Electrical conductivity and dielectric relaxation in non-crystalline films of tungsten trioxide

M.G. Hutchins a, O. Abu-Alkhair b, M.M. El-Nahass c,* K. Abdel-Hady d

a School of Engineering, Oxford Brookes University, England, UK
b Physics Department, Faculty of Science, King Abdel-Aziz University, Jeddah, Saudi Arabia
c Physics Department, Faculty of Education, Ain Shams University, Roxy Square 11757, Cairo, Egypt
d Physics Department, Faculty of Science, Minia University, Minia, Egypt

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Abstract

Amorphous tungsten trioxide (a-WO₃) thin films were prepared by thermal evaporation technique. The electrical conductivity and dielectric properties of the prepared films have been investigated in the frequency range from 100 Hz to 100 kHz and in the temperature range 293–393 K. In spite of the absence of the dielectric loss peaks, application of the dielectric modulus formulism gives a simple method for evaluating the activation energy of the dielectric relaxation. The frequency dependence of \( \sigma(\omega) \) follows the Jonscher’s universal dynamic law with the relation \( \sigma(\omega) = \sigma_{dc} + A\omega^s \), where \( s \) is the frequency exponent. The conductivity in the direct regime, \( \sigma_{dc} \), is described by the small polaron model. The electrical conductivity and dielectric properties show that Hunt’s model is well adapted to a-WO₃ films.

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1. Introduction

Thin film technology is well established and widely used in the fabrication of electronic devices. The technique has been successfully used to fabricate thin film resistors, capacitors, photoelectronic devices etc. The use of this technique in fabricating electronic devices makes it necessary to understand the electrical properties of the material in thin film form.

Tungsten trioxide (WO₃) is a wide band-gap n-type semiconductor. Films of WO₃ are considerable interest because of their potential applications in electrochromic devices [1–4] and gas sensors [5,6]. These films can be amorphous or polycrystalline depending on preparation method. These films have previously been deposited by various different techniques such as sputtering [7–10], pulsed laser [11,12], thermal evaporation [13–15], wet chemical method [16–21], sol–gel [22], and spray pyrolysis [23,24]. However, the properties of the films are significantly affected by the film crystallinity.

Development of devices based on WO₃ thin films is clearly dependent upon knowledge of general electrical behaviour of these materials. In a previous work, we observed that WO₃ films deposited by thermal evaporation technique are amorphous with optical gap of 3.28 eV [15]. According to the available literature, AC conductivity and dielectric properties of the thermally evaporated WO₃ films were not studied.

AC conductivity measurement of semiconductors, as is a powerful tool for obtaining information about the defect states in amorphous semiconductors [26,27], has been extensively used to understand the conduction process [25]. Various models have been proposed to explain the
ac conduction mechanisms [25–30]. Dielectric relaxation studies are important to understand the nature and the origin of dielectric losses, which in turn, may be useful in the determination of structure and defects in solids. The dielectric behaviour of thin film devices depends not only on their material properties, but also on the substrate used for fabrication and the type of the metal electrodes. Fringing effects at the edges of thin film dielectrics is usually negligible because the thickness of the dielectric is usually very small compared to its lateral dimensions. The magnitude of geometric and measured capacitance may differ if the electric field at the metal insulator interface varies over this region.

In this work, amorphous tungsten oxide films have been prepared by thermal evaporation technique. The temperature and frequency dependence of the electrical conductivity, the dielectric constants for a-WO3 films in the frequency range 0.1–10 kHz and in the temperature range 293–393 K have been investigated and analyzed to determine some related parameters and predict the electronic conduction mechanisms.

2. Experimental techniques

Tungsten trioxide (WO3) powder used in this study was obtained from BDH chemical Ltd Company with purity of 99.986%. Thin films of different thicknesses were deposited by vacuum thermal evaporation method, using a high vacuum coating unit (Edwards, E306A). Thin films were deposited from a molybdenum evaporator charged by WO3 in a vacuum of 10−5 Pa. The deposition rate was controlled at 1 nm s−1 using a quartz crystal thickness monitor (FTM6, Edwards). The film thickness ranged between 100 and 500 nm. Accurate thickness measurements were derived after deposition using interferometric method. For AC measurements, films of thickness 500 nm were sandwiched between ITO and Au electrodes as lower and upper electrodes respectively. A programmable automatic RCL bridge (Fluke PM6306) was used to measure the impedance Z, the capacitance C, and the loss tangent (tan δ) directly. The real part of the total conductivity was calculated from the equation: \( \sigma(\omega) = t \sin \phi/ZS \), where \( t \) is the thickness of the film, \( S \) is the cross-sectional area and \( \phi \) is the phase angle between the input and output signals. The dielectric constant was calculated from the equation: \( \varepsilon_1 = tC/\varepsilon_0 S \), where \( C \) is the capacitance of the film, and \( \varepsilon_0 \) is the permittivity of free space. The dielectric loss \( \varepsilon_2 \) was calculated from the equation: \( \varepsilon_2 = \varepsilon_1 \tan \delta \), where \( (\delta = 90 − \phi) \).

3. Results and discussion

3.1. Dielectric properties of a-WO3

Dielectric dispersion implies the variation of real and imaginary parts at fixed temperatures. The dielectric constant is associated with the polarization of the material under the influence of sub-switching AC field [31]. The frequency dependence of the real \( \varepsilon'(\omega) \) and imaginary \( \varepsilon''(\omega) \) parts of the dielectric permittivity at different temperatures for a-WO3 film are shown in Fig. 1(a,b). As the temperature increases, the dielectric constants at low frequency show a dispersive behaviour and rise rapidly and a strong dispersion is also observed at frequencies below ~400 Hz.

The study of dielectric properties is an important source for information in a thin film; since we can determine the electrical and dipolar relaxation time and its activation energy [32] but, it is very difficult to observe the dielectric relaxation peak in transition metal oxide (TMO) glasses because its dielectric loss current is masked by the dominant conduction current [33]. It has been suggested by Moynihan, Boese and Laberage [34,35] that in the absence of a well-defined \( \varepsilon''(\omega) \) peak, information about the relaxation mechanism can be obtained from the dielectric modulus representation, which is defined as the reciprocal of the dielectric permittivity [36,37]:

\[
M'(\omega) = 1/\varepsilon'(\omega) = M' + iM'',
\]

\( M' \) and \( M'' \) are defined as:

Fig. 1. Frequency dependence of the: (a) real part \( \varepsilon'(\omega) \) and (b) imaginary part \( \varepsilon''(\omega) \) of the dielectric constant for a-WO3 thin film at different temperatures.
\( M' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} \quad M'' = \frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} \).

The modulus representation suppresses the unwanted effects of extrinsic relaxation and is often used in the analysis of the dynamic conductivity of solids. It gives us an idea about the relation of dipoles that exists in different energy environments, independent of the strong effect of dc conductivity, which often masks the actual dielectric relaxation processes, active in this type of systems.

Fig. 2 shows the imaginary part of the dielectric modulus, \( M'' \), as a function of frequency for a-WO_3 film at different temperatures. It is clear that the maximum in \( M'' \) peak shifts to higher frequency with increasing temperature. The frequency region below peak maximum \( M'' \) determines the range in which charge carriers are mobile over long distances. For a frequency above peak maximum \( M'' \), the carriers seem to be confined to potential well, thus becoming mobile over a short distance [38].

The temperature dependence of the frequency at the maximum \( M'' \) represented by the Arrhenius equation:

\[
\omega_{M''} = \omega_{M''0} \exp\left(-\frac{\Delta E_{M''}}{kT}\right),
\]

where \( \Delta E_{M''} \) is the activation energy for the electrical relaxation. As shown in Fig. 3, the temperature dependence of the frequency at the maximum \( M'' \), indicates a linear relationship within the temperature and frequency ranges measured. The activation energy value for dielectric relaxation obtained from the dielectric modulus were found to be, \( \Delta E_{M''} = 0.63 \) eV.

Fig. 4 shows the variation of the normalized parameter \( M''/M''_{\text{max}} \) as a function of \( (\omega/\omega_{\text{max}}) \) at three different temperatures. It is noted that the low frequency side of the three peaks line up but the high frequency side data are significantly different. These curves show that the distributions of relaxation time are nearly the same over the temperature range investigated.

3.2. AC conductivity study of a-WO_3

Fig. 5 shows the frequency dependence of \( \sigma(\omega) \) at different temperatures for a-WO_3 thin film of thickness 500 nm. It is noticed that the general behaviour of \( \sigma(\omega) \) is nonlinear frequency dependent at frequencies below \( \sim 400 \) Hz, while linear frequency dependence appears at higher frequency range. The values obtained from extrapolation of the experimental data at low frequency \( < 400 \) Hz to zero frequency are assumed equivalent to the dc conductivity for a-WO_3 at each temperature as given in Table 1.

Fig. 6 shows the temperature dependence of \( \sigma_{\text{dc}} \) for a-WO_3 film. This figure reveals that, dc conduction is through an activated process with activation energy, \( \Delta E_{\text{dc}} = 0.63 \pm 0.03 \) eV which is almost identical to the activation energy obtained from dielectric relaxation suggesting a hopping mechanism for a-WO_3 [39] and indicating that both processes are due to the same conduction mechanism in this temperature range. This unique property was first noted by Chomka and Samatowicz [40].
The temperature dependence of electronic conductivity for amorphous semiconductors containing transition metal, which have two different valence states, namely $W^{+5}$ and $W^{+6}$ [41] is usually expressed by the following formula [29,42]:

$$
\sigma_{dc} = \frac{e^2 v_{ph} c (1 - c)}{kT} \exp(-2xR) \exp(-W/kT),
$$

where $v_{ph}$ is the optical phonon frequency, $R$ is the average spacing between the transition ions, $x$ is the localization length, $c$ is the fraction of reduced transition metal ions (the ratio of ion concentration of transition in the low valence states to the total concentration of transition metal ions) and $W$ is the activation energy for the hopping conduction. Eq. (3) describes a non-adiabatic regime of small polaron hopping and is usually used to analyze the $\sigma_{dc}$ of glasses containing transition metal oxides. According to Mott’ theory, the mechanism of electron transport in amorphous semiconductors depends on temperature. In the high temperature region ($T > \Theta/2$), where $\Theta$ is the Debye temperature, the conduction mechanism is considered as phonon-assisted hopping of small polaron (SPH) between localized states. In this temperature region the jump of an polaron occurs between nearest neighbors with $W = W_h + W_d/2$; where $W_h$ is the polaron hopping energy and $W_d$ is the disorder energy between two neighboring sites.

The electrical conductivity, $\sigma(\omega)$, of many solids including glasses, polymers and crystal was shown by Jonscher and Nagai [43–46] who called it the ‘universal dynamic response’ (UDR) because of the wide variety of material that showed such behaviour. This lead to the empirical form of the total conductivity, $\sigma(\omega)$, for different temperatures, that is expressed as:

$$
\sigma(\omega) = \sigma_{dc} + A\omega^s,
$$

where $A$ is a constant for a particular temperature and $s$ is the frequency exponent. We found that the calculated value of $s$ decreases from 0.962 at room temperature (293 K) to 0.275 at 393 K. The experimental values for $s$ for a-WO$_3$ as a function of temperature are given in Table 1. The interpretation purposed to explain the AC conduction mechanism usually involves analysis of the temperature dependence of frequency exponent, $s$, which makes it possible to find the relevance of hopping mechanism in terms of pair approximation model [25–30]. However, it is difficult to explain the dielectric loss peak and the observed power law behaviour of the frequency dependent conductivity for TMO glasses from the point of view of the pair approximation model. The theory of dielectric relaxation in TMO glasses should take into account the hopping mechanism of charge carrier transport. Although the charge carriers in TMO glasses are small polarons, their mobility is of the same order of magnitude as mobility of ions [33]. In the present paper, the results are analyzed by considering Hunt’s model [47–52] applied in ionic conducting glasses and well adapted to the oxide glasses and explains the dielectric relaxation properties of this material. This model distinguishes two frequency regions: $\omega < \omega_m$ and $\omega > \omega_m$, where $\omega_m$ is the frequency of the peak of the dielectric loss (frequency of onset of ac conductivity). The total conductivity can be expressed in these two domains by the following expressions:

$$
\sigma(\omega) = \sigma_{dc}[1 + A(\omega/\omega_m)^s], \quad \omega > \omega_m,
$$

$$
\sigma(\omega) = \sigma_{dc}[1 + k(d)(\omega/\omega_m)^s], \quad \omega < \omega_m,
$$

**Fig. 5.** Frequency dependence of the conductivity, $\sigma(\omega)$, at different temperature for a-WO$_3$ thin film.

**Table 1**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>293</th>
<th>313</th>
<th>333</th>
<th>353</th>
<th>373</th>
<th>393</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>0.962</td>
<td>0.916</td>
<td>0.772</td>
<td>0.245</td>
<td>0.259</td>
<td>0.275</td>
</tr>
<tr>
<td>$\sigma_{dc}$ (Ω·cm)$^{-1}$</td>
<td>3.89E-6</td>
<td>1.29E-5</td>
<td>4.72E-5</td>
<td>3.77E-4</td>
<td>8.01E-4</td>
<td>1.56E-3</td>
</tr>
</tbody>
</table>

**Fig. 6.** Temperature dependence of the dc conductivity ($\omega \to 0$) for a-WO$_3$ thin film.
where $r = 1 + d - d_c$, $d$ being the dimensionality and $d_c$ is the fractal dimensionality of the percolation cluster in three dimensions, $d_c = 2.66$ [50,53], $A$ and $k(d)$ are constants.

For $\omega > \omega_m$ the electrons (or ions) Jumps forth and back between sites. This is the pair-hopping region, while for $\omega < \omega_m$ the fractal structure of clusters influences the relaxation currents. It is interesting to mention that the Eqs. (5) and (6) treat the dc and ac conduction as independent macroscopic phenomena. However, both contributions should arise from the same microscopic mechanism.

Fig. 7 shows the ac conductivity, $\sigma_{ac}(\omega)$, for different frequencies as a function of reciprocal temperature for a-WO$_3$. The values of $\sigma_{ac}(\omega)$ were derived from Eq. (4), by subtracting $\sigma_{dc}$ from the total measured conductivity, $\sigma(\omega)$. It is clear from this figure that it is difficult to evaluate the activation energy for ac conductivity, $\Delta E_{ac}$, from the slopes of $\sigma_{ac}(\omega)$ curves because $\Delta E_{ac}$ is temperature dependent. This behaviour can be understood from the BNN (Barton [54], Nakajima [55], Namikawa [56]) relation:

$$\omega_m = \frac{\sigma_{dc}}{\rho_0 \Delta \varepsilon},$$

(7)

where $\Delta \varepsilon = \varepsilon(0) - \varepsilon_\infty$, is the relaxation strength and $\rho$ is a temperature independent constant of the order one. From the BNN relation and after subtracting $\sigma_{dc}$, the result obtained for $\sigma_{ac}(\omega)$ is [53]:

$$\sigma_{ac}(\omega) = A(\omega_0 \Delta \varepsilon)^s (\sigma_{dc})^{1-s},$$

(8)

Since, the activation energy of ac conductivity, $\Delta E_{ac}$, can be related to the activation energy of dc conductivity, $\Delta E_{dc}$, by Ngai relation [57], which consistent with Hunt’s model ($\sigma_{ac}(\omega) \propto \sigma_{dc}$):

$$\Delta E_{ac} = \beta \Delta E_{dc},$$

(9)

where $\beta = (1 - s)$. Using the previously obtained relations for Arrhenius temperature dependence for $\omega_m = \omega_0$ exp $(-\Delta E_{dc}/kT)$ and $\sigma_{dc} = \sigma_0 \exp (-\Delta E_{dc}/kT)$. If one substitutes these relations to the ac part of Eq. (5), one obtains [53]:

$$\sigma_{ac}(\omega) = A\sigma_0 \left( \frac{\omega}{\omega_0} \right)^s \exp \left( \frac{-(1 - s)\Delta E_{dc}}{kT} \right),$$

(10)

It is clear from this relation that the activation energy for ac conductivity is temperature dependence.

4. Conclusion

Conductivity and dielectric properties of thermally evaporated tungsten trioxide films have been measured at various temperatures and frequencies. No peak is observed in the dielectric loss, but by removing the strong effect of the dc conductivity, a peak in $\varepsilon'(\omega)$ can be observed; the dielectric relaxation time obtained from the imaginary part of the dielectric modulus, $M''$ shows an Arrhenius behaviour. The activation energy from the dc conductivity and the relaxation time are very similar, $\Delta E \approx 0.63$ eV, and we can conclude that both processes arise from the same conduction mechanism in this temperature range. We have applied the Hunt theory to the interpretation of the electrical and the relaxation properties of a-WO$_3$ thin films. Using the BNN relation, the relation between $\sigma_{ac}(\omega)$ and dc conductivity has been reported.

References