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ORIGINAL PAPER

Structural and electrochemical properties of spray deposited molybdenum trioxide (α-MoO3) thin films

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Abstract Nanostructured molybdenum trioxide (α-MoO_3) thin films were deposited to investigate effect of substrate temperature on microstructural, morphological, optical, electrical, and electrochemical properties of the α-MoO_3 thin films. X-ray diffraction results indicated deposited α-MoO_3 thin films are polycrystalline, crystallizes in orthorhombic structure, and crystalline quality improved with substrate temperature. Films show the optical band gap varied between 2.56 and 2.85 eV, the activation energy of the α-MoO_3 thin films were found to be in the range of 0.15–0.30 eV. The measured electrochemical properties of α-MoO_3 thin film electrode deposited at 673 K exhibits significantly improved supercapacitive performance in Na_2SO_4 (0.5 M) electrolyte about 73.61 F/g at current density 0.6 mA/cm^2 than the other deposition temperatures. The maximum energy density (11.13 Wh/kg) at the power density 10.54 kW/kg was observed.

Keywords Orthorhombic phase · Nanorods · Optical properties · Electrochemical

Introduction

Recently, use of nanomaterial supercapacitor electrodes has been attracting great interest due to their high power and energy densities than the respective bulk materials [1]. According to the energy storage mechanism, supercapacitors are classified into two categories, namely, electrical double-layer capacitors (EDLC) with carbon materials as electrodes and pseudocapacitors with metal oxide or conducting polymers. Previous research has shown several important factors affecting the performance of EDLC: specific area, electrical conductivity, pore size, and distribution [2]. However, the low-energy density, especially the low volumetric energy density of EDLC materials is yet to be improved. The pseudocapacitors store energy through a Faradic process that involves fast and reversible redox reactions occurring at or near the electrode surface [3–5]. The most widely explored pseudocapacitive electrode materials include transition metal oxides or hydroxides (MnO_2, V_2O_5, RuO_2, Co_3O_4, NiO, MoO_3, etc.) [6–11]; among these electrode materials for pseudocapacitors, MoO_3 has been extensively investigated due to its natural abundance, large theoretical capability, and low toxicity [12]. Moreover, MoO_3 have attracted much attention as pseudocapacitive electrode material due to its crystallographic structure, multiple oxidation states, n-type conductivity, etc. [13–15].

Different techniques like hydrothermal method [16], sputtering [17], atomic layer deposition [18], sol-gel [19], chemical vapor deposition [20, 21], molecular beam epitaxy [22], and spray pyrolysis [23–26] have been used to prepare the α-MoO_3 thin films. Among them, spray pyrolysis coating is a simple and low-cost method for the preparation of thin films with large areas. This method is convenient for preparing pinhole free, homogenous and smoother films with the required substrate temperature. It is very attractive because it has been largely used to produce oxides [27] and sulfides [28] of II–VI group semiconductors.

In this investigation, α-MoO_3 thin films with nanostructured rod are deposited on FTO substrates by spray pyrolysis method. The effect of substrate temperature on structural, morphological, and supercapacitive properties of α-MoO_3 thin films has been calculated. Further electrochemical characteristics like cyclic

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voltammetry, galvanostatic charge/discharge measurement, specific capacitance, energy density, and power density were studied and reported.

Experimental details

Deposition of α-MoO_3 thin films

Molybdenum trioxide (α-MoO_3) thin films were deposited onto glass substrates via well-known spray pyrolysis technique. The spraying solution consisted of 0.1 M molybdenum trioxide powder (AR grade, SD fine, 99.5% pure) dissolved in ammonia solution separately to form ammonium molybdate at room temperature. The undergoing chemical reaction is given in the following equation:

$$MoO_3 + 2NH_3 + H_2O \rightarrow (NH_4)_2MoO_4 \quad (1)$$

The solution was sprayed onto the glass substrates at various substrate temperatures within 573–723 K. The pyrolytic decomposition of $(NH_4)_2MoO_4$ on the surface of the substrates results in the formation of α-MoO_3 thin films according to the following equation:

$$(NH_4)_2MoO_4 \rightarrow MoO_3 + 2NH_3\uparrow + H_2O\uparrow \quad (2)$$

The temperature of the substrate controlled within ±1 K through temperature controller. During the deposition, other parameters, especially spray rate (5 cm^3/min), nozzle to substrate distance (NSD) (32 cm), etc., were kept at their fixed values [28]. The sprayed droplets undergo evaporation and solute condensation, and thermal decomposition resulted in well adherent molybdenum trioxide thin films.

Characterization

For thickness measurement, gravimetric weight difference method is used with the relation of $t = m/(\rho \times A)$, where m is the mass of the film deposited on the substrate in grams, A is the area of the deposited film in square centimeters, and ρ is the density of the deposited material (MoO_3 = 4.69 g/cm^3) in bulk form. The structural properties of α-MoO_3 thin films were carried out by x-ray diffractometer (XRD Bruker AXS D8 Advance Model) with the radiation source Cu-Kα (λ = 1.5406 Å) at 2θ in the range 20 to 80°. Surface morphology of the deposited α-MoO_3 thin films was studied with field emission scanning electron microscope (FE-SEM SU8000 Hitachi). The optical parameters were studied at room temperature in the wavelength range 400–900 nm through UV-Visible spectroscopy (PerkinElmer Lambda 1050 UV-Vis-NIR Spectrophotometer). Surface electrical study was carried out by standard two-probe resistivity method. The electrochemical measurements of the α-MoO_3 thin film electrodes were reported using cyclic voltammetry (CV) and galvanostatic analysis. A potentiostat (CHI 6005E, made in USA) and a (CHI 6002E, made in USA) were used with three-electrode electrochemical cell containing Na_2SO_4 (0.5 M) as the electrolyte, α-MoO_3 as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode.

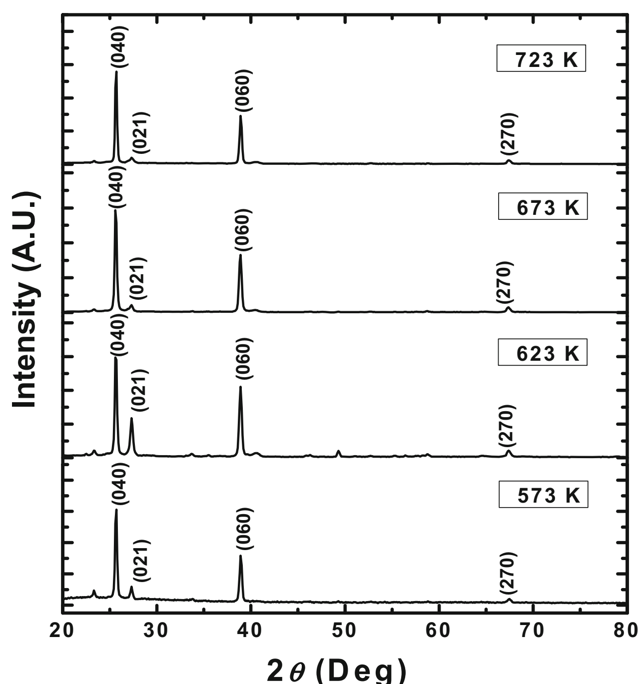


Fig. 1 X-ray diffraction patterns of α-MoO_3 thin films deposited for different substrate temperatures

Results and discussion

X-ray diffraction studies

Figure 1 shows the typical XRD pattern of α-MoO_3 thin films deposited at various substrate temperatures (573–723 K). The observed diffraction peaks at 2θ° are around 25.7, 27.3, 38.9,

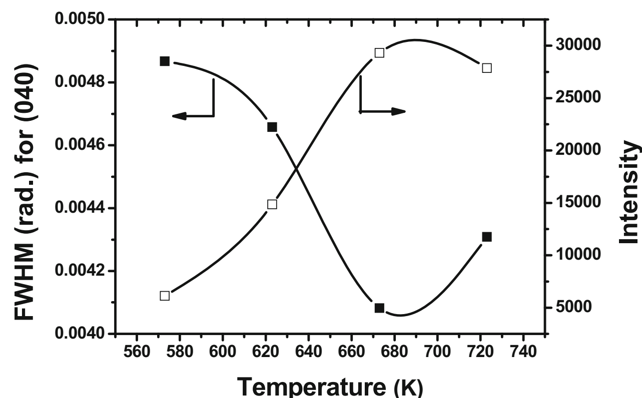


Fig. 2 Plot of FWHM and relative peak intensity of (0 4 0) diffraction peak for α-MoO_3 thin films at different substrate temperatures

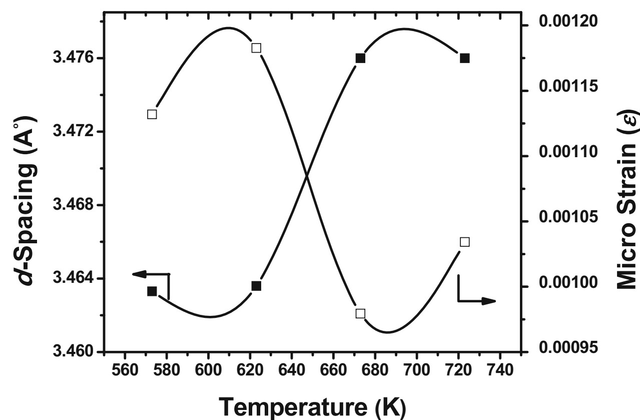


Fig. 3 The variation of microstrain and interplanar spacing of α-MoO_3 thin film for different substrate temperatures

and 67.4 with the corresponding Miller (*h k l*) planes (0 4 0), (0 2 1), (0 6 0), and (2 7 0), respectively. All these observed peaks correspond to stable orthorhombic α-MoO_3 phase according to the standard JCPDS data card: 01-0706 [29], Liqiang Mai, et al. reported the similar results [30]. Figure 1 depicts integrated intensities of the diffraction peaks suggests that α-MoO_3 thin films grow in the preferential orientation (0 *k* 0) direction where, $k = 4, 6$. The (0 4 0) peaks are dominating preferential growth with *b*-axis perpendicular to the surface of all thin films. However, other phases and structural rearrangements are not observed in the α-MoO_3 thin films prepared at temperature range of 573–723 K. The lattice parameters *a*, *b*, and *c* for orthorhombic phase was determined by using the following equation:

$$d_{(\mathrm{hkl})} = \frac{1}{\sqrt{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}} \tag{3}$$

For orthorhombic lattice, $a \neq b \neq c$, in the above relation, *h*, *k*, and *l* are Miller indices of reflector planes appearing on the diffraction spectrum and $d_{(\mathrm{hkl})}$ is their interplanar distance. The obtained average lattice constants were found to be $a = 3.95$ Å, $b = 13.84$ Å, and $c = 3.69$ Å. These values are consistent with standard JCPDS data card [29]. The interplanar distances were calculated by the following equation:

$$2d\sin\theta = n\lambda \tag{4}$$

where *d* is the interplanar distance, θ is the Bragg's angle, *n* is the order of diffraction (usually $n = 1$), and λ is the wavelength of the x-ray used (here, $\lambda = 1.5406$ Å). The average crystallite size (*D*) of the prepared films was calculated by the Scherrer relation [31]:

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{5}$$

where *k* is the shape factor with value $k = 0.94$, λ is the wavelength of the x-ray used ($\lambda = 1.5406$ Å), β is the full width at half maxima (FWHM) of corresponding peak, and θ is the Bragg's angle. The average crystallite size of the α-MoO_3 film initially increase with substrate

Table 1 The microstructural properties of α-MoO_3 thin films deposited for different substrate temperature

Temp. [°C]	*h*	*k*	*l*	$2\theta_{(\mathrm{obs.})}$	$d_{(\mathrm{obs.})}$ (Å)	FWHM	Intensity	Crystallite size (nm)	Dislocation density	Microstrain (ε) × 10^{-3}
300	0	4	0	25.607	3.4633	0.004867	6125	29.21496	1.17E + 15	1.131830388
	0	4	0	27.305	3.2636	0.005024	1188	28.40075	1.24E + 15	0.66692865
	0	6	0	38.899	2.3132	0.005251	3175	28.00478	1.28E + 15	1.101452514
	2	7	0	67.399	1.3878	0.007955	406	20.95141	2.28E + 15	1.65455839
350	0	4	0	25.607	3.4636	0.004658	14,857	30.52804	1.07E + 15	1.182700863
	0	4	0	27.305	3.2639	0.005726	5877	24.93728	1.61E + 15	0.585187588
	0	6	0	38.903	2.313	0.005338	10,519	27.54681	1.32E + 15	1.081968871
	2	7	0	67.401	1.3865	0.008077	1077	20.63459	2.35E + 15	1.67988425
400	0	4	0	25.7	3.476	0.004082	29,313	34.83979	8.24E + 14	0.979440986
	0	4	0	27.3	3.2635	0.007187	2134	19.85295	2.54E + 15	0.837143226
	0	6	0	38.906	2.3134	0.00478	16,524	30.76438	1.06E + 15	0.984915041
	2	7	0	67.503	1.3883	0.006873	1490	24.25199	1.70E + 15	1.42864767
450	0	4	0	25.702	3.476	0.004309	27,870	33.00605	9.18E + 14	1.034154469
	0	4	0	27.305	3.2636	0.003716	1983	38.40067	6.78E + 14	0.434847686
	0	6	0	38.903	2.3132	0.005007	14,566	29.37113	1.16E + 15	1.030580858
	2	7	0	67.427	1.3883	0.007885	1205	21.14939	2.24E + 15	1.63973181

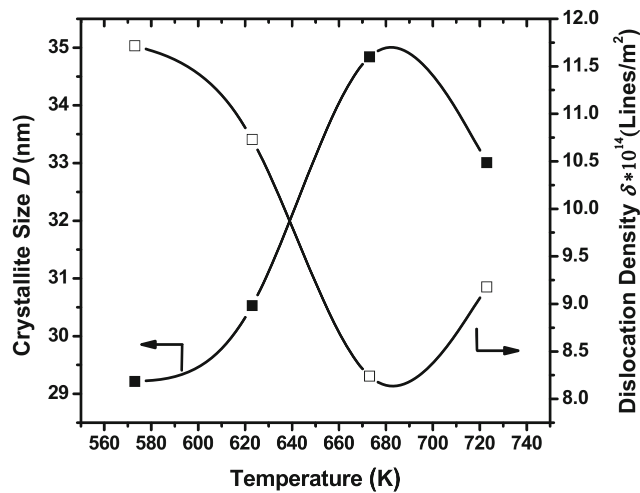


Fig. 4 Crystallite size and dislocation density of α-MoO_3 thin film for different substrate temperatures

temperature reaches maximum 34.83 nm at 673 K further decreased with high substrate temperature. Increases in crystallinity and crystallite size with substrate temperature are due to the optimum rate of supply of thermal energy for the recrystallization [32]. The graphical representation of intensity and the FWHM of the peak (0 4 0) with respect to substrate temperature is given in Fig. 2. The sum of individual intensities scattered by each grain is the total intensity of all grains [26]. The FWHM values are seen to decrease with substrate temperature up to 673 K and further found to increase at high temperature. However, the stresses are one of the most important unfavorable factors affecting the structural properties and geometric mismatch at boundaries between crystalline lattices of films and substrates [33]. The microstrains are

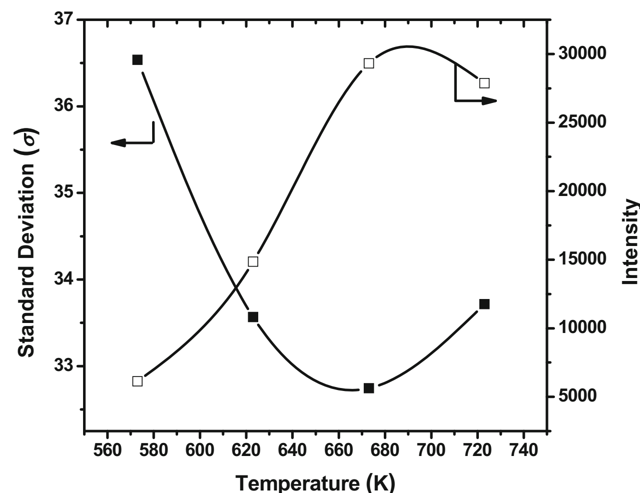


Fig. 5 The variation of standard deviation and intensity of α-MoO_3 thin film for different substrate temperatures

developed in the films due to these stresses. The microstrains are calculated by the following relation [34]:

$$\varepsilon = \frac{\beta\cos\theta}{4} \tag{6}$$

The existence of internal microstrain can easily induce the formation of defect centers [35]. The dislocation density (δ) values can be obtained by following relations [36]:

$$\delta = \frac{1}{D^2} \tag{7}$$

The variation in microstructural parameters like microstrain and interplanar spacing with substrate temperature is shown in Fig. 3. The interplanar spacing of α-MoO_3 thin films are increases with substrate temperature consequently microstrain relaxation in α-MoO_3 thin films decreases. The microstrain relaxation is steady with the contraction or expansion of the interplanar spacing of (0 4 0) plane. Table 1 gives the values of microstructural properties of the α-MoO_3 films. The graphical nature of crystallite size (D) and dislocation density (δ) with different substrate temperature of α-MoO_3 thin films is shown in Fig. 4. The dislocation density of the films decreased up to 673 K further increased with substrate temperature. In order to explain growth mechanism involved in sprayed α-MoO_3 films, the standard deviation (σ) in intensities of various planes was calculated by using the following equation (Fig. 5) [37]:

$$\sigma = \sqrt{\frac{\sum_N (\mathrm{I})^2 - \frac{\left(\sum_N \mathrm{I}\right)^2}{N}}{N}} \tag{8}$$

where I stand for the relative intensity of the ($h\,k\,l$) plane and N is the reflection number. The standard deviation (σ) value was found between 36.53 and 32.74, the decrease in standard deviation at high temperature is due to improved crystallinity and reorientational effects. The reflection intensities from each XRD pattern contain information related to the preferential or random growth of polycrystalline thin films which is studied by calculating the texture coefficient $TC_{(hkl)}$ for all planes using the following equation [38]:

$$TC_{(hkl)} = \frac{\frac{I_{hkl}}{I_{0hkl}}}{\frac{1}{N}\sum_N \frac{I_{hkl}}{I_{0hkl}}} \tag{9}$$

where I_{hkl} is the relative intensity of the observed peak, $I_{0_{hkl}}$ is the corresponding standard relative intensity from the JCPDS

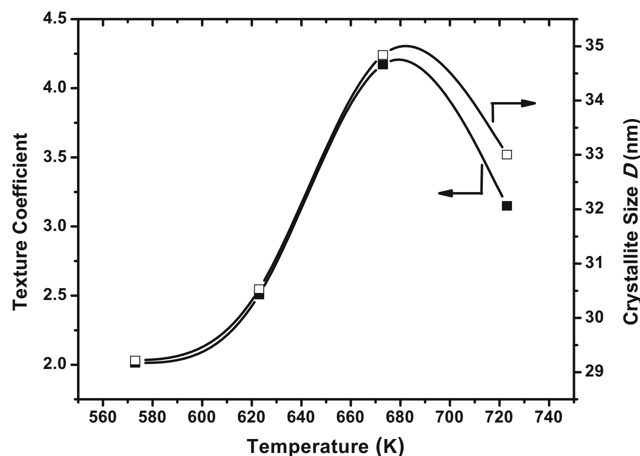


Fig. 6 Texture coefficient and crystallite size of α-MoO_3 thin film for different substrate temperatures

data and N is the number of reflections observed in the pattern. From Eq. (9), it is observed that the value of TC is greater than unity when the ($h\ k\ l$) plane is preferentially oriented. Figure 6 shows the variation of the TC for (0 4 0) plane with respect to substrate temperature for α-MoO_3 thin films. Figure 6 shows that the lower value of texture coefficient represents that the films have poor crystallinity and the crystallinity improved with substrate temperature. Further, with increase in substrate temperature above 673 K, the value of texture coefficient slightly decreases.

Field-emission scanning electron microscopy

The surface morphology was determined using field-emission scanning electron microscopy (FE-SEM) and compared with XRD data. Figure 7 shows surface morphology of α-MoO_3 thin films prepared at different substrate temperatures. At low substrate temperature (573 K), α-MoO_3 thin film shows surface morphology with dense surface and reticulated oblate-structured grains. However, at high substrate temperature, grain boundaries increased and few small nanorods were observed. At 673 K substrate temperature, typical one-

Fig. 7 Surface FE-SEM images of α-MoO_3 thin film for different substrate temperature

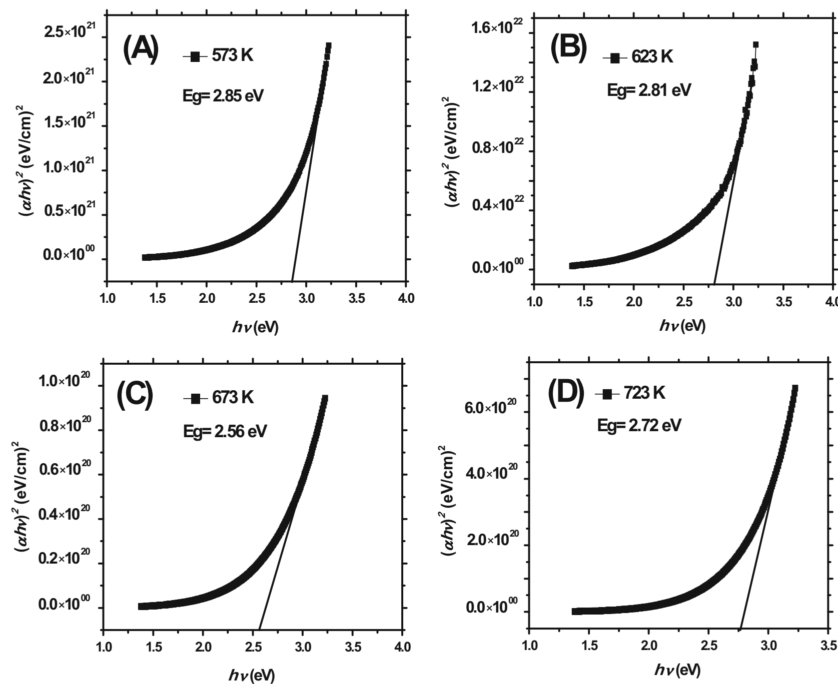


Fig. 8 **a** Plot of $(\alpha h\nu)^2$ vs. the photon energy $(h\nu)$ of α-MoO_3 thin films for different substrate temperature. **b** The variation of optical band gap of α-MoO_3 thin film for different substrate temperatures

dimensional nanorod-like morphology formed and such rods grow larger due to enhanced surface diffusion of species.

Optical properties

The optical band gap energy E_g can be determined from the experimental values of absorption coefficient as a function of photon energy $h\nu$, using the following equation: [39]:

$$(\alpha h\nu)^n = A\left(h\nu - E_g\right) \quad (10)$$

where A is the probability parameter for the transition, α is the optical absorption coefficient, E_g is the band gap energy, $h\nu$ is

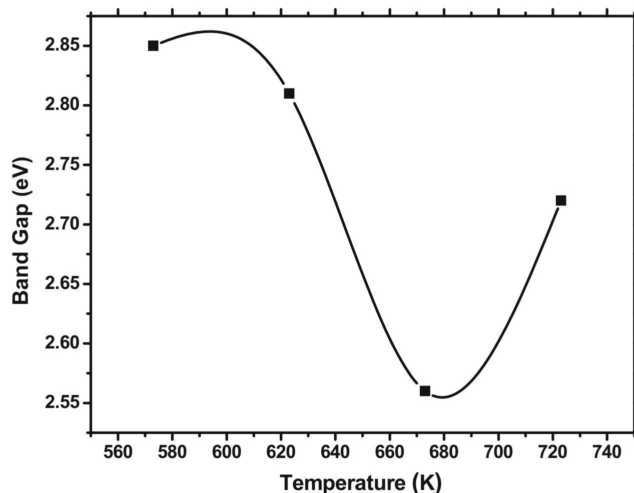


Fig. 8 continued.

the photon energy, and exponent n determines the type of electronic transitions causing the absorption and take the values (1/2 for indirect transitions and 2 for the direct transitions). The plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ is shown in Fig. 8a which is linear at absorption edge, indicating a direct allowed transition. The band gap energy is found to be in the range 2.56 to 2.85 eV depending upon substrate temperature and the variation is depicted in Fig. 8b [40]. The change in band gap energy is due to the effect of internal compressive stress and various chemical compositions [35]. At higher temperature, internal compressive stress releases the crystal, and expansion of lattice will reduce the band gap of α-MoO_3 films [41, 42]. The internal compressive stress relaxation has been confirmed by the XRD. With increasing substrate temperature, the grain size increases and the grain boundary density decreases; the scattering of electron at grain boundaries decreases resulted in electronic transition from valance band to conduction band becoming easy.

Electrical properties

The measurement of surface electrical resistance of the α-MoO_3 thin films was using standard two-probe method in the temperature range 573–723 K. A plot of inverse absolute temperature (1000/T) vs. log (ρ) for a cooling cycle is shown in Fig. 9a. Decrease in electrical resistance behavior with increasing substrate temperature may be due to the increase in the crystallite size. This is attributed to the crystallite boundary discontinuities, presence of surface states, and the change in

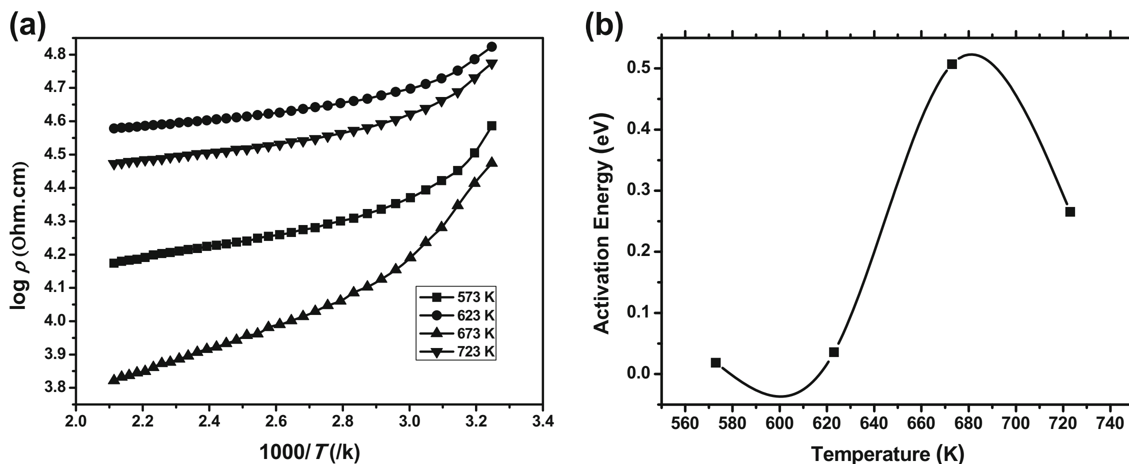


Fig. 9 **a** Plot of surface electrical resistance versus temperature of α-MoO_3 thin films at different substrate temperatures. **b** Plot of activation energy of the α-MoO_3 thin films at different substrate temperatures

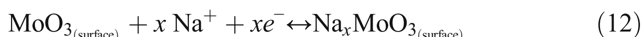
structural parameter of the thin films. Activation energy of the α-MoO_3 thin films is calculated by the following equation:

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{K_B T}\right) \tag{11}$$

where $\rho(T)$ is the resistivity at absolute temperature T, E_a is the thermal activation energy, and K_B is the Boltzmann constant. The E_a is found to be in the range between 0.15 and 0.50 eV, indicating that the prepared samples are semiconductors. This change in energy attributed to change in dislocation and the stoichiometry of the films. The graphical representation of the activation energy is shown in Fig. 9.

Electrochemical properties

To study electrochemical properties of prepared α-MoO_3 thin film electrodes, the cyclic voltammetry (CV) is carried in Na_2SO_4 electrolyte. The representation of electrochemical Na^+ insertion process is given by the following equation:



$$MoO_{3(\mathrm{surface})} + x\,Na^+ + xe^- \leftrightarrow Na_xMoO_{3(\mathrm{surface})} \tag{12}$$

where $x = QM/mF$ is the mole fraction of Na^+ insertion. Here, Q is the stored charge, M is the molar weight, m is the mass, and F is the Faraday constant. During intercalation/de-intercalation process, two mechanisms occur: the first mechanism is based on simple surface adsorption of alkali metal cations such as Na^+ in the electrolyte on the surface of electrode material, and the second mechanism involves the intercalation of alkali metal cations (Na^+) into the electrode material during reduction and de-intercalation upon oxidation [43].

Figure 10a shows the cyclic voltammograms (CVs) of α-MoO_3 thin film deposited at substrate temperature 673 K in a potential range of −0.5 to +0.2 V vs. Ag/AgCl at different scan rates. The area under the curve increased continuously with a scan rate from 5 to 100 mV/s. At low scan rate 5 mV/s, the oxidation and reduction peaks are observed approximately at −0.32 and −0.21 V vs. Ag/AgCl, respectively. This is different from the reported ordered mesoporous α-MoO_3 [44]; this may be due to the different morphology and structure. As usual, the intensities of the redox peaks increased with the scan rate. The redox peaks are shifted slightly due to the increase in over potentials. The oxidation and reduction peaks are observed at −0.35 and −0.17 V vs. Ag/AgCl reference electrode, respectively, at a scan rate of 100 mV/s. The redox peaks are still evident even at high scan rate of 100 mV/s, represents that α-MoO_3 thin film electrodes will be stable as an anode material for supercapacitors and present good rate capability [45]. The specific capacitance (C_s) was calculated using following relations [46]:

$$C = \frac{I}{\mathrm{dv/dt}}, \quad C_i = \frac{C}{A} \quad \text{and} \quad C_s = \frac{C_i}{m} \tag{13}$$

where C is the differential capacitance, I is the average current in ampere, dV/dt is the voltage scanning rate, C_i is the interfacial capacitance, A is the area of active material dipped in the electrolyte, and m is the weight of α-MoO_3 film dipped in electrolyte. The specific capacitance value found to be 118.79 F/g at the scan rate of 100 mV/s for the α-MoO_3 thin film electrode deposited at substrate temperature 673 K.

The galvanostatic charge/discharge curves at different current densities (0.6 to 0.9 mA/cm^2) of the electrode prepared at 673 K are shown in Fig. 10b. The figure shows that charge/discharge time decreases with the increase in applied current density. The galvanostatic charge/discharge (GCD) curves are almost linear and symmetrical without IR drop, indicating a rapid I–V response and good capacitance performance [47]. The inset of Fig. 10c shows galvanostatic charge/discharge curves of the last few cycles at 0.6 mA/cm^2 current density

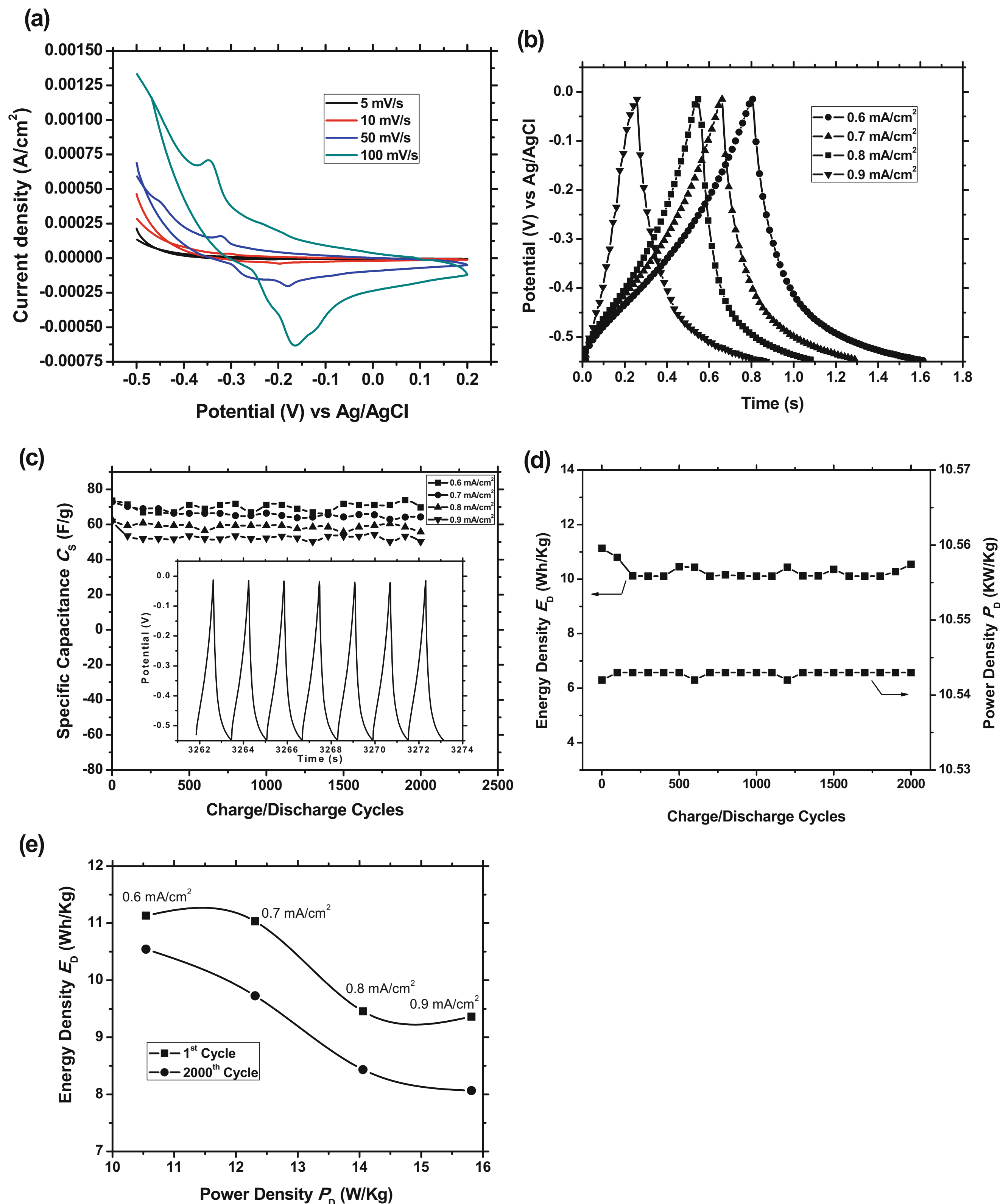


Fig. 10 **a** Cyclic Voltammograms at different scan rates of α-MoO_3 thin film prepared at 673 K substrate temperature. **b** Galvanostatic charge/discharge curves recorded at different current densities for the electrode prepared at 673 K substrate temperature. **c** Plot of specific capacitance of the α-MoO_3 thin film electrode for different applied current densities vs. cycle number and inset figure is last few cycles of fast charge/discharge at 0.6 mA/cm^2 current density. **d** Plot of energy density and power density vs. cycle number at current density 0.6 mA/cm^2 of α-MoO_3 thin film electrodes prepared at 673 K temperature at different current density. **e** Ragone plot for the 1st and 2000th cycles of GCD at different current densities of α-MoO_3 electrode prepared at 673 K substrate temperature

within potential window 0.55 V for α-MoO_3 thin film electrodes prepared at 673 K substrate temperature. Figure 10c depicts that α-MoO_3 electrodes show a nonlinear charge/discharge curve, indicating that they have a mainly pseudocapacitive behavior and same graphical nature was reported by few authors [48, 49]. The values of total specific capacitance (C_s) are calculated from Eq. (13) [50–53]:

$$C_s = \frac{I \times t_d}{m \times \Delta V} \tag{14}$$

where I (mA) is the discharge current density, ΔV (V) is the working potential window, m (g) is the actual mass deposited on the active area of the material, and t_d (s) is the discharging time. The specific capacitance values are calculated to be 73.61, 72.93, 62.51, and 61.9 F/g corresponding to the discharging current densities 0.6, 0.7, 0.8, and 0.9 mA/cm^2, respectively. It is due to the inner active sites of the electrode which can be fully accessed and diffused with alkali cations at the low current density and also attributed to the slow rate of redox reactions [54]. The variation in the specific capacitance with the cycle number for different current densities is shown in Fig. 10c. The maximum specific capacitance observed for α-MoO_3 thin film electrode for the 1st cycle is 73.61 F/g and for the 2000th cycle is 69.70 F/g at a 0.6 mA/cm^2 current density. Hence, there is about 95% stability of the α-MoO_3 thin film electrode deposited at substrate temperature 673 K.

The specific energy density (E_D) and specific power density (P_D) of the supercapacitor cell were calculated according to the following equation [52]:

$$E_D = \frac{Q \times \Delta V}{2m} \tag{15}$$

$$P_D = \frac{E}{t_d} \tag{16}$$

where $Q = (I \times t)$ is charge delivered during discharge, ΔV is the cell voltage (potential window) and t_d is the discharging time. The variation of power density and energy density with cycle number is shown in Fig. 10d. Figure 10 depicts very slight variation in energy density and power density after 2000th cycles, it resulted that deposited material have good stability. Figure 10e shows the Ragone plot of α-MoO_3 electrode deposited at substrate temperature 673 K and shows the highest energy density 11.13 Wh/kg with power density 10.54 kW/kg at applied current density of 0.6 mA/cm^2.

Conclusions

Nanostructured α-MoO_3 electrodes were deposited with different substrate temperatures on the conducting glass substrates by spray pyrolysis technique. The effect of substrate temperature on the microstructural, morphological, optical, electrical, and electrochemical properties of α-MoO_3 thin films was investigated. The XRD results revealed that microstructural properties changed with substrate temperature. The optical band gap energy varied in the range 2.56–2.85 eV is observed and it depends on the substrate temperature. The decreasing trend of electrical resistance attributed to the semiconducting nature of the α-MoO_3 electrode. The spray deposited α-MoO_3 thin film electrodes at 673 K have successfully showed as supercapacitor property with higher specific capacitance of 73.61 F/g, energy density (11.13 Wh/kg) at the power density 10.54 kW/kg. It is concluded that the electrochemical properties of α-MoO_3 electrode are temperature-dependent and it can be used for application in electrochemical supercapacitors.

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