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ELECTRICAL PROPERTIES OF THE SEMICONDUCTOR MATERIALS MOLYBDENUM AND TUNGSTEN TRIOXIDES

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ABSTRACT

Molybdenum and tungsten trioxides are widely applied as semiconductor materials. The electrical conductivity, σ, of polycrystalline MoO_3 is measured in the temperature range from liquid air to 510°C. The value of σ varied from 10^{-6} to 10^{-4} ohm^{-1} cm^{-1}. The gap width is found to be 3.42 eV. The dielectric constant, ϵ', at 2 Mc sec^{-1} and 20°C is 6.32 ± 0.02 and 12.23 ± 0.02 for MoO_3 and WO_3, respectively.

Phase changes detected by differential thermal analysis, DTA, are reflected in the ϵ' vs. T and log σ vs. $1/T$ curves, where T is the temperature.

The specific conductivity, σ_s, calculated from the measured dielectric loss is of the order of 10^{-6} ohm^{-1} cm^{-1}. From the relation between the dielectric constant and the specific resistivity, R_s, the dissociation energy, U_0, was calculated. It is found that U_0 is equal to 0.896×10^{-13} and 1.35×10^{-13} erg $mole^{-1}$ for MoO_3 and WO_3, respectively.

INTRODUCTION

From the band structure standpoint the transition metals and their compounds attract considerable interest due to their suitability for favourable applications as semiconductors because of their wide variety of magnetic, electrical, thermal and mechanical properties. These materials are characterized by an incomplete *d* shell which is usually assumed to be responsible for these properties.

Several of the properties of MoO_3 and WO_3 were studied, such as the infrared absorption of MoO_3 [1] and the X-ray [2], electrical conductivity [3], diffuse reflectance [4], infrared absorption [5] and magnetic properties [6] of WO_3. Current knowledge of the electrical and dielectrical properties of MoO_3 and the dielectrical properties of WO_3 is rather limited.

The electrical conductivity of MoO_3 was reported for the first time by Sacconi and Cini [7] in 1950. He stated that the value varied from 10^{-8} at 20°C to 10^{-3} ohm^{-1} at 350°C for the polycrystalline form. Therefore, this property was measured as a function of temperature for both the polycrystalline [8–12] and the single crystal [13–16] forms by many authors. They all

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stated that it is by nature an electronic semiconductor.

The information available on the conductivity of WO_3 is scarce. The given values range between 10^{-6} at 25°C [17] and 2×10^{-3} at 100°C, [18]. Breaks in the log σ vs. $1/T$ curve were observed by Sawada [19] at 720 and 920°C. Deren and Polaczkowa [20] concluded that the conductivity of polycrystalline powder tungsten trioxide is controlled by surface processes. James and Seinko [21] studied the behaviour of a single crystal from 100 to 500 K and observed two phase changes.

The dielectric properties of MoO_3 thin films were measured by Deb [8,22] and Simmons and Nadkarni [23,24]. That of the powder form remained largely unexplored till more recent time when it was tackled by Rapos and Calderwood [25,26]. The dielectric properties of WO_3 were measured on both single crystal [27–29] and powder [30–34] forms by many authors.

The present investigation is undertaken to study these properties for the most stoichiometric forms of MoO_3 and WO_3 to throw more light on their behaviour as a function of temperature and frequency.

EXPERIMENTAL

Molybdenum trioxide was prepared by heating A.R. ammonium heptamolybdate tetrahydrate (paramolybdate) at 350°C to constant weight [35]. Tungsten trioxide was prepared as described before [2].

Spectroscopic analysis indicated the presence of Pb, Fe and Si in very minute traces.

X-Ray diffraction analysis was carried out. The diffraction pattern reflections were indexed according to the orthorhombic system of MoO_3 given by Lars Kihlborg [36] and the monoclinic cell of WO_3 by Tanisaki [37]. To check the degree of stoichiometry for the given samples, density, lattice parameter calculation [2], diffuse reflectance [4] and infrared absorption [1,5] were carried out. These proved that these samples represent the most stoichiometric forms.

All samples were sieved through a standard 200 mesh sieve and then compressed, without using any binder, into cylindrical pellets suitable for the special cell employed.

Grain boundary effects seem to be negligible since the condensation at different pressures was found to have no effect.

For the electrical conductivity measurements, test specimens were pressed at 8 ton cm^{-2} into pellets 1 cm diameter and 3 mm thickness. The change in the resistivity of the specimen with rise of temperature from liquid air up to 510°C was studied using the technique described previously [3]. The frequency used was 100 kc sec^{-1} from the frequency dispersion experiment.

For the dielectric measurements, the sample was pressed at 1200 kg cm^{-2} into a cylindrical disc of 59 mm in diameter and 4 mm thickness. The dielectric constant, ϵ', was measured with an accuracy of ±0.02 using the technique described previously [38].

RESULTS AND DISCUSSION

The variation of electrical conductivity of MoO_3 samples with temperature from −190 to 510°C is represented in Fig. 1, curve a. As may be seen, the curve reveals a horizontal region extending from −190 to 0°C, due to frozen-in impurities where the defects are less mobile. Initially the conductivity increases slowly but above 460°C the increase becomes rapid. Some peaks and minima are detected in the σ vs. $1/T$ curve. A maximum is obtained at 50–60°C which disappears totally when the sample was previously heated to 100°C under a vacuum of 10^{-3} mmHg for 1 h. This may be due to the presence of water molecules in agreement with Ioffe et al. [15] who interpreted the instability in electrical conductivity results to the presence of OH groups. Above 110°C, the conductivity increases with temperature giving rise to activation energies of 0.6 and 0.86 eV. Slight discontinuities at 190 and 220°C are observed. These activation energies represent the extrinsic part of conductivity. Ioffe et al. [15] obtained an activation energy of 0.6 eV and Gvilova et al. [13] obtained a value of 0.87–1.12 eV which they attributed to the formation of O vacancies which act as electron-capturing centres. Interruption of the linear behaviour extends from 290 to 340°C, decreasing down to 370°C, when the σ value begins to increase again with a maximum at 450°C. Above this temperature, the linear relation $\sigma = \sigma_0 e^{-E/2KT}$ becomes applicable again and an increase of conductivity up to 510°C is observed.

The behaviour of MoO_3 above 460°C represents the intrinsic part of the

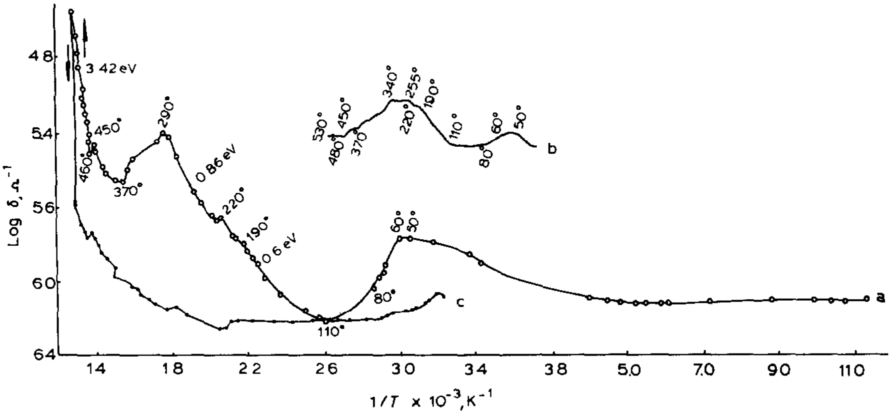

Fig. 1. Plot of log σ vs. $1/T$ for MoO_3. a, Electrical conductivity measured with increasing temperature; b, DTA curve; c, electrical conductivity measured with decreasing temperature.

oxide. This is in agreement with Elyutin et al. [10] who found that the transition to the intrinsic region begins at 460°C. Ioffe et al [15] reported a corresponding temperature of 430°C. The activation energy obtained in the high temperature region is 3.42 eV which may represent the value of the gap width for MoO_3. This is found to be in reasonable agreement with the corresponding value obtained by Ioffe et al. [15], Deb [8] and Shkol'nik and co-workers [12].

Hysteresis is observed in the course of the cooling curve, Fig. 1, curve c. The maxima and interruptions of the non-linear behaviour of the log σ vs. $1/T$ plot after 110°C, namely that at 190, 220, 290–340, 370 and 450°C, may primarily be due to a change in the carrier mobility caused by either a change in the scattering mechanism, to an increase in the effective mass or a combination of both in which case this may be due to a phase change leading to a change in the electronic structure [3].

It is noted that the literature reviewed includes neither the phase change nor the effect of temperature on MoO_3.

Thermogravimetric analysis, TGA, for MoO_3 showed that the whole run has no weight loss at all. The DTA recorded in Fig. 1, curve b revealed discontinuities or steps and e.m.f. changes at the same temperatures corresponding to conductivity changes as indicated on the curve. The behaviour indicates that the non-linear behaviour of the conductivity may be due to phase changes. This needs confirmation using high-temperature X-ray techniques, the Hall effect and thermoelectric power which are recommended for future studies.

The electrical conductivity of the WO_3 sample, published previously by the same author, was measured in the temperature range -190–580°C. The log σ vs. $1/T$ curve is formed of many segments. As a result of frozen-in impurities the electrical conductivity is independent of temperature up to 0°C. A maximum is reached at 18°C due to the triclinic/monoclinic phase transformation. Extrinsic behaviour is evident in the span 140–300°C and is followed by an exhaustion range where all impurity atoms are ionized. A decrease in conductivity is observed in the temperature range 390–480°C due to transformation into the orthorhombic modification. Log σ increases linearly with $1/T$ above 480°C. The activation energy was found to be 2.2 eV [3].

The variation of the dielectric constant, ϵ', and the dielectric loss factor, ϵ'', for MoO_3 with temperature at different frequencies is shown in Fig. 2. It is found that the dielectric constant and the dielectric loss at 2 Mc sec^{-1} and 20°C are 6.32 ± 0.02 and 1.08 ± 0.2, respectively. The effect of temperature on the dielectric behaviour of MoO_3 is very small while the frequency has a considerable effect.

The increase of ϵ' with decreasing frequency may result from some kind of space-charge polarization [26] in the medium, perhaps due to the barriers formed either by the accumulation of the free carriers on the boundaries of

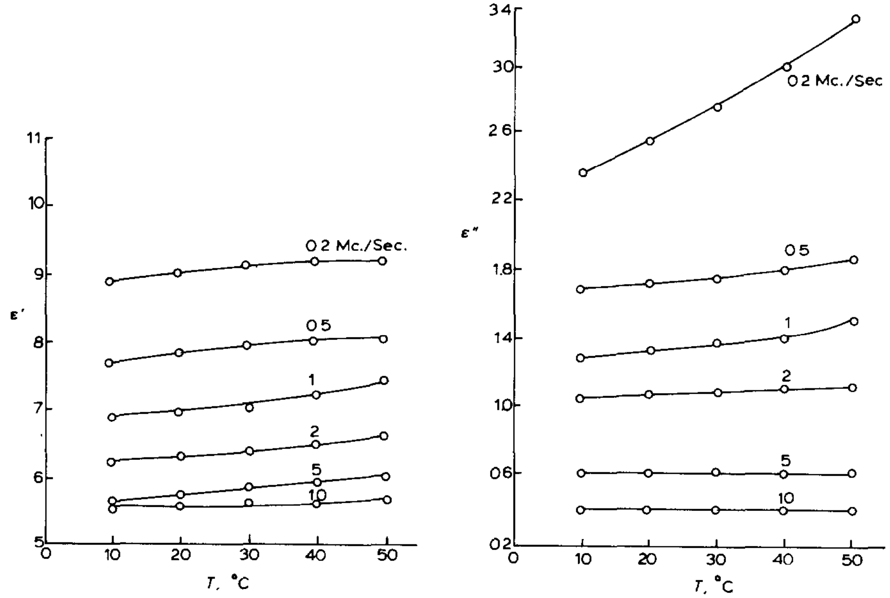

Fig. 2. Plots of ϵ' vs. T and ϵ'' vs. T for MoO_3 at different frequencies (Mc sec^{-1}).

the crystal grains or at the regions adjacent to the electrode or both. At high frequency some of the charge carriers may jump over these barriers arising at the electrode and hence the dielectric constant decreases.

It is well established that MoO_3 contains a number of oxygen vacancies capable of capturing one or two electrons unless it is ionized. Oxygen vacancies occupied by two electrons, O^{2-}, act as donors. Under the effect of an electric field, some of these oxygen vacancies are ionized giving two new charge carriers, one electron and a singly charged oxygen vacancy. These two charge carriers migrate from the medium to the barrier near the electrodes and hence the measured dielectric loss factor, ϵ'', of the bulk MoO_3 increases. When the frequency of the applied field increases the concentration of the free charge carriers becomes smaller [26] and hence the dielectric loss factor decreases.

As the temperature increases, the space charge between the MoO_3, molecules increases and the rotation of these molecules becomes flexible and hence the dielectric constant increases. The increase in the dielectric loss factor with temperature may be attributed to the increase in the number of the ionized carriers by the thermal energy [14]. The dielectric behaviour of WO_3 is represented in Fig. 3. It is found that the static dielectric constant and the dielectric loss factor measured at 20°C and 2 Mc sec^{-1} are 112.23 ± 0.02 and 0.96 ± 0.02, respectively. Both increase with increase of temperature and decrease of frequency. This change in the dielectric behaviour of WO_3 may be due to the expansion of the space between the molecules and to the thermal breaking of the associated molecules.

The anomalous change in the ϵ'' vs. T plot between 15 and 20°C may be

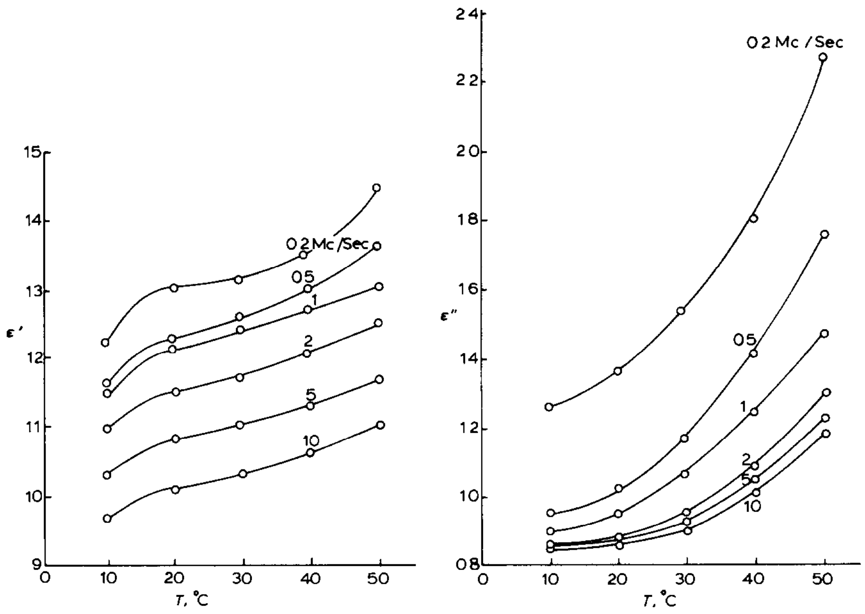

Fig. 3. Plots of ϵ' vs. T and ϵ'' vs. T for WO_3 at different frequencies (Mc sec^{-1}).

attributed to the presence of a phase transition in the WO_3 crystal structure. Other physical measurements such as microscopic observations, thermal analysis, measurements of the electrical resistivity, X-ray studies [28] and optical properties [29] indicate that phase transition from triclinic to monoclinic occurs at 17°C.

After discussing each compound individually, some general observations will be summarized for both compounds in relation to their periodicity. In general, the resistance decreases with increasing temperature. At certain specific temperatures, the rate is faster, moving from the extrinsic to the intrinsic part of the oxide.

The gap width is 3.42 and 2.27 eV for MoO_3 and WO_3, respectively. It is quite reasonable for this value to be higher for MoO_3 than WO_3 because of the variation in the strength of the chemical bond [39]. Also, the dielectric constant is 6.32 and 12.23 increasing from MoO_3 to Wo_3 according to the increase of their electronegativity [40].

The measured dielectric loss, ϵ'', has two components, the dielectric loss and the conductivity loss [41] as given by

$$\epsilon''_{(\text{measured})} = \epsilon''_{(\text{dielectric loss})} + \epsilon''_{(\text{conductivity loss})}$$

Also, the conductivity loss is equal to $1.80 \times 10^{12}\ \sigma_s\ f^{-1}$, where σ_s is the specific conductivity at frequency f. The conductivity loss can be calculated from the measured dielectric loss [42,43] by plotting the product $f\ \epsilon''_{\text{measured}}$ vs. f and extrapolating the resulting curve to zero frequency (at which frequency the dielectric loss is mainly due to the conductivity and the dielectric contribution disappears). By dividing the value of $f\epsilon_{(\text{measured})}$ when extrapolated to zero frequency over the frequencies employed, the conductivity loss can be calculated. The electrical conductivity for MoO_3 and WO_3 is calculated at 2 Mc sec^{-1} over the temperature range 10–50°C (see Table 1). The results indicate that the calculated values of the electrical conductivity, $\sigma_{(\text{cal.})}$ are in the same order of magnitude as the measured values, $\sigma_{(\text{measured})}$, (see Fig. 1).

From the relation between the dielectric constant and the electrical conductivity, the dissociation energy, U_0, can be calculated [44]. Hearle [45] proposed a relation between the dielectric constant and the specific resistivity, R_s, as given by

$$\log R_s = \frac{A}{\epsilon'} + B$$

where A and B are constants and R_s is the resistivity measured in ohm cm^{-2}. A is equal to $U_0 \log_e e/2kT$ where e is the electronic charge, k is the Boltzman constant and T is the temperature. From plotting $\log R_S$ vs. $1/\epsilon'$ the value of U_0 can be calculated (see fig. 4). By using this method, it is found that the dissociation energies of MoO_3 and WO_3 are equal to 0.896×10^{-13} and 1.35×10^{-13} erg $mole^{-1}$, respectively.

On the other hand, the dissociation energy depends on the forces between the ions in the lattice, and it will be of the same order of magnitude as the energy required to separate to infinity the electronic charges of opposite sign, which were initially a distance apart equal to the ionic diameter for the ionic compounds such as alkali halide crystals [45]. U_0 is given by

$$U_0 = \frac{e^2}{x}$$

where x is the lattice space in the crystals. By taking the mean distance of Mo–O to be 2.07×10^{-8} cm [46] and that for W–O to be 1.88×10^{-8} cm

TABLE 1

The calculated electrical conductivity, $\sigma_{(\text{cal.})}$ of MoO_3 and WO_3

T (°C)	$\sigma_{(\text{cal.})} \times 10^6$	
	MoO_3	WO_3
10	0.0277	0.0416
20	0.0303	0.0444
30	0.0327	0.0511
40	0.0350	0.0544
50	0.0372	0.0666

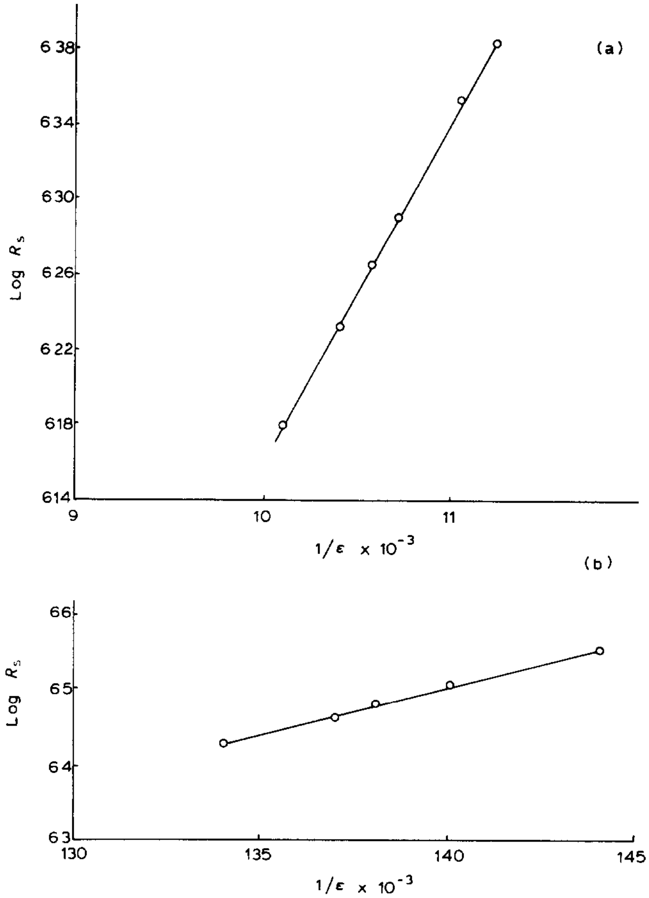

Fig. 4. Plots of log R_s vs. $1/\epsilon'$. (a) WO_3; (b) MoO_3.

[47], the calculated dissociation energies are 0.00123×10^{-13} and 0.00136×10^{-13} erg mole^{-1} for MoO_3 and WO_3, respectively.

It is found that there is good agreement between the value of the dissociation energy calculated from the dielectric constant–conductivity relation and the value calculated from the ionic diameter for the ionic compounds [45]. This agreement was not the case for MoO_3 and WO_3; this may be due to the covalent character of these oxides.

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