Phase formation polycrystalline vanadium oxide via thermal annealing process under controlled nitrogen pressure

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Abstract. This article provides an approach to improve and control crystal phases of the sputtering vanadium oxide (V\(_2\)O\(_3\)) thin films by post-thermal annealing process. Usually, as-deposited V\(_2\)O\(_3\) thin films at room temperature are amorphous phase; post-thermal annealing processes (400 °C, 2 hrs) under the various nitrogen (N\(_2\)) pressures are applied to improve and control the crystal phase of V\(_2\)O\(_3\) thin films. The crystallinity of V\(_2\)O\(_3\) thin films changes from amorphous to α-V\(_2\)O\(_3\) phase or V\(_2\)O\(_7\) polycrystalline, which depend on the pressure of N\(_2\) carrier during annealing process. Moreover, the electrical resistivity of the V\(_2\)O\(_3\) thin films decrease from 10\(^3\) Ω cm (amorphous) to 6×10\(^{13}\) Ω cm (V\(_2\)O\(_7\)). Base on the results, our study show a simply method to improve and control phase formation of V\(_2\)O\(_3\) thin films.

1. Introduction
Metal-insulator transitions (MIT) are reversible changes in the conductivity of materials when the temperature above or below the transition point, which are the smart transitions in advanced material [1]. Vanadium oxide (V\(_2\)O\(_3\)) demonstrated excellent MIT characteristics at the transition temperature (T\(_c\)) due to the lattice distortion such as VO\(_2\) (68 °C), V\(_2\)O\(_7\) (-23\(^\circ\)C), V\(_6\)O\(_{11}\) (-103 °C), V\(_8\)O\(_{17}\) (-194 °C) [2].

Several techniques have been applied to deposit vanadium oxide films such as sputtering, pulsed laser deposition and thermal evaporation. The sputtering technique demonstrated an excellent uniformity with high deposition rate, consequently the sputtering technique is promising to prepare V\(_2\)O\(_3\) thin film [3]. However, the sputtering V\(_2\)O\(_3\) thin films, which prepared at room temperature have amorphous phase. To improve the MIT or the crystallinity of V\(_2\)O\(_3\) films, the post-annealing controlled ambient processes were applied to recrystallize and control phase formation of the material.
2. Experiment and methods
Vanadium oxide thin films were deposited on glass slides from 2-inch vanadium sputtering target (Kurt J. Lesker) by pulsed DC magnetron sputtering (ATC 2000-F, AJA International, Inc.) at room temperature. High purity (99.999%) of Argon (Ar) gas and Oxygen (O_2) gas were used as the sputtering gas and the reactive gas, respectively, both of them were controlled by mass flow controller (1179A, MKS). V_2O_3 thin films have grown at base pressure 2×10^{-5} mbar. To find out the oxide mode in reactive sputtering process, the flow rate of Ar was fixed at 45 sccm and various flow rates of O_2 were controlled at 0, 5, 10 and 15 sccm before introduced into the chamber [4]. Then, the operating pressure was set at 5×10^{-3} mbar by automatic gate valve. The pulsed DC power was set at 300 W and the deposited time was 60 minutes, respectively. To improve crystallinity of V_2O_3, as-deposited thin films with O_2 flow rate 15 sccm were annealed at 400 °C for 120 minutes by using a contact heater under the various controlled nitrogen pressure in vacuum chamber. Annealing treatment was not performed higher than 400 °C to avoid the deformation of thin films at the high annealing temperature [5]. The electrical transport characteristics were evaluated by a four-point probe technique using precision DC source (6621, Keithley) and nano-voltmeter (2182A, Keithley). The temperature was controlled between 30-120 °C in the air by precision hot plate (1000-1, Electronic micro systems). After that, the crystalline phases of V_2O_3 thin films were investigated by X-ray diffraction (XRD) (Smartlab, Rigaku) using Cu-Kα (λ=1.54 Å) radiation. All measurements were taken by generator voltage of 40 kV and a current of 30 mA. Then, the chemical bondings of V_2O_3 were confirmed by confocal Raman spectroscopy using 532 nm Ar laser (NTEGRA Spectra, NT-MDT).

3. Results and Discussion
X-ray diffraction pattern by general 0-20 scanning mode shows in figure 1(a) According to database number (01-088-2322), a diffraction peak of a thin film without O_2 (0 sccm) shown at 2θ = 42.14°, which matched with the (110) plane of vanadium. The broad area between 20°-35° indicates the diffraction from the glass substrate. When we increased the O_2 flow rate (5, 10 and 15 sccm), the diffraction peaks of thin films were disappeared. Therefore, all of them were amorphous phase.

![Figure 1](image_url)

**Figure 1.** (a) X-ray diffraction pattern of V_2O_3 thin films at the O_2 flow rate 0-15 sccm. (b) Voltage bias on vanadium target with the various O_2 flow rate. (Inset: corresponding the image of thin films)

Figure 1(b) illustrated the increasing of voltage bias of target when the reactive O_2 flow rate increased during the sputtering process. The voltage bias abruptly changed from 388 V to 481 V in case of O_2 flow rate 5 sccm and slightly increasing for 10 sccm and 15 sccm. The difference in voltage biases revealed the oxide mode or the poisoning effect on target surface during the reactive sputtering [4]. The as-deposited thin films by pulsed DC magnetron sputtering with various O_2 flow rate shown as inset in figure 1(b). The sputtered thin films at the O_2 flow rate 5 sccm and 10 sccm were sub-oxide thin films, while the thin films at the O_2 flow rate 15 sccm has a yellow colour and transparent, which was possible to be the V_2O_5. Consequently, the O_2 flow rate 15 sccm was used to optimize for the post annealing process, and were used to characterize the electrical transport property, respectively.
When the operating pressure increased from $2 \times 10^{-6}$ to 1 mbar, the component peaks of mixed-phase $\alpha$-$\beta$O$_5$ decreased, while the component peaks of mix phase of $V_6$O$_{11}$ and $V_9$O$_{17}$ appeared and increased dramatically. At the nitrogen operating pressure 1 mbar, the diffraction pattern of the $V_9$O$_{17}$ film preferred to be $V_9$O$_{17}$ dominant rather than $V_6$O$_{11}$. The intensity ratios between (002) of $V_9$O$_{17}$ and (101) of $\alpha$-$\beta$O$_5$ were calculated, which were plotted as a function of nitrogen operating pressure, as presented in figure 3(b).
Further analysis was performed to confirm the chemical bonding by using Raman spectroscopy. Figure 4 illustrated nitrogen pressure-dependent Raman spectra of the V$_x$O$_y$ thin films as a function of the operating pressure. The intensity of Raman shifted spectra from the V$_2$O$_5$ thin film decreased; on the other hand the intensity of Raman shifted spectra from the V$_9$O$_{17}$ slightly increased when the operating pressure increased.

![Raman spectra](image)

**Figure 4.** Raman spectra of the post annealing V$_x$O$_y$ thin films.

According to above results, the applied thermal energy under the ambient of nitrogen contributed to deform grains and recrystallization of V$_x$O$_y$ thin films. Since, the oxygen atoms in thin films were carried out by thermal annealing process under controlled nitrogen pressure a vacuum chamber. The residual oxygen gas in annealing ambient decreased with increasing pressure of nitrogen gas, which suppressed higher valence state of V$_x$O$_y$ thin films [7]. Consequently, the crystallinity of the V$_x$O$_y$ thin films has changed from amorphous to polycrystalline structures, which leading to the reduced of resistivity when the operating pressure increased. Based on our strategy, we could improve the crystallinity and control V$_x$O$_y$ phase by the post-annealing process from as-deposited thin film growth. This method is simple and flexible for crystal phase controlling of the V$_x$O$_y$, which is an alternative method to prepared V$_x$O$_y$ materials for various applications, which depend on the transition temperature (T$_c$).

4. Conclusions
We offered a strategy to improve crystallinity and phase controlling of as-deposited sputtering V$_x$O$_y$ thin films via thermal annealing controlled nitrogen pressure. After annealing process, the crystallinity of V$_x$O$_y$ has changed from amorphous to polycrystalline phase. Consequently, we could measure the decreasing of resistivity from V$_x$O$_y$ thin film when the nitrogen operating pressure increased. Our research work has shown the flexible and simply method to improve crystallinity and phase controlling of V$_x$O$_y$ thin films for further development in advanced functional device.

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References
[1] Yang Z, Ko C and Ramanathan S 2011 *Annu. Rev. Mater. Res.* 41 337
[2] Nag J and Haglund Jr R F 2008 *J. Phys.: Condens. Matter* 20 264016
[3] Shigesato Y, Enomoto M, and Odaka H 2000 *Jpn. J. Appl. Phys.* 39 6016
[4] Saringer C, Franz R, Zorn K, and Mitterer C 2016 *J. Vac. Sci. Technol., A* 34 041517
[5] Liewhiran C and Phanichphant S 2007 *Sensor* 7 650
[6] Baddour-Hadjean R, Smirnov M B, Konstantin K S, Kazimirov V Y, Gallardo-Amores J M, Amador U, Arroyo-de Dompablo M E, and Pereira-Ramos J P 2012 *Inorg. Chem.* 51 3194
[7] Xu H, Huang Y H, Liu S, Xu K, Ma F, and Chu P K 2016 *RSC Adv.* 6 79383