

The Electrical Studies on Sol-Gel Routed Molybdenum Oxide Thin Film

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Abstract

This paper investigates electrical properties of sol-gel routed spin coated Molybdenum trioxide (MoO_3) thin films. Prepared films were annealed at 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 at 400 °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 UV-Vis spectrum the band gap of the film is found to be 3.3-3.8eV. The surface morphology of the MoO_3 films has been examined by scanning electron microscope. The resistivity of the film found to be $1.4 \times 10^{-7} \Omega\text{m}$. The AC conductivity measurement of 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, electrical conductivity, Dielectric constant, capacitance, tunability, Curie-temperature, Figure of merit.

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 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], sputtering [4] and spray pyrolysis [5] 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 thin film with required thickness. Prepared films were annealed at 400° C. This work investigates the structural, optical and electrical properties of the molybdenum trioxide thin film. The novelty of the present work is to study the effect of temperature and concentration on the electrical properties of MoO_3 thin film respectively.

1. 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 minutes at 60°C in air. The resulting yellow coloured 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 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 minutes. The solution-processed films were annealed at 400° C for 2 hours 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 for phase identification was performed using XPERT-PRO X-ray diffractometer with Cu-K α (λ = 0.154nm) radiation source. The surface morphology of MoO₃ film was examined by VEGA3 TESCAN scanning electron microscope. The optical characterization was done by Perkin Elmer Lambda - 35 UV-Visible spectrometer. The measurements of dielectric properties were carried out using a MIM structure. Capacitance vs 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 MoO₃ has been determined.

2. Structural parameters

The XRD pattern of MoO₃ thin film of thickness of 2.5 μ m (Figure 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 400°C exhibit α -orthorhombic phase with preferential orientation along (0 2 0) plane. The peak intensity increases with increase of concentration, due to the increase in grain size of the crystal lattice [7]. The various structural parameters like crystallite size (D), dislocation density (δ), strain (ϵ), and number of crystallites per unit area (N) of MoO₃ film are calculated (Table 1). The crystallite size D is evaluated from Scherrer formula:

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

where β is full width at half maximum of XRD peak. The crystallite size increases with increase of concentration. According to the theory of kinematical scattering the narrow peak is due to 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]:

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

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

$$\epsilon = \frac{\beta \cos \theta}{4} \quad \dots (3)$$

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

where, t is thickness of the thin film. The reduction of strain with increase of concentration reveals the enhancement of crystalline nature. The number of crystal lattice per unit area decreases with increases of concentration due to increase of crystallite size. The surface morphology of the film has been investigated by SEM (Figure 2). It shows that the film is homogeneous and the grain boundaries are evenly distributed though out the sample.

Table 1. Structural properties

Concentration (mol)	grain size (nm)	Dislocation density(δ)(x 10 ⁻¹⁸)	strain (ϵ)	Number of crystal lattice (N) x 10 ²¹
0.5	29	3.18	0.007	7.08
1	34	2.49	0.005	4.36
1.5	61	2.34	0.005	1.07
2	74	1.9	0.003	1.91

Crystallite size (D), Strain (ϵ), Dislocation Density (δ), Number of Crystallites per unit area(N).

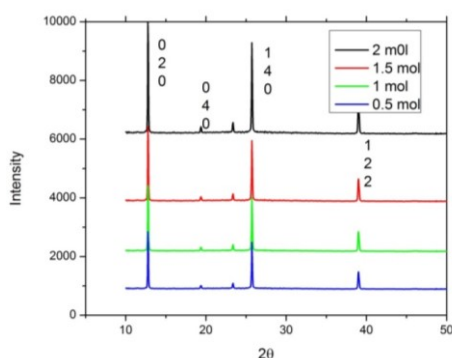
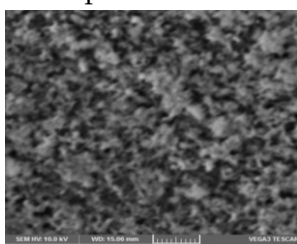
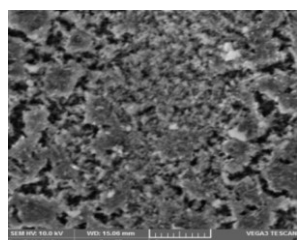


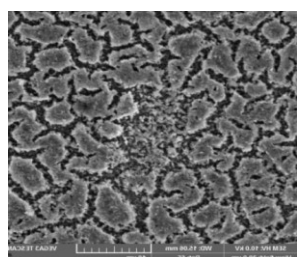
Figure 1. XRD spectrum of MoO₃ Thin film



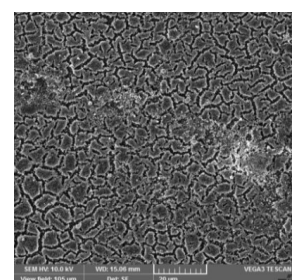
2A



2B



2C



2D

Figure 2: SEM images of MoO₃ Thin film

2.1. Micro Raman Studies

A typical Raman spectrum of the MoO₃ thin film is shown in (Figure 3). The vibration modes appearing in the frequency ranges of 1000–600 cm⁻¹ and 600–200 cm⁻¹ correspond to the stretching and deformation modes respectively. The narrow band at 994 cm⁻¹ is assignable to the anti symmetric $\nu_{as}(\text{Mo}=\text{O})_{Ag}$ stretching, in which the strong band at 830 cm⁻¹ represents the symmetric $\nu_s(\text{Mo}-\text{O}_3-\text{Mo})_{Ag}$ stretching. The weak and broad bands at 666 and 470 cm⁻¹ are ascribable to the anti symmetric $\nu_{as}(\text{Mo}-\text{O}_2-\text{Mo})_{B_{2g}}$ stretching and bending respectively. The bands at 377 and 364 cm⁻¹ correspond to the $\delta(\text{O}_2=\text{Mo}=\text{O}_2)_{B_{1g}}$ scissor. The Raman band at 830 cm⁻¹ reveals the formation of α orthorhombic phase in MoO₃ film at higher annealing temperature [10].

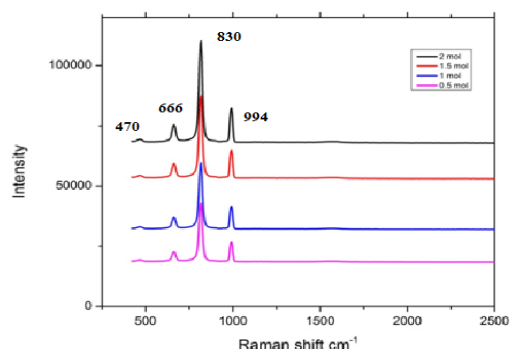


Figure 3. Raman Spectrum of MoO₃ Thin film

3. Optical Properties

The optical transmission spectra of MoO₃ films prepared at 400°C with various concentration exhibit good transparency at 570 nm (Figure 4). The film prepared at 0.5 mol exhibits maximum transparency of 80%. The transparency of the film decreases with increase of the concentration. The films prepared at 2 mol exhibits only 40% of transparency at 570 nm that might be due to the free carrier absorption and formation of micro crystallites leading to the scattering of light[11]. The higher transmittance in the higher wave length region indicates the reduction in optical band gap (E_g) with increase of the concentration.

From the transmission spectrum the absorption coefficient (α) is determined by the relation [12].

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

where t is thickness of the film and T is transmittance. The band gap of the film is determined from the relation [13].

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

A is the energy dependent 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 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 $(\alpha h\nu)^2$ vs $h\nu$ for MoO_3 at different concentration. It reveals that the optical band gap of the MoO_3 film decreases with increase of the concentration that may be due to the formation of oxygen ion vacancies and the improvement of crystallinity in the film [11]. This inference is consistent with our XRD finding. The optical band gap value of MoO_3 film prepared at 0.5 mol, 1.5 mol and 2 mol are 3.8, 3.5 and 3.3 eV respectively.

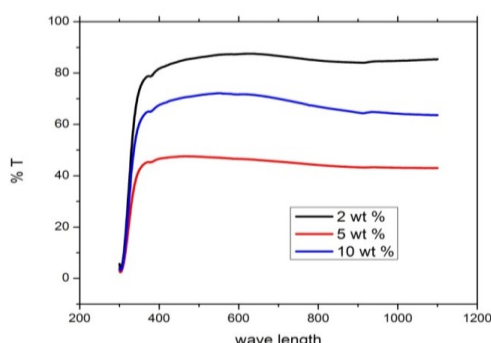


Figure 4. UV Transmittance spectrum of MoO_3 Thin film

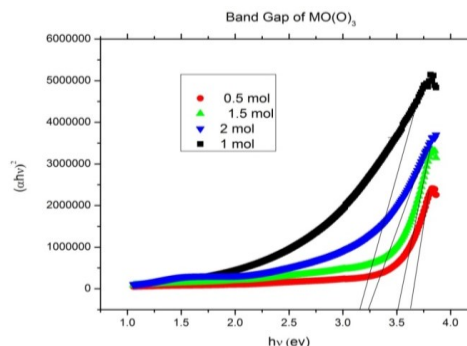


Figure 5. The Band gap of MoO_3 Thin film

4. Electrical Properties

The resistivity measurement of MoO_3 film carried out by two-probe method, V-I plot of MoO_3 (Figure 6A) film with different concentration shows the increment in the conductivity with increase of concentration. The resistivity of the film found to be $1.4 \times 10^7 \Omega\text{m}$ for higher concentration. The measurements of dielectric properties were carried out using a MIM structure. The value of dielectric constant decreases with increase of frequency (Figure 6B). It might be due to 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 (Figure 8). The increment in the dielectric constant with increase of temperature is attributed to bulk effect of the system and also due to increase of energy absorption by the dielectric material [14] (Figure 7).

Table 2. Electrical Properties

Concentration (mol)	$(\rho) \Omega\text{m}$	$(\sigma) \times 10^{-8} \Omega^{-1} \text{m}^{-1}$
0.5	3.7×10^8	2.6
1	5.5×10^7	1.8

1.5	3.5×10^{-7}	1.5
2	1.4×10^{-7}	1.3

Resistivity (ρ) Ωm , conductivity (σ) $\times 10^{-8} \Omega^{-1} \text{m}^{-1}$

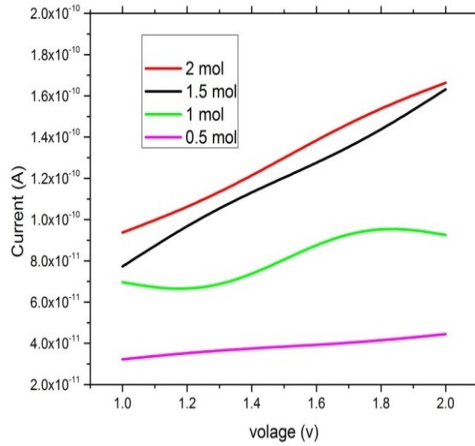


Figure 6A. Resistivity measurement of MoO₃ Thin film

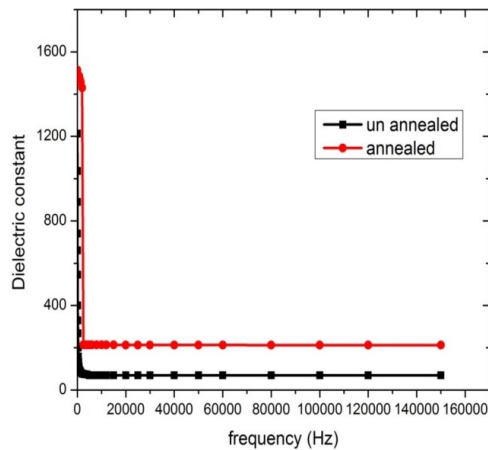


Figure 6B. Frequency dependent Dielectric constant of MoO₃ Thin film

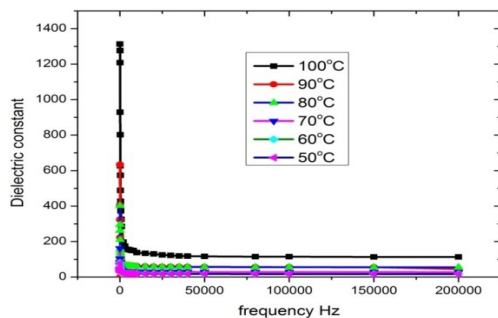


Figure 7. Temperature dependent Dielectric constant of MoO₃ Thin film

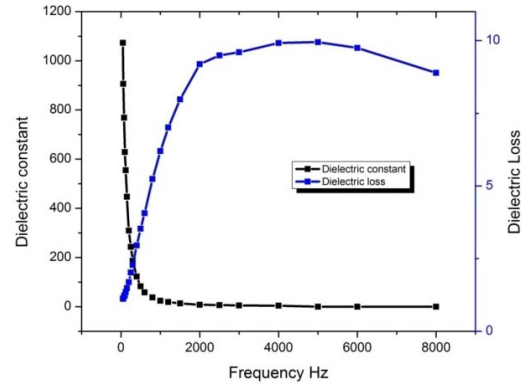


Figure 8. Dielectric constant Vs Dielectric Loss

Figure 9A & 9B shows that the variation of the capacitance and dielectric constant of the MoO₃ thin film with respect to temperature, it fits very well with Curie–Weiss 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.

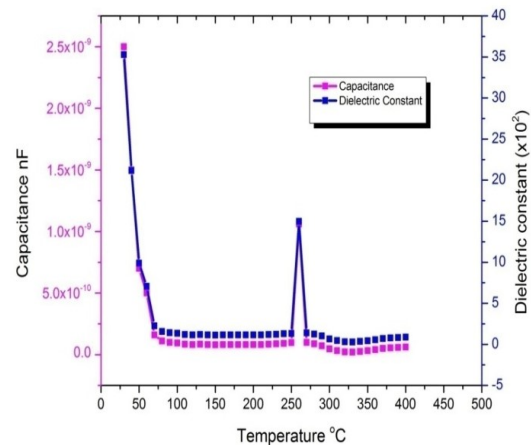


Figure 9A. Curie temperature

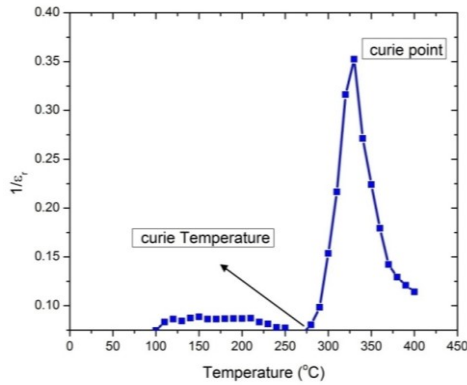


Figure 9B. Curie temperature

The measurement of capacitance with respect to dc electric field was carried out at room temperature for 1 KHz and 100 KHz (Figure 10). The tunability and figure of merit were determined from the following relations [16]:

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

$$Figure\ of\ merit = \frac{\% Tunability}{\% dielectric\ loss} \quad \dots (8)$$

where, C_{max} is the capacitance value for zero bias fields. 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 increase with increase of applied potential (Figure 11). The tunability of the dielectric properties of the material might be attributed to internal stress among the grains [17].

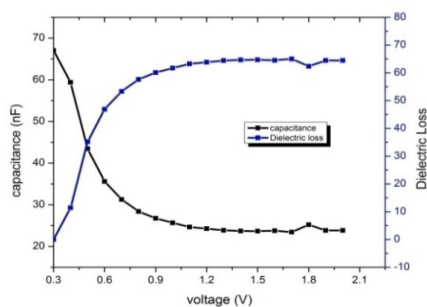


Figure 10. variation of capacitance and dielectric Loss with respect to Voltage

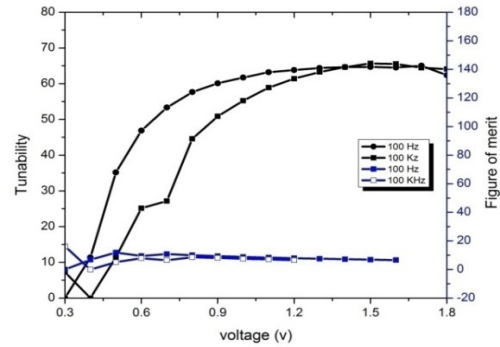


Figure 11. Variation of tunability and figure of merit with respect to Voltage

4.1. 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]

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

where $\omega = 2\pi f$.

The above equation can be expressed as

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

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} (Figure 12 Nyquist plot) is a semi circle of radius $R_{gb}/2$. The R_{gb} and R_b values derived from the intercept at low and high frequency impedance values respectively. The capacitance C_{gb} can be obtained from the maximum value of the reactance. A semicircle at high frequency indicates that the relaxation time of the bulk and the grain boundaries are closer to

each other [19]. In the mid frequency region linear progress of the diffusion characteristic of MoO_3 is observed. At low frequency region, the capacitive behavior is observed which reveals the characteristic response of blocked diffusion. 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 semicircular to real axis z' at low frequency indicates the sum of resistance of grain R_g and grain boundaries R_{gb} . The intercept at the high frequency depicts the resistance of the grain only. The Figure 12(B) shows that the increment in the resistance of the bulk and grain boundaries have been observed, it might be due to increase of grain size by heat treatment.

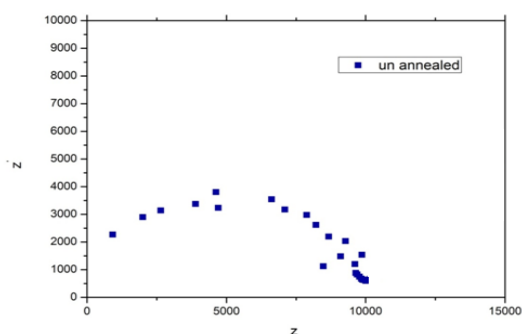


Figure 12 A. Nyquist plot of unannealed MoO_3 Thin film

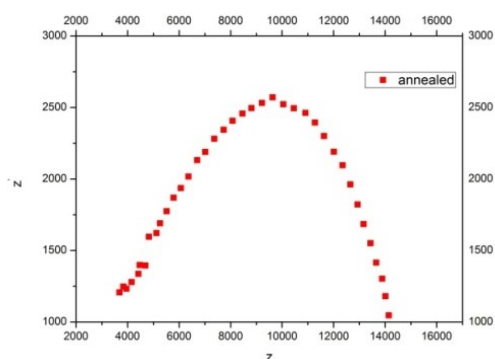


Figure 12 B. Nyquist plot of annealed MoO_3 Thin film

Conclusion

The effect of concentration and temperature on the Electrical properties of sol-gel routed spin coated Molybdenum trioxide (MoO_3) 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 MoO_3 thin film has been found at the frequency ranges of $1000\text{--}600\text{ cm}^{-1}$. The band gap of the film is found to be $3.3\text{--}3.8\text{ eV}$. SEM image shows that the film is homogeneous and the grain boundaries are evenly distributed though out 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 MoO_3 film with respect to temperature and frequency has been analyzed. Tunability and figure of merit of the film are also determined. The obtained data can be utilized for fabrication of dielectric devices.

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