The dielectric studies on sol-gel routed molybdenum oxide thin film

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The influence of temperature on the dielectric properties of sol-gel routed spin-coated molybdenum trioxide (MoO_3) thin film has been investigated. Prepared films were annealed at temperatures 250°C, 350°C and 400°C. The phase transformation from amorphous to α -orthorhombic phase with preferential orientation (0 2 2) has been found by XRD for the film annealed above 250°C. The vibration modes of α -orthorhombic MoO_3 have been examined by Raman spectrum. The predominant Raman's band of α -orthorhombic MoO_3 thin film has been found at the frequency range 1000–600 cm^{-1} . Using the UV-Vis spectrum, the band gap of the film is found to be 3.3–3.8 eV. The surface morphology of the MoO_3 films has been examined by scanning electron microscope. The AC conductivity measurement of the MoO_3 film has been carried out in the frequency range 10–10⁶ Hz. The frequency dependence of the impedance has been plotted in the complex plane. The variation of the capacitance and dielectric constant of MoO_3 film with respect to temperature and frequency has been analyzed. Tunability of capacitance and figure of merit of the film are also determined.

Keywords: Sol-gel; dielectric constant; capacitance; tunability; Curie-temperature; figure-of-merit.

1. Introduction

In modern technological era, the need for new materials with good dielectric behavior has increased. The wide band gap transition metal oxides with notable dielectric behavior have attracted the researchers to fabricate the device with low leakage current level for their operations. The metal oxides exhibit different optoelectronic properties such as electrochromic, photochromic, gas sensing and some of them exhibit high dielectric constant and low dielectric loss that make them a best alternative for conventional SiO_2 in the fabrication of DRAM and super capacitors. The molybdenum trioxide (MoO_3) is one of the transition metal oxides which exhibit good dielectric behavior. Different deposition techniques such as chemical vapor deposition,¹ electrode deposition,² electron beam deposition,³ sputtering⁴ and spray pyrolysis⁵ have been employed to produce MoO_3 films. The sol-gel technique has been receiving considerable attention to prepare the high quality films at low cost with simpler deposition procedure.⁶ In this present work, the sol-gel routed spin coating technique has been used for obtaining MoO_3 thin films at room temperature with required thickness. Prepared films were annealed at the temperature range 250–400°C to convert MoO_3 thin film from amorphous to crystalline nature. This work investigates the structural, optical and dielectric properties of the MoO_3 thin film. The novelty of the present work is to study the effect of temperature on the dielectric properties of MoO_3 thin film in amorphous form.

2. Materials and Method

The precursor solution was prepared by mixing MoO_3 powder (99.999%, SigmaAldrich) into excess H_2O_2 (30%, Sigma-Aldrich) and the solution was refluxed for 30 min at 60°C in air. The resulting yellow colored solution was cooled to room temperature and left for gellation and during the gellation time, the viscosity and concentration of the solution were adjusted by adding polyethylene glycol (average Mn 200, Sigma-Aldrich) and 2-ethoxyethanol (Sigma-Aldrich). The solution with sufficient viscosity was spin-coated on clean commercially available fluorine-doped tin oxide (FTO) substrates with a sheet resistance of 10 Ω /square. The film was coated as multiple layers to obtain the required thickness. After each layer of coating, the film was dried at 100°C for about 5 min. The solution-processed films were annealed at the temperature range of 250–400°C for 2 h by keeping the rate of temperature at 4°C per minute. The thickness of the film was measured by stylus profilometer (Mitutoyo, SJ-301). The X-ray diffraction (XRD) for phase identification was performed using XPERT-PRO X-ray diffractometer with $\text{Cu-K}\alpha$ ($\lambda = 0.154$ nm) radiation source. Raman spectra were recorded using a micro-Raman spectrometer ($\lambda = 514.5$ nm, Acton Spectra Pro 2500i, Princeton Instruments, Acton Optics & Coatings). The surface morphology of MoO_3 film was examined by VEGA3 TESCAN scanning electron microscope (SEM). The optical characterization was done by Perkin Elmer Lambda-35 UV-Visible (UV-Vis) spectrometer. The measurements of dielectric properties were carried

out using an MIM structure. Capacitance versus voltage, dielectric constant and dielectric loss measurements were carried out using Impedance analyzer (Princeton Applied Research, VersaSTAT MC) and LCRZ meter. Using the impedance data, the Nyquist plot was plotted and the possible equivalent circuit has been identified. Using the temperature variable capacitance measurement set-up, the phase transition temperature of the MoO_3 has been determined.

3. Structural Parameters

The XRD pattern of MoO_3 thin film of thickness of $2.5 \mu\text{m}$ (Fig. 1) exhibits amorphous nature for the film annealed below 250°C and crystalline nature for the film annealed at higher temperatures. The films annealed at 350°C and 400°C exhibit α -orthorhombic phase with preferential orientation along (0 2 0) plane. The peak intensity increases with the

Fig. 1. XRD spectrum of MoO_3 thin film.

increase of annealing temperature, due to the increase in grain size of the crystal lattice.⁷ The various structural parameters like lattice constants (a , b , c), crystallite size (D), dislocation density (δ), strain (ε) and number of crystallites per unit area (N) of MoO_3 film are calculated (Table 1). The lattice constants (a , b , c) of MoO_3 films annealed at higher temperature were evaluated by using Check Cell software and cross-verified by JCPDS data (JCPDS Card no.: 89-5108). The crystallite size D is evaluated from Scherrer formula:

$$D = \frac{0.94\lambda}{\beta \cos \theta}, \quad (1)$$

where β is full width at half maximum of XRD peak. The crystallite size increases with the increase of annealing temperature. According to the theory of kinematical scattering, the narrow peak is due to the larger crystallite size and fewer defects present in the crystals. In the present work, the sharp and higher peak of XRD confirm larger crystallite size and improvement in crystalline nature.⁸ The dislocation density is evaluated from the relation:⁹

$$\delta = \frac{1}{D^2}. \quad (2)$$

The decrease of dislocation density with the increase of annealing temperature indicates the reduction of defects due to annealing. The strain (ε) and number of crystallites per unit area (N) of the film is calculated from the relations:⁹

$$\varepsilon = \frac{\beta \cos \theta}{4}, \quad (3)$$

$$N = \frac{t}{D^3}, \quad (4)$$

where t is thickness of the thin film. The reduction of strain with the increase of annealing temperature reveals the enhancement of crystalline nature. The number of crystal lattice per unit area decreases with the increase of annealing temperatures due to the increase of crystallite size. The surface morphology of the film has been investigated by SEM

Table 1. Structural properties.

Annealing temperature ($^\circ\text{C}$)	Structure/Lattice	Lattice constant ($\text{\AA}$)	Crystallite size (D)(nm)	Dislocation density (δ) $\times 10^{15}$ (lines/ m^2)	Strain (ε) $\times 10^{-2}$ ($\text{line}^{-1}\text{m}^{-4}$)	Number of crystallites per unit area (N) $\times (10^{16}/\text{m}^2)$
250	Amorphous	—	—	—	—	—
350	Orthorhombic/primitive	$a = 3.7$ $b = 13.9$ $c = 3.3$	51.78	3.55	6.56	11.37
400	Orthorhombic/primitive	$a = 4.3$ $b = 13.8$ $c = 3.5$	63.87	2.26	6.32	9.41

Note: Lattice constant (a, b, c), crystallite size (D), strain (ε), dislocation density (δ), number of crystallites per unit area (N).

Fig. 2. (a) SEM images of MoO_3 thin film before annealing, (b) SEM images of MoO_3 thin film before annealing, (c) SEM images of MoO_3 thin film annealed at 400°C and (d) SEM images of MoO_3 thin film annealed at 400°C .

(Fig. 2). It shows that the film is homogeneous and the grain boundaries are evenly distributed throughout the sample and it also indicates that the heat treatment increases the size of grain boundaries (Figs. 2(c) and 2(d)).

3.1. Micro Raman studies

A typical Raman spectrum of the MoO_3 thin film is shown in (Fig. 3). The vibration modes appearing in the frequency ranges of $1000\text{--}600\text{ cm}^{-1}$ and $600\text{--}200\text{ cm}^{-1}$ correspond to the stretching and deformation modes, respectively. The narrow band at 994 cm^{-1} is assignable to the anti-symmetric $\nu_{\text{as}}(\text{Mo}=\text{O})A_g$ stretching, in which the strong band at 830 cm^{-1} represents the symmetric $\nu_s(\text{Mo}-\text{O}_3-\text{Mo})A_g$ stretching. The weak and broad bands at 666 cm^{-1} and 470 cm^{-1} are ascribable to the anti-symmetric $\nu_{\text{as}}(\text{Mo}-\text{O}_2-\text{Mo})$

Fig. 3. Raman spectrum of MoO_3 thin film.

B_{2g} stretching and bending, respectively. The bands at 377 cm^{-1} and 364 cm^{-1} correspond to the δ ($\text{O}_2 = \text{Mo}=\text{O}_2$) B_{1g} scissor. The Raman band at 830 cm^{-1} reveals the formation of α orthorhombic phase in MoO_3 film at higher annealing temperature.¹⁰

4. Optical Properties

The optical transmission spectra of MoO_3 films annealed at various temperatures exhibit good transparency at 575 nm (Fig. 4). The films annealed at 250°C manifests clearly the maximum transparency of 85%. The film annealed at 400°C exhibits only 65% of transparency at 575 nm due to the free carrier absorption and scattering of light by formation of micro crystallites.¹¹ The optical behavior of the film annealed at 350°C is different from the others indicating the phase transformation around 300°C which causes more absorption by charge carriers. The higher transmittance in the higher wavelength region indicates the decrement in optical band gap (E_g) with the increase of the annealing temperatures. From the transmission spectrum, the absorption coefficient (α) is determined by the relation.¹²

$$\alpha = \frac{1}{t} \ln T, \quad (5)$$

where t is thickness of the film and T is transmittance. The band gap of the film is determined from the relation¹³

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g). \quad (6)$$

where A is the constant, E_g optical band gap energy of the material and $n = 1/2, 2, 3/2$ and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and

Fig. 4. UV transmittance spectrum of MoO_3 thin film.

Fig. 5. The plot of $(\alpha h\nu)^3$ as a function of $h\nu$.

forbidden indirect transitions, respectively. The optical band gap depends upon the absorption coefficient (α). The MoO_3 is found to be direct band gap material ($n = 1/2$). The extrapolation of linear portion ($\alpha = 0$) gives the optical band gap energy of the film. Figure 5 shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for MoO_3 at different annealing temperatures. It reveals that the optical band gap of the MoO_3 film decreases with the increase of the annealing temperature that might be due to the formation of oxygen ion vacancies and the improvement of crystallinity in the film.¹¹ This presumption is consistent with our XRD finding. The optical band gap value

Fig. 6. The plot of dielectric constant as a function of frequency and temperature.

of MoO₃ film at 250°C, 350°C and 400°C are 3.8, 3.5 and 3.3 eV, respectively.

5. Dielectric Properties

The value of dielectric constant decreases with the increase of frequency (Fig. 6). It might be due to the alignment of permanent dipoles along with the direction of electric field at lower frequency and it contributes to the total polarization of the dielectric material. On the other hand, at higher frequency as the field rapidly vary, the dipole can no longer follow the field.¹⁴ Hence, their contribution to the

polarization becomes negligible and it leads to increment in the dielectric loss and decrement in dielectric constant (Fig. 7). The increment in the dielectric constant with the increase of temperature is attributed to the increase of grain size and more electrical polarizability of the material.¹⁴ (Fig. 6).

Figure 8(a) and 8(b) show that the variation of the capacitance and dielectric constant of the MoO₃ thin film with respect to temperature, it fits very well with Curie–Wiess law. At 260°C, the capacitance and dielectric constant reach a maximum value which indicates the phase transition in the material.¹⁵ This temperature is the transition temperature or Curie temperature (T_c), beyond which the material behaves as paraelectric. The above fact is supported by the XRD data. The XRD spectrum of the sample annealed above 250°C reveals the crystalline nature of MoO₃ thin film. The measurement of capacitance with respect to DC electric field was carried out at room temperature for 1 KHz and 100 KHz (Fig. 9). The tunability and figure of merit (FoM) were determined from the following relations:¹⁶

$$\text{Tunability} = \frac{C_{\max} - C_{\min}}{C_{\min}} \times 100, \quad (7)$$

$$\text{FoM} = \frac{\% \text{Tunability}}{\% \text{dielectric loss}}, \quad (8)$$

where $C_{\max}$ is the capacitance value for zero bias field. $C_{\min}$ denotes the capacitance of applied field. The applied field is in the order of 10^6 V/m. The tunability and FOM of the MoO₃ film increases with the increase of applied potential (Fig. 10). The tunability of the dielectric properties of the material might be attributed to internal stress among the grains.¹⁷

Fig. 7. The plot of dielectric constant and dielectric loss as a function of frequency.

Fig. 8. (a) The plot of capacitance and dielectric constant as a function of temperature, (b) The plot of $1/\epsilon_r$ as a function of temperature.

Fig. 9. The plot of capacitance and dielectric loss as the function of voltage.

Fig. 10. The plot of tunability and FoM as the function of voltage.

5.1. The impedance studies

The impedance spectroscopy studies on MoO₃ thin film were carried out by using the complex impedance spectra. It can be fitted with a simple electrical model $R_b (R_{gb}C_{gb})$, where R_b and R_{gb} are bulk and grain boundary resistance, respectively, and C_{gb} is the capacitance across the grain boundary. The impedance of the film with resistance R_{gb} in parallel with a capacitance C_{gb} is given by the expression.¹⁸

$$Z_{gb} = \frac{1}{R_{gb}^{-1} + j\omega C_{gb}}, \quad (9)$$

where $\omega = 2\pi f$.

Fig. 11. (a) Nyquist plot of unannealed MoO₃ thin film, (b) Nyquist plot of annealed MoO₃ thin film.

The above equation can be expressed as

$$\left(\frac{Z'_{gb} - R_{gb}}{2}\right)^2 + Z''_{gb} = \left(\frac{R_{gb}}{2}\right)^2, \quad (10)$$

where Z'_{gb} and Z''_{gb} are the real and imaginary components of the Z_{gb} , respectively. The corresponding plot of the real Z_{gb} against the imaginary component of Z_{gb} (Fig. 11(a) Nyquist plot) is a semicircle of radius $R_{gb}/2$. The R_{gb} and R_b values were derived from the intercept of the semicircle with real axis at low and high frequencies, respectively. In the mid-frequency region, linear progress of the diffusion characteristic of MoO₃ is observed. At the low frequency region, the capacitive behavior is observed which reveals the characteristic response of blocked diffusion.¹⁹

The impedance response of the grain dominates at high frequency and resistance of the grain R_g is deduced from the left intercept to real axis. The right intercept of the semicircle to real axis Z' at low frequency indicates the sum of resistance of grain R_g and grain boundaries R_{gb} . Figure 11(b) shows that the resistance of the bulk and grain boundaries increases due to the increase of grain size by heat treatment.

6. Conclusion

The effect of temperature on the dielectric properties of sol-gel routed spin-coated MoO₃ thin film has been investigated. The phase transformation from amorphous to α -orthorhombic phase has been found by XRD for the film annealed at higher temperature. The Raman spectrum reveals that the predominant Raman's band of α -orthorhombic MoO₃ thin film has been found at the frequency ranges of 1000–600 cm⁻¹. The band gap of the film is found to be 3.3–3.8 eV. SEM image shows that the film is homogeneous and the grain boundaries are evenly distributed throughout the sample. The impedance plot in the complex plane reveals semicircular arc. The system could be represented by an equivalent circuit of parallel resistance–capacitance combination. The variation of the capacitance and dielectric constant of MoO₃ film with respect to temperature and frequency has been analyzed. Tunability and FoM of the film are also determined. The obtained data can be utilized for the fabrication of dielectric devices.

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