

## Hall Effect Parameters of Aluminium and Tungsten Co-Doped VO<sub>2</sub> Thin Films

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### Abstract

The Hall Effect parameters of Al and W co-doped VO<sub>2</sub> thin films were studied in order to explain the effect of co-doping on the electrical properties of thermochromic VO<sub>2</sub> films. The carrier concentrations and conductivity of the films were found to increase with increase in temperature while carrier mobility decreased reaching a minimum around the transition temperature then slightly rose and became stable at high temperatures. Tungsten doped films displayed higher carrier concentrations and conductivity on both sides of the metal insulator transition and lower mobility compared to undoped and Al and W co-doped VO<sub>2</sub> thin films.

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Keywords: Vanadium dioxide, Hall effect, Carrier concentration, carrier mobility

### Introduction

Vanadium dioxide is one of the thermochromic transition metal oxides which transform from metal to semiconductor upon cooling or heating across a transition temperature,  $\tau_c$  (Alder 1968, Kivaisi and Samiji 1999). The transition may involve changes in structural, optical, electrical as well as electronic properties. At temperatures below the transition temperature of 68 °C, VO<sub>2</sub> is a semiconductor having a monoclinic structure, while above the transition temperature it is a metal having a rutile or tetragonal structure (Goodenough 1971, Zylbersztejn and Mott 1975). In low temperature semiconducting state, VO<sub>2</sub> thin films are transparent in the infrared part of the solar spectrum whereas in high temperature metallic state the films become infrared reflecting (Lee and Choo 2000, Mlyuka and Kivaisi 2006). This optical property switch can be employed in smart windows for automatic control of solar throughput into buildings. Some of the challenges facing VO<sub>2</sub> films for smart window applications are too high transition

temperature and low luminous transmittance (Mlyuka and Kivaisi 2006, Li et al. 2012).

Tungsten (W) doping has been reported to lower the transition temperature of VO<sub>2</sub> films to comfort levels but with compromised luminous transmittance (Burkhardt et al. 2002, Jiazhen et al. 2008). Co-doping of tungsten and aluminium on VO<sub>2</sub> thin films showed an increase in solar and luminous transmittance compared to undoped films. The transition temperature was lower than that of undoped VO<sub>2</sub> films, but not as low as those doped with W (Lyobha 2013). Doping of VO<sub>2</sub> thin films also affects the Hall Effect parameters such as carrier mobility, carrier concentration, conductivity and resistance (Lin et al. 2013, Ruzmetov et al. 2009). This paper reports on the effect of aluminium and tungsten co-doping on the Hall Effect parameters of vanadium dioxide thin films.

### Materials and Methods

The VO<sub>2</sub>, VO<sub>2</sub>:W thin films were deposited on soda lime glass substrates by reactive dc magnetron sputtering of 99.9% pure metallic

V, V (99%) – W (1%) alloy targets. VO<sub>2</sub>:W:Al films were prepared from V–W targets with aluminium pellets. The sputtering and reactive gases, argon and oxygen of purities 99.999% and 99.9%, respectively, were used for films deposition. The deposition time, power and temperature were fixed at 25 minutes, 200 watts and 450 °C, respectively. The working pressure was about  $5.6 \times 10^3$  to  $6.2 \times 10^3$  mbar. Deposition rates were used to predetermine film thickness at a fixed value of 150 nm that was later confirmed by Tencor Alpha step IQ surface profiler. The Ecopia- HMS–3000 Hall Effect measurement system was used to determine the electrical conductivity, carrier concentration and carrier mobility of VO<sub>2</sub>, VO<sub>2</sub>:W and VO<sub>2</sub>:W:Al thin films using van der Pauw geometry (van der Pauw 1958). These parameters were recorded at different temperatures from 25 °C to 100 °C for both heating and cooling cycles. Before taking the measurements, the samples were cut into 1 × 1 cm square and Sn/In ohmic contacts were mounted on each corner of the film to ensure good film conductivity. The current used was 1 μA which suits for semiconductor/insulator materials. The temperature of the sample was monitored using an autonics temperature controller.

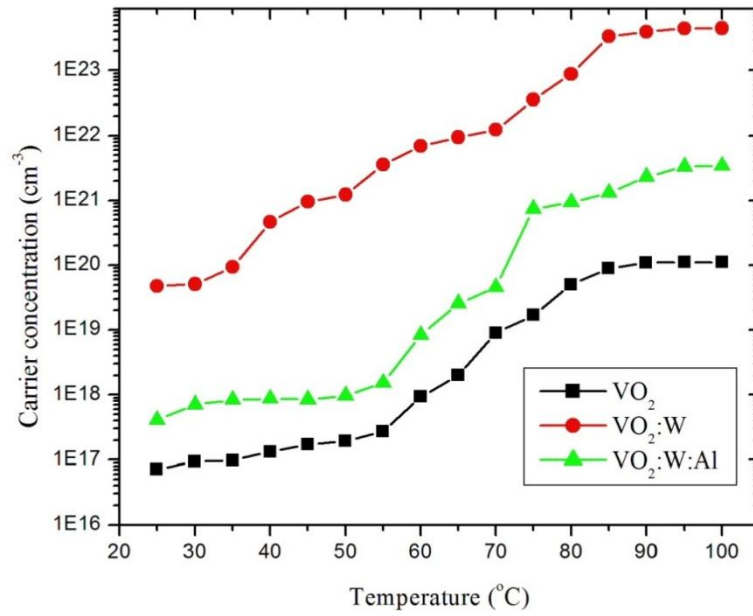
### Results and Discussion

The variation of carrier concentrations with temperature for undoped, tungsten doped and tungsten-aluminium co-doped VO<sub>2</sub> thin films are shown in Figure 1. The films exhibited an increase in carrier concentration with increase in temperature. At room temperature the films exhibited carrier concentration of  $2.4 \times 10^{16}$ ,  $6.3 \times 10^{19}$  and  $4.1 \times 10^{17} \text{ cm}^{-3}$  and increased rapidly with temperature to about  $1.1 \times 10^{20}$ ,  $5.5 \times 10^{23}$  and  $3.5 \times 10^{21} \text{ cm}^{-3}$  at 100 °C for VO<sub>2</sub>, VO<sub>2</sub>:W and VO<sub>2</sub>:W:Al thin films, respectively. The change in concentration is about three orders ( $10^3$ ) of magnitude across

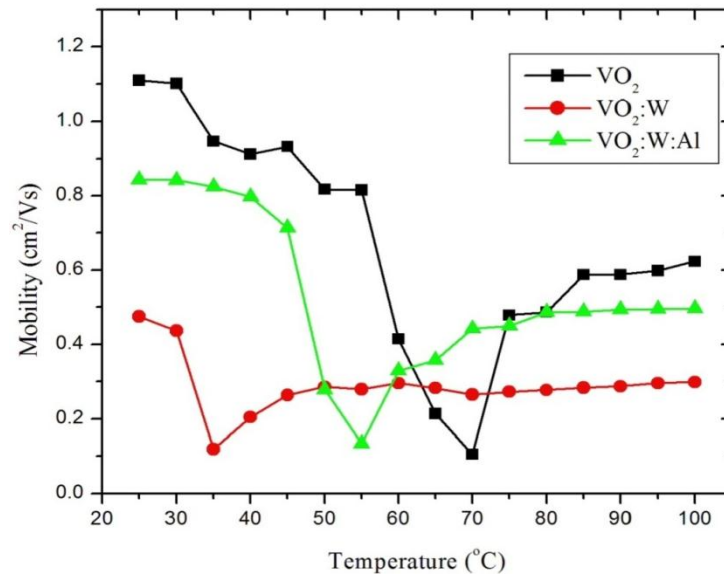
the metal insulator-transition for undoped, W-doped as well as W and Al co-doped VO<sub>2</sub> thin films. These results are consistent with the values found in VO<sub>2</sub> thin films reported by other authors (Ruzmetov et al. 2009). VO<sub>2</sub>:W films have higher carrier concentrations on both sides of the metal insulator transition (MIT) compared to the undoped VO<sub>2</sub> and VO<sub>2</sub>:W:Al thin films fabricated using the same deposition parameters. The presence of higher carrier concentrations in VO<sub>2</sub>:W thin films was also observed by Batista et al. (2011). This is due to the fact that tungsten dopant (W<sup>6+</sup>) can donate two extra electrons in VO<sub>2</sub> crystal increasing the carrier density and consequently the band structure of VO<sub>2</sub> films (Tang et al. 1985, Wu et al. 2015).

The addition of Al dopant into the VO<sub>2</sub>:W thin films lowered the carrier concentration and raised the transition temperature compared to VO<sub>2</sub>:W. The substitution of Al ions in W doped VO<sub>2</sub> gives rise to stabilization of the insulating phases resulting to the increase in transition temperature of co-doped VO<sub>2</sub> films compared to W-doped VO<sub>2</sub> thin film (Ghedira et al. 1977, Strelcov et al. 2012).

The variations of carrier mobility with temperature for undoped and doped VO<sub>2</sub> films were plotted on the same pair of axes as shown in Figure 2. It was observed that carrier mobility of all the films in the semiconducting phase is higher than that in the metallic phase and varies slightly across the MIT. Electrons were found to be the majority carriers on both sides of the MIT. These observations are similar to those reported by Ruzmetov et al. (2009). The mobility of doped films was less than undoped VO<sub>2</sub> thin films mostly due to scattering by the impurities Al and W atoms.



**Figure 1:** Variation of carrier concentration with temperature for  $\text{VO}_2$ ,  $\text{VO}_2:\text{W}$  and  $\text{VO}_2:\text{W}:\text{Al}$  thin films.



**Figure 2:** Carrier mobility for  $\text{VO}_2$ ,  $\text{VO}_2:\text{W}$  and  $\text{VO}_2:\text{W}:\text{Al}$  thin films as function of temperature.

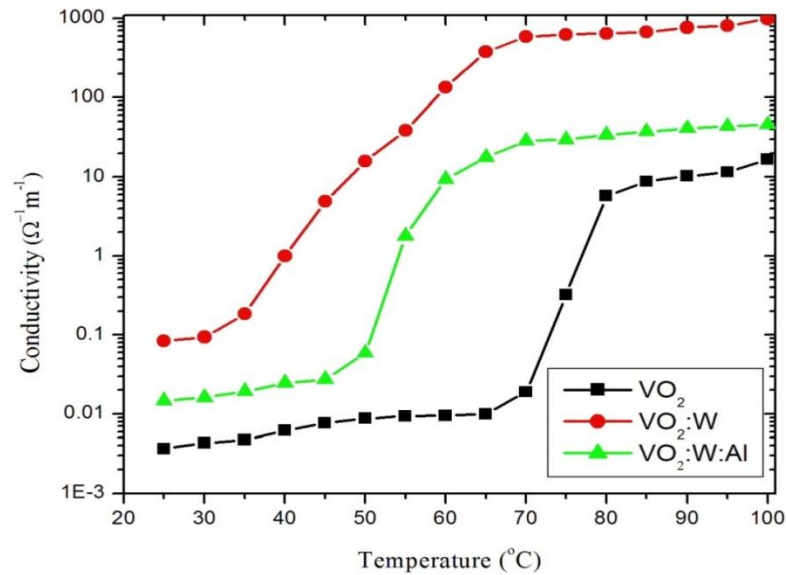
The mobility of the VO<sub>2</sub>, VO<sub>2</sub>:W and VO:W:Al thin films as shown in Figure 2 were 1.1094, 0.4753 and 0.8431 cm<sup>2</sup>/V sec at the insulating phase and 0.6235, 0.2985 and 0.4965 cm<sup>2</sup>/V sec at the metallic phase, respectively.

Figure 3 shows conductivities,  $\sigma$  ( $\Omega^{-1}m^{-1}$ ) as a function of temperature for VO<sub>2</sub>, VO<sub>2</sub>:W and VO<sub>2</sub>:W:Al thin films. Conductivity is observed to increase with increase in temperature as was also reported by other authors (Nazari et al. 2011). The conductivities of the W-doped VO<sub>2</sub> films were higher on both sides of the MIT compared to the co-doped and undoped VO<sub>2</sub> thin films. The changes in conductivities across the MIT were of about two orders of magnitude for all the films. This was also

reported by other authors for high-quality polycrystalline VO<sub>2</sub> thin films (Rozgonyi and Hensler 1968).

The carrier concentrations, conductivities and mobility for three samples of VO<sub>2</sub> thin films at 25 °C and 100 °C are summarized in Table 1.

The conductivities for all the films correlate well with the career concentrations of the films as expected since the two parameters are directly proportional to each other. However, mobility did not significantly influence conductivity as has been reported by other authors (Fu et al. 2013).



**Figure 3:** Temperature dependent conductivity of VO<sub>2</sub>, VO<sub>2</sub>:W and VO<sub>2</sub>:W:Al thin films.

**Table 1:** The conductivities, carrier concentrations and mobility for VO<sub>2</sub>, VO<sub>2</sub>:W and VO<sub>2</sub>:W:Al thin films in the semiconducting and metallic phases

Semiconducting phase (25 °C)				Metallic phase (100 °C)		
Sample	n (cm <sup>-3</sup> )	σ (Ω <sup>-1</sup> m <sup>-1</sup> )	μ (cm <sup>2</sup> /V sec)	n (cm <sup>-3</sup> )	σ (Ω <sup>-1</sup> m <sup>-1</sup> )	μ (cm <sup>2</sup> /V sec)
VO <sub>2</sub>	2.36 x 10 <sup>16</sup>	3.64 x 10 <sup>-3</sup>	1.1094	1.12 x 10 <sup>20</sup>	1.66 x 10 <sup>1</sup>	0.6235
VO <sub>2</sub> :W	6.31 x 10 <sup>19</sup>	8.34 x 10 <sup>-2</sup>	0.4753	5.47 x 10 <sup>23</sup>	9.85 x 10 <sup>2</sup>	0.2985
VO <sub>2</sub> :W:Al	4.07 x 10 <sup>17</sup>	1.47 x 10 <sup>-2</sup>	0.8431	3.46 x 10 <sup>21</sup>	4.57 x 10 <sup>1</sup>	0.4965

### Conclusion

The reactive DC magnetron sputtering method was used to deposit VO<sub>2</sub>, VO<sub>2</sub>:W and VO:W:Al thin films on soda lime glass slides at 450 °C in a mixed Ar/O<sub>2</sub> atmosphere. The films were fabricated from metallic vanadium target (99.9 % pure), V–W alloy target (V 99% - W 1%) and V–W alloy target attached with aluminium pellets (99.99% pure). The Hall Effect measurements across the metal insulator transition (MIT) of the films were successfully studied and showed a strong correlation between carrier concentrations and conductivities of the films. Career mobility did not significantly influence conductivity.

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