

# Electrical Conducting Behavior of W- Doped VO<sub>2</sub> Thin Films / La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> Heterostructure

Chun-Chi Lin, Yi Hu, and Jiun-Shing Liu

**Abstract**—W-doped vanadium oxide thin films were obtained by sol-gel spin coating process on the pre-heat treated silicon wafer. The precursor for thin film coating is prepared with vanadium methanol solution. These films were post annealed at 580°C for 30 min under controlled air pressure. The average thickness of the films was about 60 nm. The predominant phase of the films is monoclinic VO<sub>2</sub> from Raman spectra analysis. These thin films exhibit a metal-semiconducting transition. The transition temperature was lowered from 68°C to 34°C by doping with tungsten cation with 15%W. A heterostructure was made by stacking the VO<sub>2</sub> films on the La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (LSCO) thin films. The LSCO thin film of about 300nm thickness was obtained by r.f. magnetron sputtering deposition process. An apparent rectifying behavior was observed for a p-n junction of VO<sub>2</sub>/La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (LSCO). The reverse bias current is characterized by a reverse threshold voltage of ~4.2V at 40°C and decrease to ~3V at 80°C. The rectifying properties show temperature dependence under the metal-semiconducting transition of VO<sub>2</sub>.

**Index Terms**—Thin films, sol-gel method, phase transition, heterostructure.

## I. INTRODUCTION

The material vanadium oxide is particularly interesting for their novel potentials on many application fields. In this family, vanadium dioxide (VO<sub>2</sub>) is one of the most extensively studied transition-metal oxide, which undergoes first-order thermal induced Insulator to Metal-Transition (IMT) at 68°C [1]. The IMT of VO<sub>2</sub> comes from a structural phase change from monoclinic phase (T<68°C) to a tetragonal phase (T>68°C). The low temperature monoclinic phase is semiconducting phase (or insulator) and infrared transparent while the high temperature tetragonal phase is metallic phase and infrared reflective. This change from semiconducting to metallic properties and related changes in optical properties makes VO<sub>2</sub> an ideal candidate for many potential applications including intelligent window coatings [2], [3], optical switch [4], data storage [5], [6] and infrared modulators in missile guidance systems [7].

For the more practical applications, there have been many approaches to reduce the transition temperature of VO<sub>2</sub> such as doping element with higher valence, different substrate type and various fabrication techniques [8]-[11]. In this study, we prepare VO<sub>2</sub> thin films by sol-gel method with W element doping of different doping concentrations.

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In the last decades, many techniques for thin film growth including sputtering [12], [13], evaporation [14], [15], pulsed laser deposition [16], and sol-gel process [17], [18], etc. have been adopted to deposit VO<sub>2</sub> films on various substrates. Among these techniques of thin-film deposition, sol-gel technique is potentially the most practical for its specific properties, especially its low-temperature synthesis route for both homogeneous and co-doped films at a comparatively low cost. This paper describes the properties of vanadium dioxide (VO<sub>2</sub>) synthesized by sol-gel dipping process with vanadium oxyacetylacetonate. These films exhibit good rectifying behavior when they were made into heterostructure with La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (LSCO) thin films and appear to be good candidates for the production of smart thin films.

## II. EXPERIMENTAL PROCEDURE

For a switch device, the structure of the p-n heterojunction as fabricated is SiO<sub>2</sub>/(LSCO)/VO<sub>2</sub>, where LSCO is a p-type semiconductor. The LSCO thin films were first deposited with the wafer mask on the top of annealed Si wafer by r. f. magnetron sputtering at a working power of 100W with a 1.067 Pa working pressure in different Ar:O<sub>2</sub> sputter gas ratio mixture (Ar=10 sccm, O<sub>2</sub>=10 sccm) for 45 min. The VO<sub>2</sub> thin films were deposited on the LSCO thin films by sol-gel method.

The precursor for the thin film coating was prepared by dissolving vanadium (IV) oxyacetylacetonate in methanol with concentration of 0.125M. To prepare the impurity-doped films, the appropriate amount of WCl<sub>6</sub>, which was dissolved in ethanol, was added into the vanadium solution. The molar percentage of doped tungsten varied in the range of from 0 to 15mol%. The precursor sol was aged for a week and became usable for thin films coating. On the other hand, the Si wafer substrate was preheated at 1000°C for one hour to make a silica layer. The film was coated on the substrate with a spin rate of 1500 rpm for 15s. The films were then dried at 80°C for 10 min to drive off the solvent. The above procedure was repeated once. Finally, the films were then heat annealed first at 300°C for 20min in air and then increased the temperature to 530°C for 30 min in nitrogen.

The surface morphology of the deposited vanadium oxides thin films was examined by field-emission scanning electron microscope (FE-SEM, JEOL, JSM-6700F). Raman spectra were performed on a Renishaw inVia Raman Microscope with He-Ne laser. The electrical measurements were conducted by the standard four-point probe method using an electrometer (Jiehan, SRS-4020) at varied temperature. The I-V characteristics were measured by the standard two-probe

method using the Keithley 4200 characteristic system.

### III. RESULTS AND DISCUSSION

Typical SEM cross-sectional images of the films were shown in Figure 1. The thin film are dense and the thickness of the LSCO thin film is about 450nm as in Fig. 1 (a). The thickness of VO<sub>2</sub> thin films is about 60 nm as in Fig. 1(b). The microstructure shows the LSCO films very dense and uniform. The heterostructure shows the good contact between LSCO and VO<sub>2</sub> films.

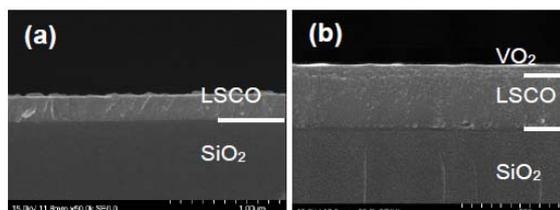


Fig. 1. The SEM cross-sectional images of VO<sub>2</sub> thin films on the LSCO films.

Fig. 2 shows the SEM surface images of the VO<sub>2</sub> thin films as function of the doped W content. It was found that the grains are densely packed with abnormal grain size for the sample without doping as in Fig. 2(a). The abnormal grain growth was due to the heat treating temperature is close to the melting temperature of Vanadium oxide (690°C) and the volatile behaviour of vanadium oxide. The grain size of the films was evidently decreased with w-doping as in Fig. 2(b) ~ (f). The film as in Fig. 2(e) are made of small crystals (~20nm) separated by well-defined grain boundaries. The addition of W into thin film can depress the volatile property of VO<sub>2</sub> and thus decrease the growth rate.

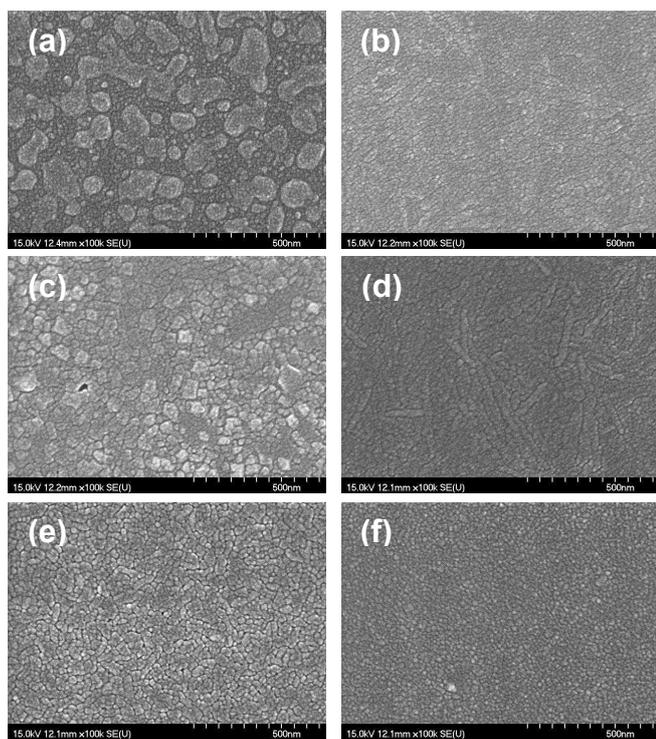


Fig. 2. The SEM morphology of the annealed VO<sub>2</sub> thin films with different amount of doped W: (a) 0 wt%; (b) 2wt%; (c) 4wt%; (d) 6wt%; (e) 8wt%; (f) 10wt%.

Fig. 3 shows the typical Raman spectra of the thin films and different temperature. It was found that the vanadium oxide films has the monoclinic structure, which VO<sub>2</sub> has a distorted rutile with altogether 15 IR-active modes and 18 Raman ones [19]. It was found that samples show the peaks 305, 370, 617 and 645 cm<sup>-1</sup>, which are the Raman phonon mode of VO<sub>2</sub>. The peak at 520cm<sup>-1</sup> is from the Si optical phonon of the substrate. The intensity of these peaks at 304 and 626 cm<sup>-1</sup> for VO<sub>2</sub> phase increased apparently as the temperature increased as seen in Fig. 3. This is suggested from the metal-to-semiconductor (IMT) phase transition. There are no apparent differences among the Raman spectra to be found against the variation of W-doping content. However, the intensity of the 645 cm<sup>-1</sup> peak would increase at low temperature when the W-doping content increases. This mode was depressed when the temperature was higher than the transition temperature as in Fig. 3. This indicates the crystalline orientation of the VO<sub>2</sub> thin film would vary for phase transition. The apparent change of the Raman mode for thin film with higher W-doping content as suggested resulting from the change of the microstructure into nano-size grains as in Fig. 2(d). The nano-size grain can easily bear the internal stress caused from the phase transition and the rearrangement of the ions.

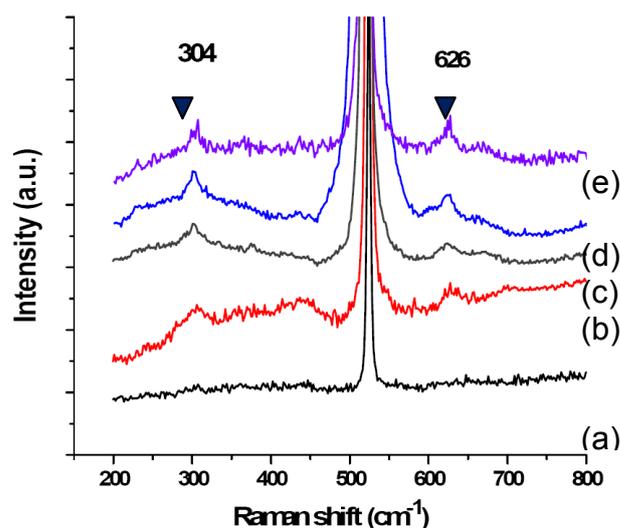


Fig. 3. Typical Raman spectra of the samples with 6% W-doping content at different temperatures of (a) 40 °C, (b) 50 °C, (c) 60°C, (d) 70 °C, (e) 80°C.

Fig. 4 shows the temperature dependence resistance of the vanadium oxide films with different content of W. The films qualities were very sensitive to the W-doping content. Semiconductor-to-metal phase transitions are clearly seen for all samples. The transition temperatures for films without doping are 68 and shift to lower temperature by W-doping as 45°C for 3mol%W, 40°C for 9mol%W, and 34°C for 15mol%W. The samples show a typical semiconductor characteristic of a decreasing electrical resistance with increasing temperature below the transition temperature. However, electrical resistance still slightly decreases with increasing temperature above the transition temperature and do not follow the metallic conducting behaviour. Two major reasons were believed to be responsible for phenomena. One is due to crystallinity of the film. An increased number of atoms distributed randomly at grain boundaries and/or a large

surface/interface ratio for a very thin VO<sub>2</sub> film, may damage the zigzag chains of the V–V pairs characteristic and result in the increase of resistance at certain range of temperature. The second is that the total stress in the film would be also a possible reason attributed to the different thermal expansions between the VO<sub>2</sub> thin films and substrate.

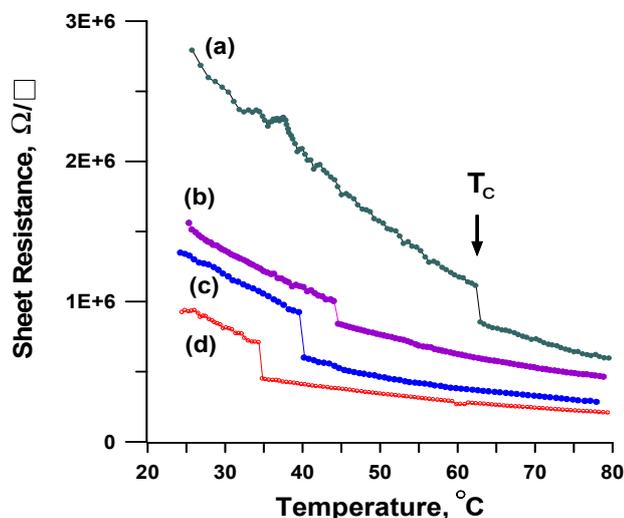


Fig. 4. Comparison of electrical switching curves for VO<sub>2</sub> films with various amount of doped W of (a) 0mol%, (b) 3mol%, (c) 9mol%, (d) 15mol%, via annealing temperature.

Fig. 5 shows the transition temperature of the samples as a function of the doped W content. The transition temperature of the VO<sub>2</sub> thin film decreased as the doped W content increased. According to the model of Tang *et al.* [19], the incorporation of W atoms leads to the loss of V<sup>4+</sup>–V<sup>4+</sup> pairs, which are essential for the crystal structure of the semiconducting phase [20], [21].

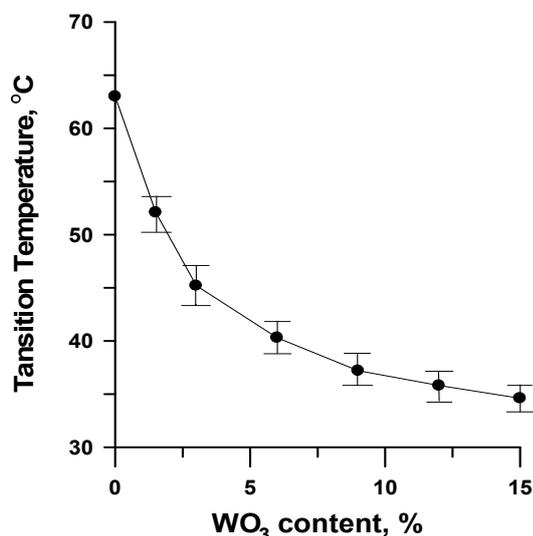


Fig. 5. Transition temperature of the samples as a function of the doped W content.

Tungsten is also an electron donor, and thus the destabilisation of the semiconducting phase is supported.

For VO<sub>2</sub> semiconductor phase, the resistance  $R$  was determined by the intrinsic carrier concentration and mobility as [20]:

$$R = R_0 \exp(E_a/kT) \quad (1)$$

where  $R_0$  was the resistance at  $T \rightarrow \infty$ ,  $E_a$  was the activation energy, which was the forbidden band gap, and  $k$  is Boltzmann constant. By calculation the corresponding conduction activation energy  $E_a$  from eq. (1) was about 0.37 eV for the low temperature phase and about 0.06 eV for the high temperature phase. The large difference of the activation energies between the two phases confirms the semiconductor-metal transition.

A heterojunction composed of La Sr CoO and VO<sub>2</sub> without doping was fabricated and exhibited good rectifying properties (I-V characteristics) as in Fig. 6. The asymmetric current-voltage relations for the junctions display forward shape and can be viewed as a Schottky diode. However, the forward-to-reverse current ratio is about 1.1 for higher applied voltage. This indicates that the p-type and n-type semiconductors have almost equivalent conductivity. An apparent but rather ill-defined forward threshold voltage occurs at  $\sim 0.8V$ , which is often identified as the diffusion or built-in potential for carriers to surmount. In addition, it was found that the threshold voltage decreased as the temperature increased. The I-V curve becomes linear at large forward voltage and the diode shows a relative large current can be obtained at the temperature higher than the phase transition temperature as in Fig. 6(e).

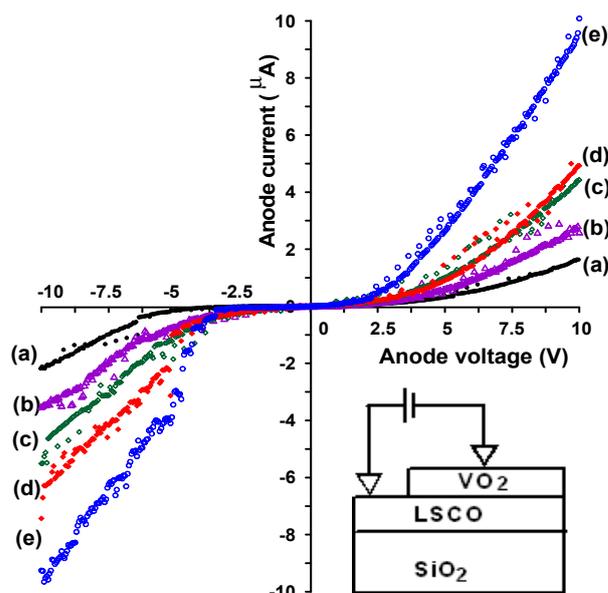


Fig. 6. The I-V characteristics of the LSCO/VO<sub>2</sub> heterojunction as a function of temperature at (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, (e) 80°C

On the other hand, the reverse bias current is characterized by a reverse threshold voltage of  $\sim 4.2V$  at 40°C and decrease to  $\sim 3V$  at 80°C. It has been reported that the chemically stoichiometric La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> behaviour like a metal without energy gap [22]. The reverse threshold voltage is ascribed to the difference of the Fermi energies between LSCO and VO<sub>2</sub>. The temperature dependent I-V behaviour ascribed to the phase transition has a potential application as temperature sensitive diode.

#### IV. CONCLUSION

W-doped VO<sub>2</sub> thin films were successfully prepared by

sol-gel spin coating process. The films qualities were very sensitive to the W-doping content. The thickness of the VO<sub>2</sub> films was in the range of 50~60 nm. The transition temperatures for films without doping are 68 and shift to lower temperature by W-doping as 45°C for 3mol%W, 40°C for 9mol%W, and 34°C for 15mol%W. A heterojunction composed of La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> and VO<sub>2</sub> with W-doping was fabricated and exhibited good rectifying properties. The rectifying properties show temperature dependence under the metal-insulating transition of VO<sub>2</sub>. The forward and reverse threshold voltages were about 0.8V and 4.2V, respectively, and both decreased as the temperature increased.

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