoO\(_3\))\(_{0.25}\) films which corresponds to V\(_2\)O\(_5\). Moreover, the observed peak (0 0 2) position is shifted towards lower value of 2\(θ\) when compared to pure V\(_2\)O\(_5\) films. This indicates the enhancement in the inter planar spacing in V\(_2\)O\(_5\) due to MoO\(_3\). With increasing composition, no crystallographic orientations correspond to either V\(_2\)O\(_5\) or MoO\(_3\) is observed. This indicates the films were amorphous at a composition of \(x = 0.5\). With further increasing the MoO\(_3\) composition (\(x = 0.75\),

the crystallographic peaks are observed at 2\(θ\) = 12°, 20 = 25° and correspond to MoO\(_3\). But there is no shift in the peak position of MoO\(_3\) films due to V\(_2\)O\(_5\). These results suggest that at lower composition of MoO\(_3\), the crystallographic peaks correspond to V\(_2\)O\(_5\), are significant and vice versa for higher composition of MoO\(_3\).

3.2 Infrared analysis

The infrared spectra of the films have been studied to understand the modes of vibrations of (V\(_2\)O\(_5\))\(_{1-x}\)-(MoO\(_3\))\(_x\) thin films. The IR spectra of mixed oxides deposited at 300 K were broad which indicates the films were amorphous. The IR spectra of (V\(_2\)O\(_5\))\(_{1-x}\)-(MoO\(_3\))\(_x\) thin films deposited at 5×10\(^{-4}\) mbar and at a substrate temperature of 500 K is shown in Figs 2 and 3. It was observed that in the wavenumber range 500-2000 cm\(^{-1}\), there were a strong and weak absorption bands corresponding to transversal bending, deformation, stretching modes of vibrations. The bands at 559 cm\(^{-1}\); 1427 cm\(^{-1}\) were weak and the bands at 612 cm\(^{-1}\); 1109 cm\(^{-1}\) were comparatively strong.

The band at 559 cm\(^{-1}\) is attributed to the transverse optical vibration mode\(^1\) of MoO\(_3\). The band at 612 cm\(^{-1}\) is due to deformation mode of MoO\(_3\) and the intensity of this deformation mode is decreasing with increasing V\(_2\)O\(_5\) composition. The combination mode with strong intensity \(^6\) was observed at 1109 cm\(^{-1}\). These combination modes are strong for lower V\(_2\)O\(_5\) concentrations in MoO\(_3\). The absorption peak at 1427 cm\(^{-1}\) is attributed to the bending vibration of Mo hydrates. It was observed that the intensity of
absorption peak 1427 cm$^{-1}$ is decreasing with $V_2O_5$ composition. This indicates that $V_2O_5$ prevents the hydration of MoO$_3$ films. The weak band at 1603 cm$^{-1}$ corresponds to lattice imperfections but this band is very weak except for lower $V_2O_5$ concentrations. So this indicates that a film does not have lattice imperfections.

The band at 2337 cm$^{-1}$ is strong due to stretching vibration of CO and CO$_2$ in ($V_2O_5$)$_{1-x}$(MoO$_3$)$_x$. The band observed at 3416 cm$^{-1}$ is weak in case of pure MoO$_3$ thin films and the intensity of this peak is increasing with increasing $V_2O_5$ composition and is attributed to the stretching and bending of V-O vibration. The intensity of this mode is decreased with further increase of $V_2O_5$ composition in MoO$_3$.

3.3 Optical properties

The optical transmittance spectra of the pure and mixed oxide ($V_2O_5$)$_{1-x}$(MoO$_3$)$_x$ films deposited at $5 \times 10^{-4}$ mbar and at a substrate temperature of 300 K is shown in Fig. 4. It was observed that there is no significant variation in the transmittance of $V_2O_5$ with MoO$_3$ doping except at lower concentrations of MoO$_3$. The absorption edge shifts towards lower wavelengths with increasing MoO$_3$ composition. This is attributed to the decrement in the electron concentration in ($V_2O_5$)$_{1-x}$(MoO$_3$)$_x$ mixed oxide films.

The optical transmittance spectra of ($V_2O_5$)$_{1-x}$(MoO$_3$)$_x$, thin films deposited at a fixed oxygen partial pressure of $5 \times 10^{-4}$ mbar and at a substrate temperature of 500 K is shown in Fig. 5. The transmittance showing oscillating variations beyond the absorption edge due to the optical interference.

The optical absorption coefficient of the films was evaluated using the relation:

$$\alpha = \frac{1}{t} \ln \frac{T}{T(1-R)^2} \quad \ldots (1)$$

where $T$ is the transmittance, $R$ reflectance and $t$ is the film thickness.

The optical absorption coefficient of the films at the fundamental absorption edge was found to be exponentially dependent on the photon energy. For incident photon energy greater than the band gap and above the exponential tail, the optical absorption follows a power law$^5$:
transitions causing the absorption thin film $V_{2}$O$_{5}$ films deposited at various substrate temperatures. It was observed that the pure $V_{2}$O$_{5}$ films exhibit broad absorption around 800 nm due to oxygen deficiency and it was observed that the pure $V_{2}$O$_{5}$ film were stoichiometric (Table 1). The band gap curve for different concentration of MoO$_{3}$ is observed non-linear and can be explained by using pseudo potential approach$^{12}$. In this approach, the pseudo potential lead to the following expression for the band gap is $E_{g}$,

$$E_{g} = E_{g0} + x(E_{g0}^{2} - E_{g}) + \gamma(x)$$  \hspace{1cm} \ldots(3)$$

where the last term generate from the pseudo-potential factor. According to Philips$^{13}$ this factor will always lower the value of $E_{g}$ and is expressed as $\gamma_{0}(1-x)x$ where $\gamma_{0}$ is the bowing factor responsible for lowering the value of $E_{g}$. The experimental value of $\gamma_{0}$ is always positive. Hence, at higher concentration of MoO$_{3}$, the $E_{g}$ value saturates and approaches the value of $E_{g}$ for MoO$_{3}$ films. Such type of non-linear behaviour of band gap in Cd$_{1-x}$Zn$_{x}$S was also observed by Mbow. The plots of $\ln \alpha$ versus $h\nu$ were used to estimate the width of localized states. The variation of $\ln \alpha$ with incident photon energy of ($V_{2}$O$_{5}$)$_{(1-x)}$(MoO$_{3}$)$_{x}$ films were found to be linear in the absorption region near the fundamental absorption edge. The optical absorption coefficient near the fundamental absorption edge is found to be exponentially dependent on the incident photon energy and obeys the empirical Urbach rule$^{14}$.

$$\alpha = \omega_{0} \exp[\frac{h\nu}{E_{g}}]$$  \hspace{1cm} \ldots(4)$$

where $\alpha$ is the optical absorption coefficient, $\omega_{0}$ a constant and $E_{g}$ the energy. The $E_{g}$ is often interpreted as the width of the localized states associated with the amorphous state in the band gap of the material. The exponential dependence of the optical absorption coefficient with photon energy may arise from the electronic transitions between the localized states, which have tailed off in the band gap. The density of these states falls off exponentially with energy, which is consistent with the theory of Tauc$^{15}$. However Dow$^{15}$ believed that the exponential dependence of

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\text{Fig.5 — Optical transmittance spectra of } \left(V_{2}O_{5}\right)_{1-x}\left(MoO_{3}\right)_{x} \text{ films deposited at various substrate temperatures.
}
\[
\alpha h\nu = B(h\nu - E_{g})^{n} \hspace{1cm} \ldots(2)\]

where $B$ is a constant, $E_{g}$ the optical band gap of the material and ’$n$’ is the exponent.

The exponent ‘$n$’ determines the type of electronic transitions causing the absorption$^{9}$.

The value of the optical band gap for $V_{2}$O$_{5}$ ($x = 0$) for direct forbidden ($n = 3/2$) transition is found to be 2.42 eV which represents the transfer of electronic charge from O 2$p$ to V 3$d$ band following a process of direct forbidden transitions. The energy gap slightly increases with increasing substrate temperature to 500 K and is 2.49 eV. This is attributed to the enhancement of crystallinity of the films at higher substrate temperatures. The results are found to be good agreement with the values reported for bulk and thin film $V_{2}$O$_{5}$ by several researchers$^{10}$. The optical band gap evaluated for MoO$_{3}$ thin films ($x = 1$) were better fit for $n = 1/2$ which indicates the direct transition of electron from valance band to conduction. The energy gap is found to be 3.30 eV, and decreases with increasing substrate temperatures due to oxygen deficiency. The values are found to be in good agreement with the reported values$^{11}$.

The estimated optical band gaps of ($V_{2}$O$_{5}$)$_{(1-x)}$($MoO_{3}$)$_{x}$ films the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ were in the range 2.10-2.56 eV. The films deposited at lower substrate temperatures have higher energy gaps when compared to the films deposited at higher substrate temperature. It was observed that the pure MoO$_{3}$ films exhibit broad absorption around 800 nm due to oxygen deficiency and it was observed that the pure $V_{2}$O$_{5}$ film were stoichiometric (Table 1). The band gap curve for different concentration of MoO$_{3}$ is

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\begin{array}{|c|c|c|c|c|}
\hline
\text{Composition} & \text{Optical band gap } E_{g} (eV) & \text{Width of localized states } E_{g} (eV) \\
\text{Composition} & \text{Ts = 300 K} & \text{Ts = 500 K} & \text{Ts = 300 K} & \text{Ts = 500 K} \\
0 & 2.42 & 2.49 & 0.92 & 0.36 \\
0.25 & 2.10 & 2.22 & 0.76 & 0.43 \\
0.5 & 2.38 & 2.09 & 0.33 & 0.5 \\
0.75 & 2.10 & 2.56 & 1.07 & 1.2 \\
1 & 3.30 & 3.09 & 0.42 & 0.36 \\
\hline
\end{array}
\]

\(E_{g} = E_{g0} + x(E_{g0}^{2} - E_{g}) + \gamma(x)\)
the optical absorption coefficient on energy might arise from the random fluctuations of the internal fields associated with the structural disorder in many amorphous materials. The width of localised states is 0.92 eV for pure V$_2$O$_3$ amorphous materials. The width of localised states is 0.92 eV for pure V$_2$O$_3$ and decreasing with increasing MoO$_3$ concentration in V$_2$O$_3$. These results are found to be in good agreement with that reported values for amorphous V$_2$O$_3$ thin film bronzes.$^{16-18}$

3.4 Electrical properties

The room temperature electrical conductivity of the films deposited at 300 K, 500 K and at a pressure of $5 \times 10^{-4}$ mbar is shown in Fig. 6. The electrical conductivity of V$_2$O$_3$ films ($x = 0$) was about $2 \times 10^{-3}$ ohm$^{-1}$cm$^{-1}$. The electrical conductivity decreases with increasing MoO$_3$ concentration. The interference of the non-periodic Columbic field produced by Mo$^{6+}$ will dominate the electrical conductivity with the increase of molybdenum$^{19}$ content in V$_2$O$_3$. This interference may lead to the decrease of the number of V$^{4+}$ ions when compared to that of Mo$^{6+}$ ions which is responsible for the decrease of the electrical conductivity with increase of Mo concentration in (V$_2$O$_3$)$_{1-x}$(MoO$_3$)$_{x}$ thin films. The interference of Columbic fields may not be so significant at lower concentration of molybdenum in (V$_2$O$_3$)$_{1-x}$(MoO$_3$)$_{x}$. The distance between Mo$^{6+}$ ions is also large which may be responsible for the observed weak dependence of conductivity on the composition at lower concentrations. The d-band in (V$_2$O$_3$)$_{1-x}$(MoO$_3$)$_{x}$ has an appreciable electron density at lower concentrations, which decreases further as molybdenum concentration increases.

4 Conclusions

The mixed oxide films of (V$_2$O$_3$)$_{1-x}$(MoO$_3$)$_{x}$ for $0 < x < 1$ were deposited by flash evaporation technique at a fixed oxygen partial pressure of $5 \times 10^{-4}$ mbar at various substrate temperatures of 300 K and 500 K. The structural study reveals that the films were observed amorphous for $x = 0.5$ when deposited at a substrate temperature of 500 K. The optical study reveals that the direct allowed transition of electron in individual oxides changes to indirect allowed in case of mixed oxides. The films deposited at higher substrate temperature were having lower energy gaps, when compared to the films deposited at lower substrate temperatures. The width of localized states $E_{\text{loc}}$ is decreased by increasing MoO$_3$ concentration. The electrical study suggests the conductivity of V$_2$O$_3$ can be reduced with increasing MoO$_3$ concentration. In conclusion, the structural, optical and electrical properties of V$_2$O$_3$ thin films were observed to be changed by MoO$_3$.

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