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Temperature dependence of the electrical conductivity of dry lithiated Tungsten trioxide thin films

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ABSTRACT

A great deal of basic and applied research has been dedicated in the past couple of decades to the transition metal oxide (TMO) thin films such as those of tungsten trioxide (WO_3). This is due to the interesting reversible optical and electrical switching that occurs in these materials under various external influences. These switching properties are interesting both from the physics point of view as well as for their application. In particular, the tungsten trioxide (WO_3) thin films exhibiting electrochromic properties have been studied extensively. While their optical switching properties are very well studied, not much study is focussed on their electrical properties, especially as a function of temperature. In this work we have studied the temperature coefficient of resistance (TCR) behavior of lithium atom intercalated WO_3 thin films. Using the variable range hopping model we have calculated the density of states at the Fermi level of samples prepared by thermal evaporation and lithiated by a dry process. The TCR measurements were performed in the temperature range between 298 and 353 K. The understanding of this temperature dependent electrical behavior is expected to enhance our knowledge of the electrochromic process in these films and lead to better design WO_3 based electrochromic (EC) devices.

1. Introduction

Among all the transition metal oxides (TMO) exhibiting electrochromic (EC) behavior, tungsten trioxide (WO_3) is found to be the most promising material. WO_3 thin films have been studied extensively because of their application in EC devices with application potential in smart windows for efficient energy management, display devices, gas-sensors and more [1–8]. WO_3 is a semiconductor in the temperature range between 293 and 353 K. Many investigations have been carried out on the mechanism associated with variations in optical [9], electrical [10], and structural properties during the EC process [11]. Although the exact mechanism of the EC coloration is still debated, two of the theoretical models that are most widely accepted are the intervalence charge transfer (IVCT) and the small polaron models [12]. As per these models and the experimental observations, WO_3 can incorporate metal atoms or ions such as Li or Li^+ as substitutional atoms in the lattice to form tungsten bronze, Li_xWO_3 [13]. The reversible optical and electrical switching from an initial transparent and non-conductive state to an intensely blue colored and conductive state takes place with the double insertion of electrons and lithium ions into the WO_3 film according to the reaction:

$$\underset{\text{Transparent}}{WO_3} + xLi^+ + xe^- \leftrightarrow \underset{\text{Blue}}{Li_xWO_3}\,. \tag{1}$$

The inserted electrons are localized on the tungsten sites instead of oxygen vacancies. This phenomenon has been attributed to the optical transfer of the electrons from their self-induced potential wells to one of the neighboring undistorted states (from W^{5+} to W^{6+}), so that these structural defects are responsible for the color center [12]. It has been demonstrated that the insertion of lithium atoms by a dry process leads to the same EC reaction as shown in Eq. (1) above [14].

WO_3 thin films can be prepared by various deposition techniques, such as thermal evaporation [15], RF-sputtering [16], chemical vapor deposition [17] and others [18–20]. The most frequently used preparation technique for WO_3 films is the thermal evaporation. In their early efforts, Miyake et al. [21] used the thermal evaporation technique to deposit WO_3 thin films. They found that all films deposited at substrate temperature below 625 K were amorphous in structure with a resistivity in the range of 10^9–10^5 Ω cm, while films deposited at the substrate temperature higher than 673 K were mainly crystalline in nature with resistivity of 10^2–10^{-3} Ω cm. The authors reported that the resistivity is almost constant and equal to 1.5×10^9 Ω cm for the substrate temperature between 323 and 473 K, and which decreased from 10^9 to 10^{-3} Ω cm with increasing substrate temperature from 473 K to 773 K.

Despite the profuse amount of basic and applied research work carried out in the last couple of decades on the EC properties of WO_3 thin films, only a handful of work is devoted to the study of the electrical properties of these films in the colored state, especially on the dependence of the resistivity on temperature. This aspect could be very

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important for the understanding of the transport kinetics of electrons, ions and/or atoms involved in the EC mechanism in device operation at higher than room temperature. M.G. Hutchins et al. have studied the electrical conduction mechanism in the as-deposited amorphous and polycrystalline WO_3 thin films prepared by thermal evaporation in the temperature range between 298 K and 625 K [22]. They have discussed the TCR behavior in these thin films in light of the variable range hopping (VRH), polaron and Arrhenius models. Lars Berggren et al. [23] and G.A. Niklasson et al. [24] have measured the TCR behavior in the temperature range between 77 and 300 K in their sputter deposited amorphous WO_3 thin films inserted with lithium. The experimental results concerning TCR in their electrochemically formed Li_xWO_y are examined in light of the VRH model. In this work we have examined the TCR behavior of thermally evaporated amorphous thin films of WO_3 in their colored state i.e. WO_3 films inserted with lithium atoms, in the temperature range between 298 K and 353 K. The lithium atom insertion has been carried out using a dry process which greatly facilitates such conductivity related work without the need to bring the WO_3 films in contact with any liquid. To the best of our knowledge such a work on the TCR behavior of dry lithiated WO_3 (Li_xWO_3) has not been carried out. The study of the kinetics associated with the transport of the inserted species as a function of temperature has been carried out using the VRH model and to calculate the density of states at the Fermi level in these dry lithiated films.

2. Experimental details

Thin films of WO_3 were deposited by the thermal evaporation technique using Tungsten filaments. High purity (99.9%) WO_3 powder obtained from Alfa Aesar was used for this work. Thin films were deposited onto pre-cleaned glass substrates at room temperature in a vacuum chamber pumped down to a pressure of 1.3×10^{-3} Pa. The film thickness as measured by quartz crystal monitor was maintained around 200 nm for all samples. The deposition rate was fixed at 7.2 nm/min for all the films. Subsequent to this, all the WO_3 films were lithiated in the same vacuum chamber with different amounts of lithium by a dry process [25]. Dry lithiation is a clean method for lithium atom insertion developed in our lab to do many measurements for one sample unlike the electrochemical method where a sample has to be prepared for each measurement. In addition, in the dry process unlike in the electrochemical process, there is no need to bring the sample in contact with any liquid which would further necessitate the cleaning of the sample before any characterization. Lithium niobate ($LiNbO_3$) powder was heated under a pressure of 1.3×10^{-3} Pa to a critical temperature to give off lithium atoms for insertion into the exposed WO_3 film. The quantity of lithium inserted was measured in terms of the effective mass thickness deposited on the quartz crystal and later calibrated against the electrochemical insertion. Following this two gold electrodes spaced 2 mm apart were deposited onto the surface of the samples. The electrical resistivity of the lithiated WO_3 samples was measured under a vacuum of 6.6×10^{-3} Pa by the two-probe method in the temperature range between 298 and 473 K using an electric resistance heater. A *610CR Solid State Keithley Instruments* electrometer was used for the resistance measurements. The temperature was measured using a K-type thermocouple.

3. Results and discussion

Variable range hopping (VRH) model is a physical theory that describes the electrical conductivity of amorphous semiconductors [26–28]. This theory is based on the assumption that the charges are localized on one site in the lattice but can jump or "hop" to another localized state under some form of activation. In other words, the electrical transport of phonon-assisted hopping of charge carriers from occupied to unoccupied localized states takes place. The nearest-neighbor hopping conductivity is given by Mott [29]:

$$\sigma = \sigma_0 exp\left(-\frac{T_0}{T}\right)^{\frac{1}{(n+1)}} \tag{2}$$

$$\text{where } \sigma_0 = 3q^2\gamma_{ph}\left(\frac{N(E_F)}{8\pi\alpha K_B T}\right)^{\frac{1}{2}} \tag{3}$$

$$\text{and } T_0 = \frac{\lambda\alpha^3}{K_B N(E_F)}. \tag{4}$$

Here T is the temperature in Kelvin, n is the dimension of the conduction path ($n = 3$ for three dimensions), q is the electronic charge, $\gamma_{ph} = 8.67 \times 10^{12}\ s^{-1}$ is the phonon frequency at the Debye temperature associated with the hopping process, $N(E_F)$ is the density of states at Fermi level, K_B is Boltzmann's constant, $\lambda = \frac{2^9}{9\pi} \approx 18.1083$ is a factor in the correlated hopping case, and $\xi = \frac{1}{\alpha} = a_B = \frac{4\pi\varepsilon_r\hbar^2}{m_e^* e^2} = 12.11 \times 10^{-8}\ cm$ is the coefficient of the exponential decay of the wave function.

Fig. 1 shows the measured resistance of lithiated samples normalized (R/R_{473}) as a function of temperature during heating. The temperature range was between 298 and 473 K. A systematic decrease in resistance with increase in temperature as well as with increasing content x of lithium inserted is seen. The x values varied between 0.03 and 0.5.

Using this data and the variable range hopping model in its simplest form [29],

$$R(T) = R_0 \exp\left(\frac{T_0}{T}\right)^{1/4} \tag{5}$$

the plot of normalized resistance (R/R_{473}) as a function of $T^{1/4}$ has been made as shown in Fig. 2. These figures clearly show that the electron transport in the amorphous tungsten bronze films occurs by hopping between localized states.

With the increase of the lithium content x from 0.03 to 0.5 the resistance of the WO_3 samples decreased from $43 \times 10^6\ \Omega$ to $0.02 \times 10^6\ \Omega$ at room temperature. This insertion of lithium was also followed by an increasingly deep coloration of the WO_3 sample.

In Fig. 3 is shown the normalized resistance of the lithium inserted amorphous WO_3 films at room temperature. It can be seen clearly that the resistance decrease follows the exponential relation noted in the figure.

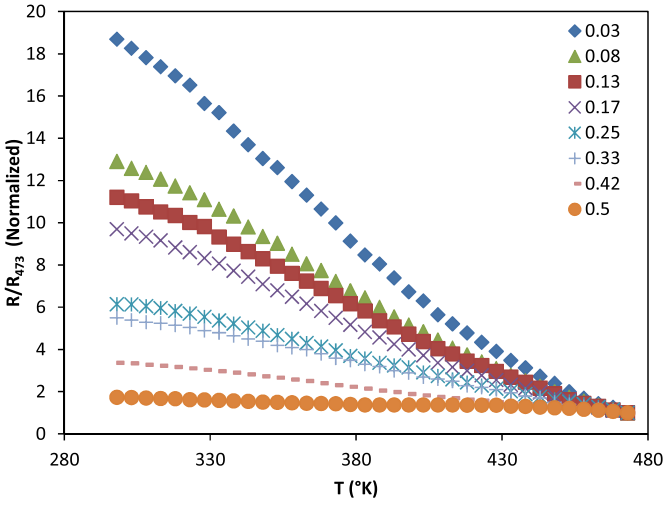

Fig. 1. The normalized resistance (R/R_{473}) as a function of temperature for amorphous WO_3 samples inserted with different Li content, x.