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An Inexpensive Method for Producing Oxygen Deficiency in Thin Films of WO_3 and Their Characterization with the Help of Electrical Properties

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In the present work we describe the method for producing oxygen deficiency in thin films of WO_3 and their characterization.

INTRODUCTION

A simple and inexpensive set up is reported for the creation of oxygen deficiency in WO_3 thin films. The studies carried out here on thin films of WO_3 show that an insulator but vacuum evaporated WO_3 if made oxygen deficient becomes conducting. The conductivity depends upon the amount of oxygen deficiency. The activation energies calculated on the basis of the temperature dependence of conductivities are found to be in agreement with those reported by others. Thus a theoretical model has been suggested for determining the extent of oxygen deficiency in the present experiment quartz crystal thickness monitor.

A thorough study has been made on the electrical properties of WO_3 and WO_{3-x} and a comparison is made with the reports of other workers. The cause of variations in the results presented here and those reported by others has also been explained.

EXPERIMENTAL

Preparation of thin films of WO_3

Thin films of WO_3 are deposited by using the vacuum evaporation technique and their thickness is measured by an inbuilt device at a pressure of 10^{-15} torr. These films are then annealed at different temperatures and for different time intervals. A number of these annealed films are then made oxyen deficient by high temperature heat treatment in hydrogen atmosphere at normal pressure and for different durations.

RESULTS AND DISCUSSIONS

Conductivity measurements and dependence of electrical conductivity on the amount of oxygen deficiency

Dependence of room temperature conductivity on the duration of hydrogen reduction of these films is shown in Fig. 1. It is observed that the films deposited

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at substrate temperature, $T_s = 475$ K and annealed in air at 825 K are highly resistive ($\rho > 10^{12}$ onm-cm). Fig. 1 indicates that the increase in the time of hydrogen reduction decreases the resistivity (ρ) of the films. Initially, the increase in the electrical conductivity is small (up to films reduced for 2.5 h). There is manifold[1] increase in the conductivity of the films reduced for 3 h compared to the films reduced for 2.5 h or lesser periods.

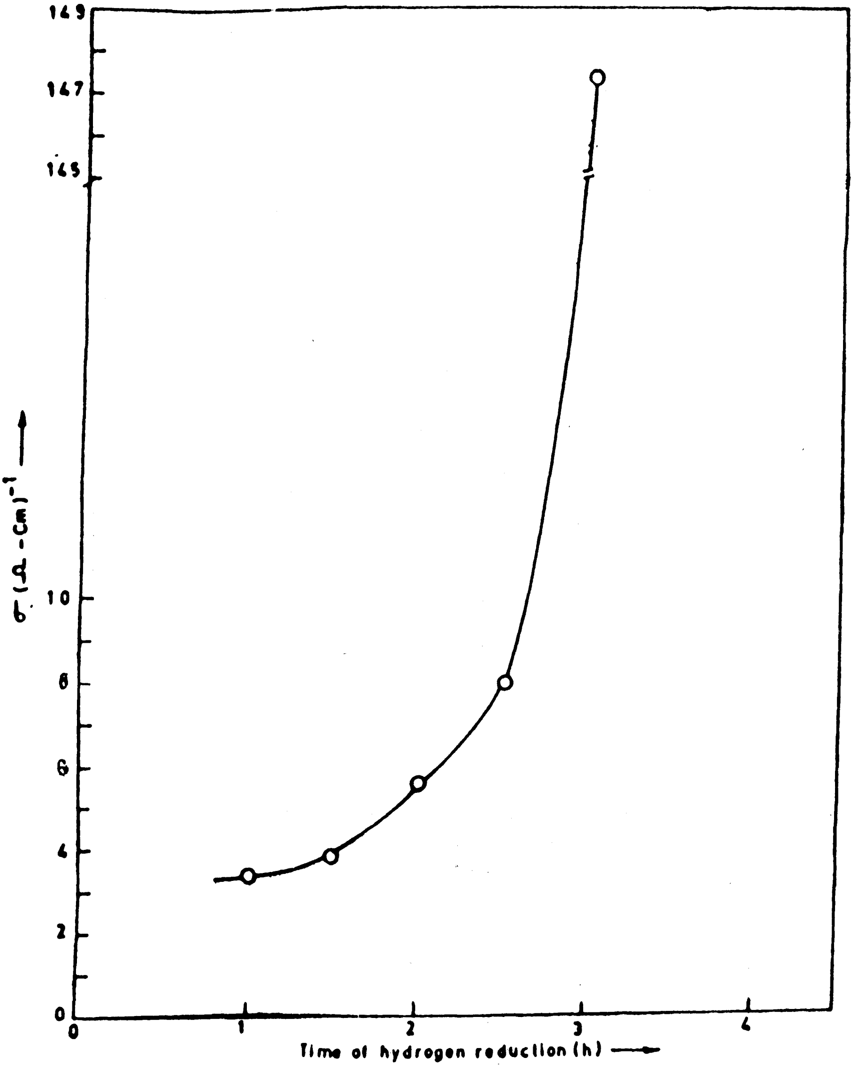

Fig. 1 Conductivity *vs.* time of reduction of WO_3 films

Stoichiometric WO_3 is a highly resistive compound formed by the corner sharing of the WO_3 octahedra. Removal of oxygen atoms produces discs of edge sharing octahdra connected together by the corner sharing octahedra.[2, 3] The conductivity does not increase appreciably. As the amount of oxygen deficiency in WO_3 increases these discs of edge sharing octahedra grow in size. At a particular value of the oxygen deficiency $(WO_{2.98})^{4,5}$ these discs of edge sharing octahedra grow into infinite strings of edge sharing octahedra extending throughout the thin film and the conductivity increases abruptly.

Temperature dependence of electrical conductivity of reduced films

These studies are carried out from 200 K to 500 K on a number of films of each group *i.e.*, 1 h, 1.5 h, 2 h, 2.5 h and 3 h reduced in hydrogen atmosphere. The representative graph (σ *vs.* 1000/T) is shown in Fig. 2, where the curves (a), (b), (c), (d) and (e) represent the variation of conductivity *vs.* 1000/T for the 1 h, 1.5 h, 2 h. 2.5 h and 3 h reduced films repectively. These graphs show the typical hoping type[6] semiconducting nature of the material of the films.

The activation energies (E_a), the frequency factors, (σ_o) and the phase transition temperatures are shown in Table 1.

TABLE-1
THE ACTIVATION ENERGY (E_a), THE FREQUENCY FACTOR (σ_0) AND PHASE TRANSITION TEMPERATURES

Films reduced for	Low temperature region		High temperature region		Phase transformation temperature (K)
	Activation energy E_a (ev)	Frequency factor ohm cm	Activation energy E_a (eV)	Frequency factor ohm cm	
(a) 1.0 h	0.05 ± 0.004	35.59 ± 0.07	0.02 ± 0.004	8.08 ± 0.07	264
(b) 1.5 h	0.035 ± 0.005	19.16 ± 0.06	0.04 ± 0.003	26.33 ± 0.07	223
(c) 2.0 h	0.05 ± 0.005	27.43 ± 0.09	0.06 ± 0.005	41.49 ± 0.09	223
(d) 2.5 h	0.05 ± 0.006	74.26 ± 0.03	0.05 ± 0.006	74.26 ± 0.03	No break
(e) 3.0 h	0.01	191.39	0.013	288.19	213

The nature of the curve for Fig. 2, (1 h reduced films) is similar to that reported by Sienko *et al*[7] for single crystal of $WO_{2.999925}$ except that the conductivity jump, the transition temperature and the high temperature metallic phase of the films have not been observed. The high temperature activation energy is the same but the low temperature activation energy is less than that (0.21 eV) reported by them. The room temperature monoclinic phase to the triclinic phase transition which ideally occurs at 290 K is also absent. For this film the triclinic low temperature monoclinic phase transition appears at 264 K which ideally occurs[7] at 233 K. During heating, Seinko *et al.*[7] have observed this transition to occur at 253 K.

The nature of the Fig. 2 (2 h reduced films) is similar to that reported[7] for the single crystals of $WO_{2.90980}$ except that the jump in the conductivity at the transition temperature is absent. However, the activation energy of these films (0.05 eV) is less than the values reported by Sienko *et al.*[7]

For 2.5 h reduced films (Fig. 2), the conductivity *vs.* {T^{-1} plot is similar to that reported by Sienko *et al.*[7] for single crystal of $WO_{2.9877}$. Sienko *et al.*[7] have observed a smooth bend in the curve while a break at 223 K is observed in the

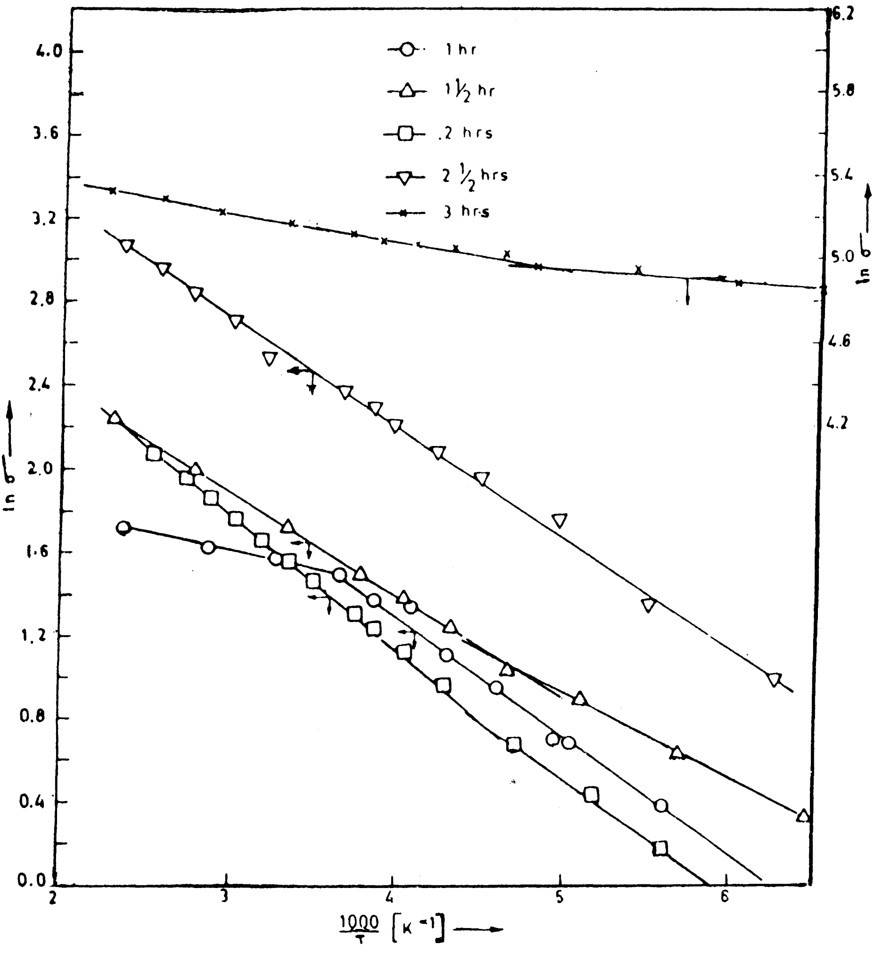

Fig. 2 ln σ *vs.* 1000/T of the WO_3 films annealed at 825 K and reduced at 775 K.

present studies. However, the activation energies in the two regions (0.05 eV and 0.06 eV) are in agreement with those reported by them.

The variation in the conductivity for the films reduced for 3 h (Fig. 2) tallies with those reported by Miyake *et al.*[8] for the amorphous films produced by the reactive sputtering technique. The low temperature activation energy (0.01 eV) appears to be similar to those reported by Miyake *et. al.*[8] For these films (3 h reduced) the triclinic low temperature monoclinic phase transition appears at 213 K.

The jump in the conductivity at the phase transition temperature has been reported by various authors[7, 9, 13, 14] and this has been attributed to the fact that in the single crystal various domains undergo transition at different temperatures.[7]

Thus it appears that in thin films (0.2 mm) various domains are exposed simultaneously to the same temperature. They undergo transition at a constant temperature and so no jump is observed. However, such jumps in the conductivity have not been observed by Crowder *et al.*[10, 11] and Miyake *et al.*[8] for the oxygen deficient single crystals and thin films of tungsten trioxide respectively. Thus the results being reported in this paper are in conformity to the findings of Miyake *et al.*[8] and Crowder *et al.*[10, 11] It is seen that the activation energy (0.05 eV) in the low temperature phase remains unaffected (Table 1) by increasing oxygen deficiency. However, in the high temperature region it drops down to 0.02 eV for the 1 h reduced films and increases to 0.05 eV (2.5 h reduced film). The activation energies, just before and after the triclinic-low temperature monoclinic phase transition, approach each other as x in WO_{3-x} increases. It appears therefore that for reduced films another type of conductivity process is becoming operative which decreases as the temperature increases and the resultant effect is the decrease in the activation energy in this region (triclinic). It suggests that even though the experiment is carried out in argon gas the presence of traces of oxidizing gases in the Dewar-flask decreases the carrier concentration at higher temperatures and a decrease in the activation energy is observed. The decrease in the carrier concentration appears to be due to an annealing out of the oxygen defects due to traces of oxidizing gases present in the Dewar flask. The lowest temperature of first appearance (Table 1) of the low temperature phase (monoclinic) is 213 K (3 h recuded film). This transition occurs at 233 K for single crystals. This derease in the transition temperature can be explained on the constraining effect of the lattice defects. Evidently the strain associated with these defects must become greater as the polycrystalline lattice structure cools through the transition. Assuming other factors constant, successive increase in this contribution to the free energy can be offset if the transition temperature is lowered in comparison to the case where the additional strain terms are small.

Conclusion

The experiment has been carried out on a number of each type of samples and the results have been found to be reproducible. Thus on the basis of discussion it can easily be concluded that the films anealed at 825 K and reduced in hydrogen atmosphere at normal pressure for 1 h are $WO_{2.999925}$. The films reduced for 2 h under similar conditions are $WO_{2.99980}$ and those reduced for 2.5 h are $WO_{2.9877}$. The 3 h reduced films are those of $WO_{2.98}$.

Thus it is also cleared that by simply controlling the time of hydrogen reduction of WO_3 thin films, one can produce oxygen deficiency in them according to one's requirement and the properties can also be achieved. A theoretical model relating the time of hydrogen reduction and the value of x in WO_{3-x} is given below in the form of an equation:

$$x = -0.013 + 0.01\ t$$

where t is time in hours.

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