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Preparation and properties of vanadium dioxide thermochromic thin films

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Abstract. Deposition of vanadium dioxide and the study of its electrical and optical properties at varying deposition conditions have been presented. The materials have been deposited by reactive r.f. magnetron sputtering technique in Ar, O_2 ambient followed by annealing post-treatment. Electrical conductivity measurements indicate that oxygen pressure plays an important role in obtaining VO_2 and at $P_{O_2} = 2{\cdot}4\%$ stoichiometric VO_2 can be obtained. The deposition rate of oxides decreases with increasing O_2 pressure and the rate of VO_2 was about 130 Å/min. Optical studies show that VO_2 films exhibit thermochromism and it has the potential application for energy efficient solar energy utilization.

Keywords. Sputtering; vanadium dioxide; thermochromism.

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1. Introduction

Chromogenic materials (Lampert and Granqvist 1990) offer new options for energy efficient solar energy utilization, for large-area information displays, and for many other applications. Vanadium dioxide is well-known in this context and among the several transition metal oxides, VO_2 crystals exhibit an abrupt structural transformation at a critical temperature $\tau_c = 68°C$ (Adler 1968; Goodenough 1971; Mott 1974). VO_2 is of particular interest since it exhibits a transition from semiconducting to metallic state at 68°C. The low temperature phase is monoclinic, semiconducting and infra-red transparent. The high temperature phase is tetragonal, metallic and infra-red reflecting for wavelength $> 1\ \mu m$. The semiconductor-metal cross over may be caused by a Mott-Hubbard-like transition (Zylberstejn and Mott 1975) or by electron trapping in homopolar bonds (Chudnovskii 1975, 1976).

Literature reports indicate that thin films of vanadium dioxide have been produced by a number of techniques by many researchers. These include reactive evaporation (Steensel *et al* 1967; Kiode and Takei 1967), chemical vapour deposition (MacChesney *et al* 1968), spray pyrolysis (Ryabova *et al* 1972) and reactive sputtering (Fuls *et al* 1967; Duchene *et al* 1972). Most of the reports address themselves to the structural aspects of these films, emphasizing the inter-relation between the substrate materials, film structure and electrical performances. Although there have been a number of investigations on the optical properties of the films (Verleur *et al* 1968; Borisov 1971; Smith 1973; Jorgenson 1984 and Babulanam *et al* 1987) no systematic study appears to have been done on electrical and optical properties at varying deposition conditions. Moreover, there is a considerable disagreement (Verleur *et al* 1968; Smith 1973)

concerning the visible and near infra-red absorptance of both below and above transition temperature. Different microstructures caused by different deposition conditions could be the probable reasons for the disagreement. Hence, there is a need to study how varying deposition conditions affect the physical properties of VO_2 to assess its usefulness for the application in energy efficient devices. In this paper we present and discuss the effect of oxygen pressure on the production of stoichiometric VO_2 and study the electrical and optical properties of the films.

2. Experimental

2.1 *Sample preparation*

Thin VO_2 films were prepared by reactive r.f. magnetron sputtering followed by annealing post-treatment by use of a versatile thin film deposition unit as described by Eriksson and Granqvist (1986). The sputtering chamber was evacuated to the pressure range $< 1{\cdot}2 \times 10^{-6}$ torr by cryopumping. After evacuation, argon (purity 99·9997%) was introduced into the chamber. The pump rate was regulated by a throttle valve so that the total pressure was kept at $7{\cdot}2 \times 10^{-3}$ torr. The substrate was heated by a resistive heater whose temperature was determined by a chromel-alumel thermocouple at the middle of the substrate table. Sputtering was carried out from a 10 cm diameter planar vanadium target (purity 99·8%) on the substrate of Corning 7059 glass positioned 4·5 cm below the target surface. The r.f. power was 200 watt at 13·56 MHz. Before depositing the films onto the substrates, presputtering was carried out for about 15–20 min and the substrates were protected by a movable shutter from possible deposition. After presputtering with argon, oxygen gas (purity 99·998%) was introduced into the chamber and the total gas pressure was maintained at about $7{\cdot}4 \times 10^{-3}$ torr. The constituent gases in the mixture were controlled via gas flow regulators at the set values of flow rate in standard cubic centimeters per minute (sec/m) (table 1).

After setting the optimum deposition parameters for VO_2, vanadium dioxide thin films were prepared onto the substrates of Corning 7059 glass, CaF_2, sapphire, Si and carbon covered copper grids for electron microscopy. The sputtering parameters are listed in table 1.

2.2 *Annealing*

The As-deposited vanadium oxide thin films did not exhibit thermochromism. The films were blackish and had poor electrical conductivity. To establish thermochromism

Table 1. Sputtering condition for vanadium dioxide thin films.

Target	Vanadium
Target diameter	10 cm
Target substrate separation	4·5 cm
r.f. power on target	200 W
Sputtering gas pressure	$7{\cdot}4 \times 10^{-3}$ torr
Presputtering time	15–20 min
Substrate temperature	400–450°C
Argon flow rate	28 scc/m
Oxygen flow rate	0·7 scc/m

the films were heated. Heat treatments of these coatings changed the optical and electrical properties substantially.

Heat treatments were carried out in a temperature-regulated oven consisting of a gas-tight ceramic pipe with surrounding heating elements. The two ends of the gas-tight pipe were cooled by circulating cold water to protect the rubber O-rings from excessive heating. To make thermochromic VO_2 films, thin films of vanadium oxides were put in the oven containing 1·2 torr of air and were heated to 420°C for a limited time period. After turning off the power of the heater, the samples were cooled down for more than 24 h in the same ambient as they were heated in. To optimize parameters for thermochromism we adopted a trial and error procedure. The required duration of the annealing period varied from sample to sample. It was found from experiment that the thicker samples required longer annealing times than the thinner ones.

2.3 *Deposition rate*

The thicknesses of the deposited coatings were measured by an alpha-step surface profiling instrument (Tencor Alpha-step instrument). The thickness was obtained by letting a fine stylus scan across a part of the coating where a thickness profile had been made. From sputter time and film thickness after annealing, as determined by mechanical surface profilometer, an effective deposition rate was obtained. Figure 1

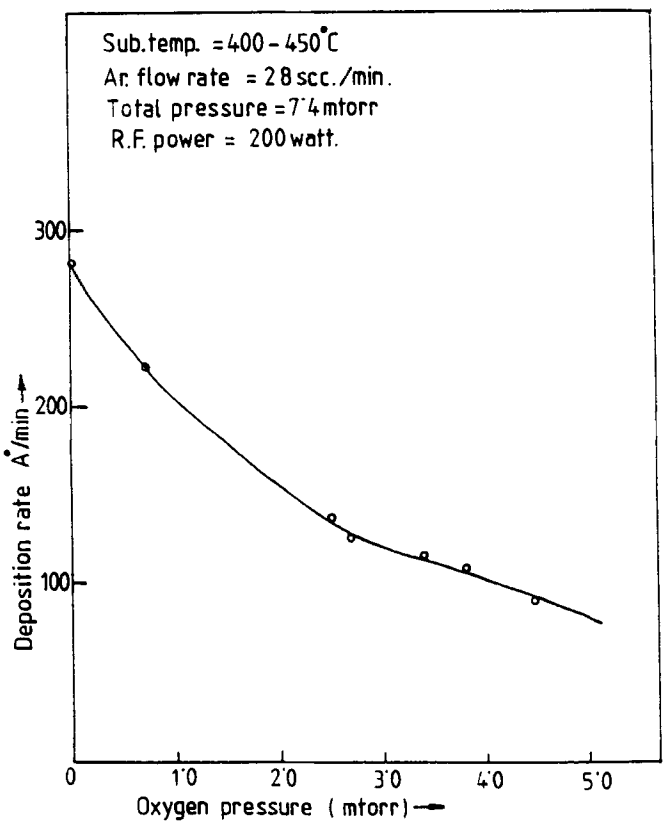

Figure 1. Deposition rate vs. oxygen pressure of the oxides of vanadium.

shows the deposition rate vs O_2 partial pressure for films deposited at a discharge power of 200 W. The argon flow rate was 28 scc/m and the total pressure was $7{\cdot}4 \times 10^{-3}$ torr. It is seen from the figure that the deposition rate of the oxides strongly depends on O_2 pressure. The deposition rate is 280 Å/min at zero oxygen and the rate decreases sharply with increasing oxygen pressure, reaching a value of 220 Å/min at $P_{O_2} = 0{\cdot}75\%$, 130 Å/min at $P_{O_2} = 2{\cdot}4\%$, respectively, and then the rate decreases very slowly with increasing oxygen pressure. The pressure-dependent variation of the oxides plays an important role in obtaining stoichiometric VO_2 and it also has great impact on the lifetime of the sputtering condition of the target. At higher oxygen pressure the target itself oxidizes and ultimately it hinders the deposition.

2.4 *Electrical properties*

The oxides of vanadium exist in two series (Bugayev *et al* 1986; Chudnovskii 1976). The first $V_nO_{2n-1}(n = 3-9)$, lies between V_2O_3 and VO_2 and contains a mixture of V^{3+} and V^{4+} ions. The second series $V_nO_{2n+1}(n = 3-6)$ is located between VO_2 and V_2O_5 and has alternating V^{4+} and V^{5+} ions. The occurrence of these oxides and their phase transitions depend strongly on preparation condition such as oxygen pressure P_{O_2} and substrate temperature. In order to prepare stoichiometric VO_2, we made a number of experiments with oxygen pressure as a variable, keeping all the other sputtering parameters constant. Figure 2 shows the electrical conductivity vs. temperature curves for a series of vanadium oxides coating. The conductivity measurements were done by applying a voltage of 1·5 V between indium press contacts

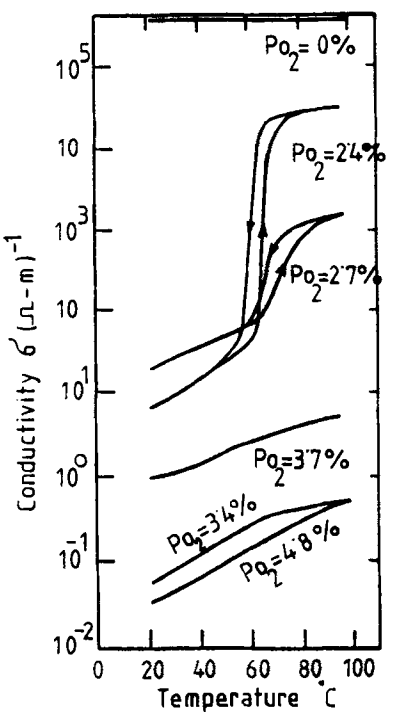

Figure 2. Electrical conductivity vs. temperature for oxides of vanadium at different oxygen partial pressure.

on the film and recording the current. The detailed measurement techniques have been discussed in our earlier studies (Khan *et al* 1988, 1989). These experiments were carried out to determine the desired oxygen pressure for the production of stoichiometric VO_2. The top and bottom curves in the figure indicate the results for $P_{O_2} = 0{\cdot}0\%$ and $P_{O_2} = 4{\cdot}8\%$. The other curves indicate the conductivity and the nature of the hysteresis for several other O_2 pressure. It is apparent that the O_2 pressure is crucial for obtaining stoichiometric VO_2. The O_2 optimum pressure is at 2·4%. All the samples in this experimental series were prepared and annealed under the same conditions, the only difference being in their O_2 pressure.

2.5 *Optical properties*

Spectral transmittance $T(\lambda)$ and near normal reflectance $R(\lambda)$ were measured at $0{\cdot}3 < \lambda < 2{\cdot}5\ \mu m$ using a Perkin-Elmer Lambda-9 double beam spectrophotometer with accessories (Babulanam *et al* 1987) for substrate heating. Figure 3 shows the spectral transmittance vs. wavelength spectra for the same five films as mentioned in figure 2. The top spectrum shows a result for film deposited at $P_{O_2} = 4{\cdot}8\%$ and the other spectra for films deposited at reduced O_2 pressures. It is seen that spectra for $P_{O_2} = 4{\cdot}8\%$, $P_{O_2} = 3{\cdot}7\%$ and $P_{O_2} = 3{\cdot}4\%$ show several absorption peaks in the infra-red and they may be caused because of the optical interference. Film deposited at $P_{O_2} = 2{\cdot}4\%$ shows the spectrum for VO_2 and it has a monotonic increase at wavelength

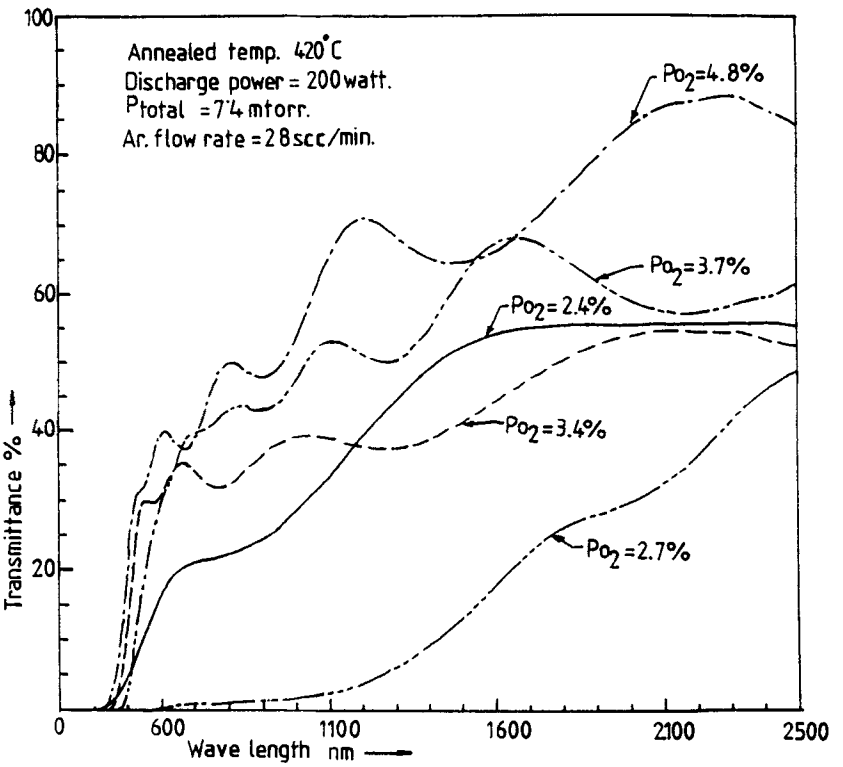

Figure 3. Spectral transmittance vs. wavelength spectra for films deposited at different oxygen pressure.

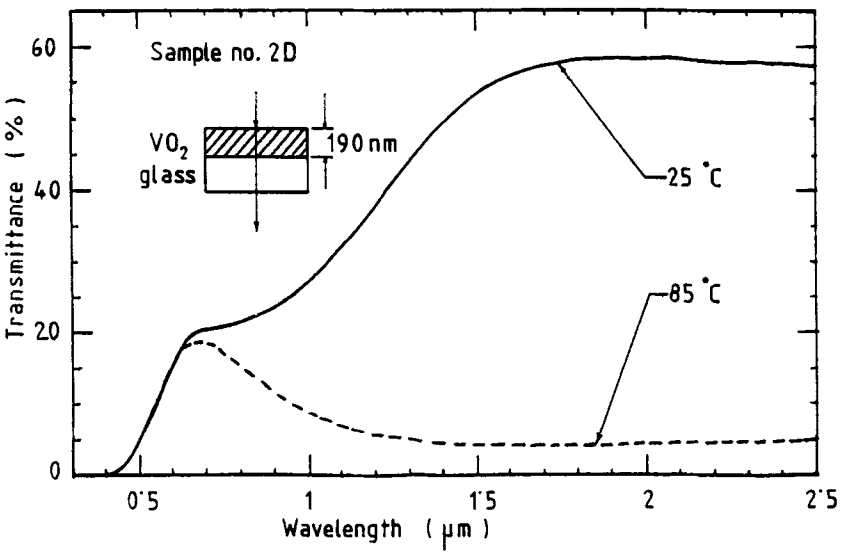

Figure 4. Transmittance vs. wavelength curves for a 190 nm thick VO_2 film on glass.

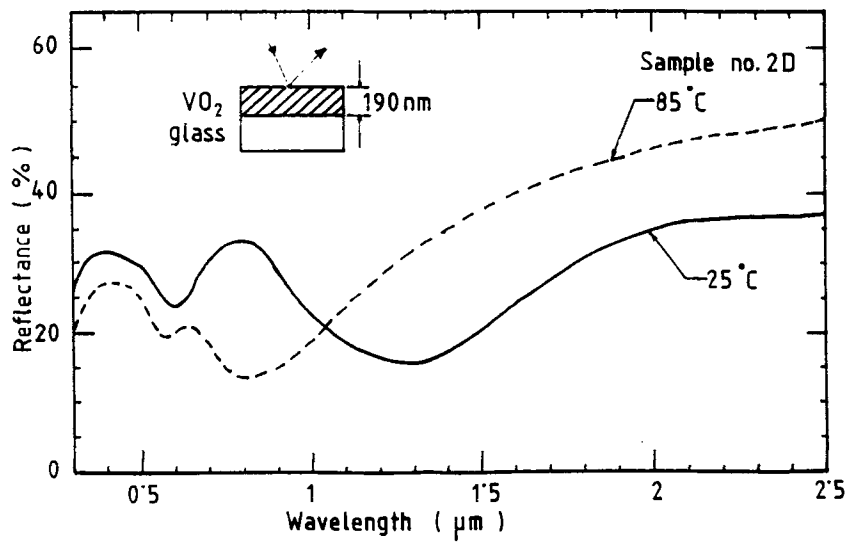

Figure 5. Reflectance vs. wavelength curves for a 190 nm thick VO_2 film on glass.

greater than 0·9 μm. Figures 4 and 5 show the results of transmittance and reflectance as a function of wavelength for VO_2 film on glass substrate. The film thickness was 190 nm and transmittance and reflectance spectra were obtained at temperature $\tau = 25°C$ and $\tau = 85°C$ below and above the transition temperature $\tau_c = 68°C$. It is seen from figure 4 that $T(\lambda)$ depends strongly on τ, particularly in the infra-red. At $\tau < \tau_c$, $T(\lambda)$ shows an almost monotonic increase with increasing wavelength and reaches at $\sim 60\%$ at $\lambda > 1{\cdot}5\,\mu$m. At $\tau > \tau_c$, $T(\lambda)$ shows a peak at $\lambda = 0{\cdot}65\,\mu$m and approaches $\sim 10\%$ at $\lambda > 1{\cdot}0\,\mu$m. The property that $T(\lambda)$ falls off abruptly above a certain critical temperature is a characteristic feature of thermochromism. In figure 5 it is seen that $R(\lambda)$ depends on τ, particularly in the infra-red, but not in the same

way as $T(\lambda)$. At $\tau > \tau_c$, $R(\lambda)$ increases at $\lambda > 0{\cdot}8\,\mu m$ and reaches $\sim 50\%$ at $2{\cdot}5\,\mu m$. This feature is consistent with metallic behaviour. At both $\tau < \tau_c$ and $\tau > \tau_c$, $R(\lambda)$ has several peaks. They are caused by interference in the thick film.

3. Discussion and conclusion

Vanadium dioxide thin films were prepared by reactive r.f. magnetron sputtering in argon and oxygen ambient. The As-deposited films did not exhibit the desired property of VO_2 and they were post-treated. Electrical measurements suggest that the phase transition of the oxides depend entirely on preparation condition such as oxygen pressure and substrate temperature. The study also indicates that stoichiometric VO_2 can be achieved at O_2 pressure of 2·4%. The deposition rate of the oxides is strongly dependent on O_2 pressure and the rate decreases with increasing O_2 pressure. In our experiment the deposition rate of VO_2 of about 130 Å/min at O_2 pressure of 2·4% was obtained. Optical studies of VO_2 films in the whole solar range (0·3–2·5 μm) were carried out and it was found that both transmittance and reflectance spectra exhibited the property of thermochromism. The experimental evidence therefore suggests that reactive r.f. magnetron sputtering is a suitable technique for obtaining good quality vanadium dioxide thin films and they exhibit the property of thermochromism which is suitable for potential application in the utilization of energy-efficient devices.

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