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Characterization of vanadium oxide thin films with different stoichiometry using Raman spectroscopy

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ABSTRACT

Vanadium oxides (VO_x) have been widely studied as "smart materials" because of their capability of going through a reversible metal-insulator-transition. They are of considerable technological interests for applications in optoelectronics, ultrafast optical switches, electrochomic devices, and lithium microbatteries. However, vanadium-oxygen system is complicated due to the multivalency of vanadium, which makes preparation of VO_x with single stoichiometry difficult. Therefore, structural characterization of vanadium oxides of different stoichiometriesis highly desirable and would provide helpful guideline to both materials preparation and their structural characterization. In the present work, VO_x thin films with different stoichiometries under various bonding states were successfully prepared by reactive sputtering with and without post oxidation or reduction and characterized using Raman spectroscopy. Characteristic Raman spectra of single and multi- valence states of VO_x including V_2O_3, VO_2, V_6O_{13}, and V_2O_5 are presented and discussed. The results have demonstrated that high purity VO_x thin films with single stoichiometry can be obtained under well controlled conditions.

1. Introduction

Vanadium oxides (VO_x) have attracted extensive attention because of their capability of going through a reversible metal-insulator-transition (MIT), during which the electrical conductivity can change by several orders of magnitude [1]. This remarkable and reversible transition makes them of considerable technological interests. For example, VO_2 undergoes an MIT at 68 °C, along with a dramatic change in its optical properties in the near infrared band, making it highly suitable for applications such as optoelectronics, ultrafast optical switches, and smart windows [2–4]. V_2O_3 and V_2O_5 have been widely used as catalysts in gas sensors, lithium ion battery as well as a variety of industrial processes [5–7]. V_2O_5 can also be found in electrochromic devices as electrochromic layers [8].

However, it remains a great challenge to deposit VO_x thin films with single stoichiometry. First, this is because the vanadium-oxygen system is highly complicated due to the multivalency of vanadium. In phase diagram, there are nearly twenty stable VO_x phases, such as VO, V_2O_3, V_4O_7, V_6O_{11}, VO_2, V_6O_{13}, V_4O_9, and V_2O_5, while each VO_x is stable only within a narrow window [9]. Second, structural characterization of VO_x of different stoichiometry is complicated and incomplete due to its complex valence states. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy are usually used to identify their bonding states and the phase structure. However, XRD is not highly sensitive and cannot identify minor amount of impurity phases [10]. And the XPS analysis of VO_x materials usually involves curve fitting because of the overlapping of the peaks and need the assistance of XRD analysis [11]. Relatively, Raman spectroscopy is a more powerful structure characterization technique for VO_x because of its high sensitivity. However, the interpretation of Raman spectra relies on comparing the measured spectra with reference spectra and available Raman data for VO_x are limited and in some cases unclear [12,13]. Those obstacles in structural characterization of VO_x add difficulties to the synthesis of VO_x thin films with single stoichiometry. VO_x thin films with unidentified impurity phases usually lead to unexpected poor performance in applications.

In this research, VO_x thin films with different stoichiometries under various bonding states are successfully prepared by reactive sputtering with and without post oxidation or reduction. The samples were then characterized using Raman spectroscopy and thus the phase evolution could be clarified. The results presented would facilitate both vanadium oxide materials preparation and their structural characterization.

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Table 1
Deposition parameters for preparation of vanadium and vanadium oxide thin films using sputtering and their thickness.

Power (W)	Voltage (V)	O_2 flow rate (sccm)	Ar flow rate (sccm)	Temperature (°C)	Gas pressure (kPa)	Deposition time (min)	Film thickness (nm)
75	120	0	35	30	1.33	70	115
200	379	1.5	100	500	1.33	120	178
200	360	1.5	50	500	1.33	120	175
100	361	1.3	100	500	1.33	120	164
200	426	2	50	500	1.33	120	187
200	437	2.5	50	500	1.33	120	189
200	454	3	50	500	1.33	120	180

2. Experimental details

Vanadium and VO_x thin films were deposited on Si (100) wafers by magnetron sputtering of high purity vanadium target (99.95%) in the environment of Argon (Ar) without and with oxygen (O_2), respectively. The deposition conditions and the thickness of the as-deposited thin films are listed in Table 1. A series of VO_x thin films with different x were obtained by changing the gas flow ratio of O_2/Ar at a constant substrate temperature of 500 °C.

In addition to sputter deposited VO_x samples, VO_x thin films of different stoichiometries were also prepared by oxidation of vanadium (V) thin films and reduction of V_2O_5 thin films. The oxidation involves annealing the as-deposited V thin films in a furnace at 400 °C in air with a period ranging from 10 min to 4 h to develop different stoichiometries (the heating and cooling rate were 17.9 °C/min and 7.2 °C/min respectively). The reduction involves annealing the as-deposited V_2O_5 thin films in a furnace in protected Ar environment at either 450 °C or 500 °C in atmospheric pressure with a period ranging from 20 min to 10 h to develop different stoichiometries (the heating and cooling rate were 15.7 °C/min and 5.5 °C/min respectively). The equilibrium has been reached because longer treatment did not make any difference. And each experiment and its result have been repeated for three times and they were reproducible.

After sample preparation, the as-prepared VO_x thin films were characterized by Raman spectroscopy with assistance of XRD (Cr target). The Raman spectra were taken at room temperature using a Renishaw micro-Raman system 2000 spectrometers located at the Saskatchewan Structural Science Center (SSSC), University of Saskatchewan. The operating laser wavelength was 514.5 nm, which gives approximately 1 cm^{-1} spectral resolution, the laser power at the sample was 1.45 mW to prevent changing the structure of the samples, the spot size was approximately 2 μm, and the spectral position was verified by internal Si (110), which is 520 cm^{-1}. It is important to note that the Raman measurement could cause oxidation and change the result by thermal effect. Therefore, we started the measurements with very low laser power and large spot size and controlled the surrounding atmosphere temperature low, and then adjusted the laser power in small increments to the set value in order to reduce the thermal effect. The laser power for this research should be low enough to prevent changing the structure of the samples because we repeated the Raman measurements of each sample for many times and the spectrum always remained the same.

3. Results and discussion

Oxidation of V thin films would allow oxygen in air gradually diffuse into the thin films and thus VO_x thin films of different stoichiometries with gradual increased oxygen fraction could be prepared, which were then characterized by Raman spectroscopy. The Raman spectra of such prepared VO_x samples with different oxidation during are shown in Fig. 1. Most of the VO_x thin films are multi-phases as shown in Fig. 1 (2)-(8) with annealing time ranging from 30 min to 3.5 h due to the complex valence states of vanadium. Single phase VO_2 and V_2O_5 thin

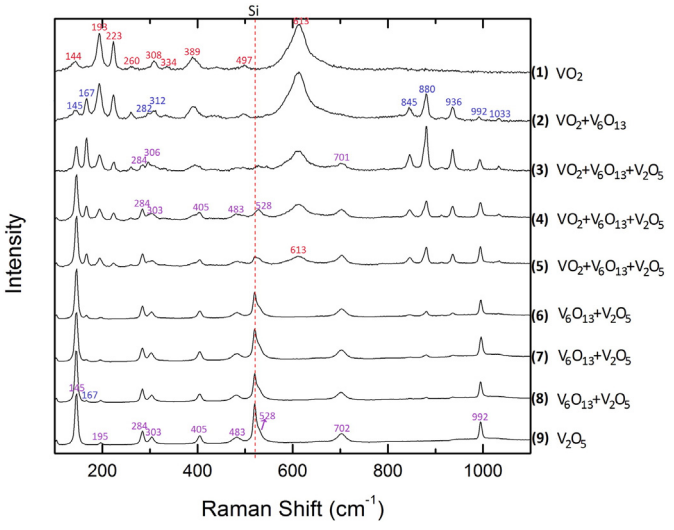

Fig. 1. Raman spectra of vanadium oxide thin films on Si prepared by oxidation of vanadium thin films at 400 °C for (1) 10 min, (2) 30 min, (3) 1 h, (4) 1.5 h, (5) 2 h, (6) 2.5 h, (7) 3 h, (8) 3.5 h, (9) 4 h.

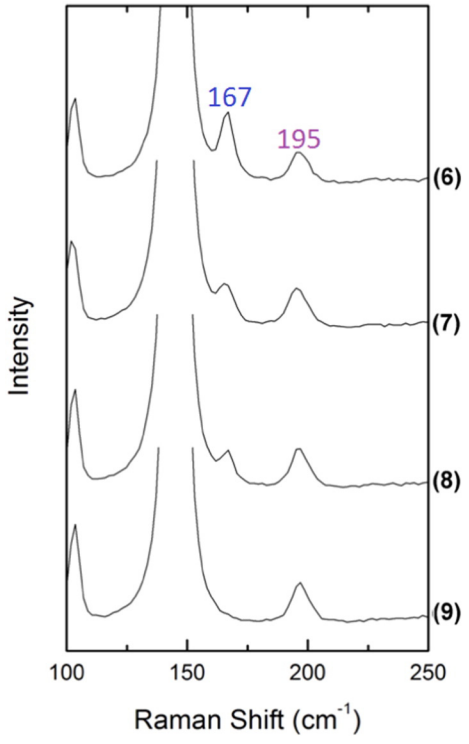

Fig. 2. Magnified view (100–250 cm^{-1}) of Raman spectra of vanadium oxide thin films on Si prepared by oxidation of vanadium at 400 °C for (6) 2.5 h, (7) 3 h, (8) 3.5 h, (9) 4 h.

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