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ORIGINAL PAPER

Raman spectroscopic characterization of the microstructure of V_2O_5 films

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Abstract The vanadium pentoxide (V_2O_5) films were deposited on silicon wafer by DC magnetron sputtering. By Raman scattering measurements, the microstructure properties of the V_2O_5 films prepared with different O_2–Ar gas flow ratios and annealed at different temperatures were studied, respectively. The results revealed that the increase of O_2–Ar gas flow ratio during sputtering was of advantage to prepare the V_2O_5 film with desired layer structure. A high post-annealing temperature (below 500 °C) induced the crystallization and the formation of the integrated structure of V_2O_5 film. However, it was found that both intensities of Raman scattering peaks at 146 cm^{-1} and 994 cm^{-1}, respectively, decreased for samples annealed at a temperature of 550 °C. The peak at 146 cm^{-1} was attributed to skeleton bent vibration and that at 994 cm^{-1} was due to the stretching vibration of vanadyl V=O_A bond. It showed that the high-temperature annealing was believed to have distorted the microstructure of V_2O_5 films. The oxygen vacancies were, therefore, induced, which benefited the formation of V-O_A-V bonds between layers. The result of X-ray diffraction measurements was in good agreement with that of Raman scattering spectra.

Keywords V_2O_5 films · Raman spectroscopy · Microstructure · Oxygen vacancy

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Introduction

Vanadium pentoxide (V_2O_5) has attracted much attention and been significantly studied recently due to its novel potentials as cathodes of rechargeable batteries such as rechargeable lithium battery [1–3], especially one of rare cathode materials of rechargeable magnesium battery [4–6]. As the cathodes of rechargeable batteries, the layer-type structure of V_2O_5 films may play an important role during the process of insertion or de insertion of metal ions such as Li^+ in the electrodes [7]. While the electrochemical properties of V_2O_5 films are tightly dependent on the film structure, it is very significant to study the microstructure of V_2O_5 film in relation to various preparation conditions.

In bulk V_2O_5, there are three structurally different oxygen atoms in each layer [8]: vanadyl oxygen, O_A; bridging oxygen atoms, O_B; threefold coordinated oxygen atoms, O_C (Fig. 1 [8, 9]). V_2O_5 crystallizes in the orthorhombic space group P_{mnm} (D_{2h}^{13}) with a=11.512, b=3.564, c=4.368 Å [9]. Under the D_{2h} factor group (k=0), the crystal modes can be classified as follows:

$$\Gamma_{opt} = 7A_g + 7B_{1g} + 3B_{2g} + 4B_{3g} + 3A_u + 3B_{1u} + 6B_{2u} + 6B_{3u}$$

All the g modes are Raman-active, while only B_u modes are infrared-active [10].

In literature, the microstructures of V_2O_5 film were reported to be very sensitive to the growth conditions [11]. Rajendra Kumar et al. had reported that V_2O_5 films deposited by vacuum evaporation at the depositing temperature of 573 K crystallized in orthorhombic symmetry, and the structural degradation observed with increase in the substrate temperature beyond 573 K was possibly due to

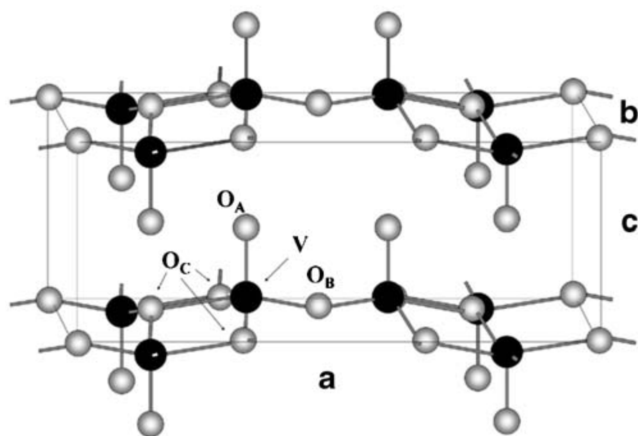

Fig. 1 V_2O_5 crystal structure. Vanadium atoms are depicted as the *black circles* and oxygen atoms are depicted as the *gray circles*. *a*-, *b*-, and *c*-axes of the orthorhombic unit cells are parallel to the [100], [001] and [010] plane, respectively [8, 9]

increase of non-stoichiometry [11, 12]. Moreover, Ganduglia-Pirovano et al. [8] had theoretically studied the vanadyl oxygen vacancy formation energy at the V_2O_5 (001) surface and proposed some models for the vacancy structure.

In this study, V_2O_5 films were deposited by DC magnetron sputtering at different preparing conditions. The aim of our study was to investigate the microstructure of V_2O_5 films, especially the formation of the oxygen vacancy on the V_2O_5 (001) surface using Raman scattering measurements and X-ray diffraction (XRD).

Experimental

The V_2O_5 films were prepared on silicon (111) wafers by DC magnetron sputtering with vanadium metal target (purity of 99.97%). The sputtering power was about 42 mW and sputtering duration was 1 h. During deposition, pure oxygen and argon gas were introduced into the chamber, and the flow ratio of O_2 to Ar was changed from 1/4 to 3/2. The preparation pressure was about 7.2 Pa, and the total gas flow during sputtering was maintained at 30 sccm. To investigate the effect of thermal stability of as-deposited films, V_2O_5 films prepared at an O_2/Ar gas flow ratio of 3/2 were annealed at different temperatures: 200 °C, 400 °C, 500 °C, 550 °C, respectively, for 2 h in air.

Raman scattering spectra were acquired at room temperature using the HORIBA Jobin Yvon HR800 laser micro-Raman spectrometer with a 532 nm laser. The spectral resolution was better than 1 cm^{-1}. XRD measurements were performed by using a Rigaku D/MAX-2400 diffractometer with monochromatized Cu Kα radiation (λ= 1.5406 Å).

Results and discussion

From Raman scattering measurements, a total of 21 vibration modes of V_2O_5 structures located in the high- and low-wave-number regions can be well distinguished [13, 14]. Raman scattering spectra of sputtered V_2O_5 films deposited with different O_2–Ar gas flow ratios are shown in Fig. 2. The sharp peak centered at about 520 cm^{-1} is a characteristic peak of single silicon substrate. The predominant low-wave-number band at 146 cm^{-1} is attributed to the skeleton bent vibration. The peaks at 198 and 286 cm^{-1} are due to the bending vibrations of the O_C-V-O_B bond. The bending vibration of V-O_C, the bending vibration of V-O_B-V bond and the stretching vibration of V-O_C bond occur at about 300, 404, and 706 cm^{-1},

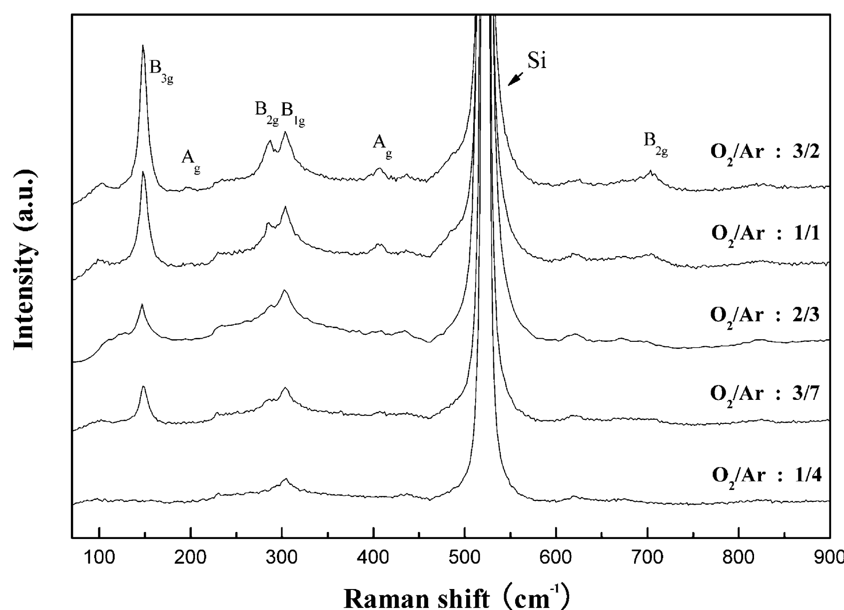

Fig. 2 Raman scattering spectra of sputtered V_2O_5 films deposited at different O_2/Ar gas flow ratios

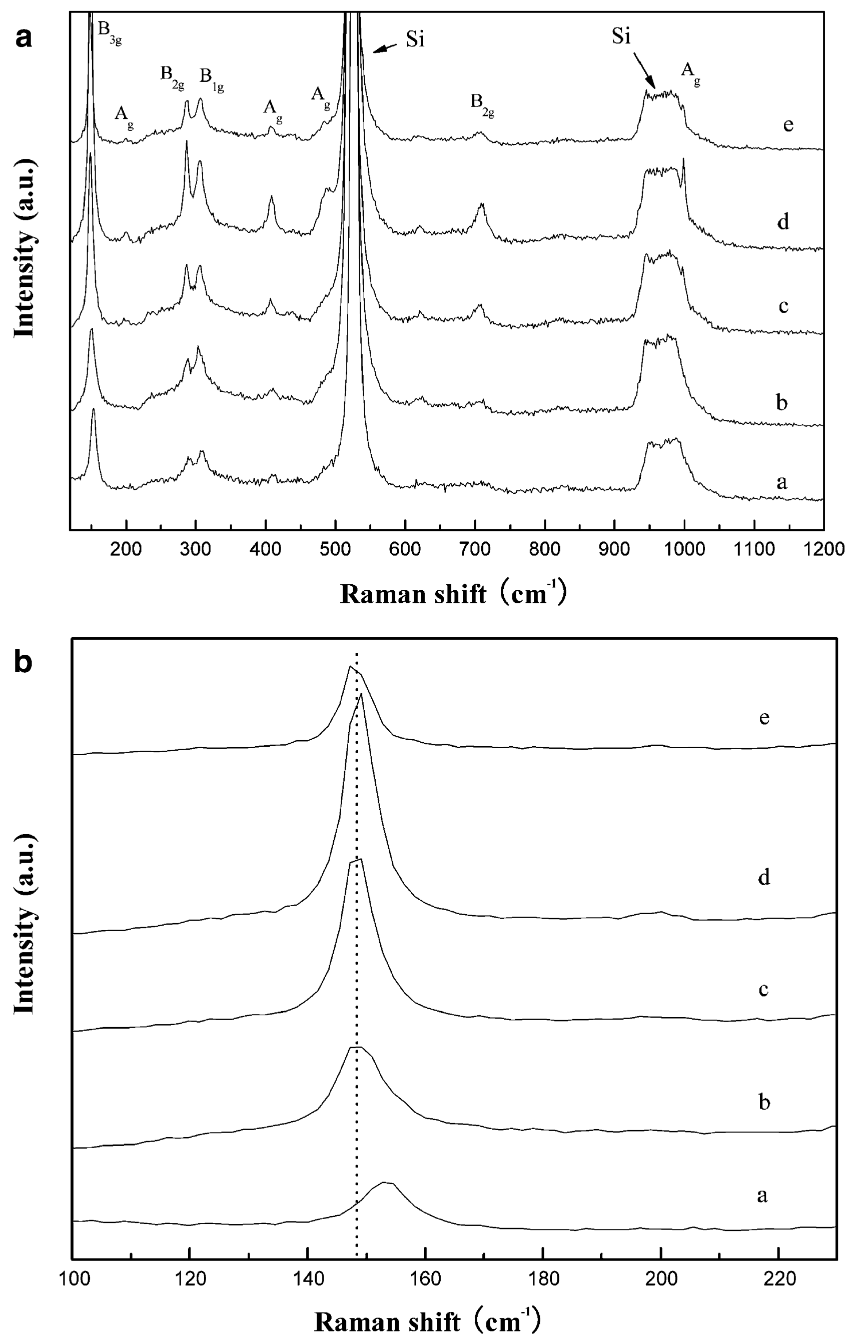

Fig. 3 Raman scattering spectra of sputtered V_2O_5 films annealed at different temperatures: *a* as-deposited, *b* 200 °C, *c* 400 °C, *d* 500 °C, *e* 550 °C. The full-survey Raman spectra are shown in (**a**) and the low wave number Raman spectra are shown in (**b**)

respectively[10, 15]. When the O_2–Ar gas flow ratio was beyond 3/7, a scattering peak appeared at Raman shift of 146 cm^{-1}. The newly appeared peak was related to the formation of layer-type structure in V_2O_5 films. The intensity of this peak gradually increases with the increase of O_2–Ar gas flow ratio. It implies that the incorporation of oxygen atoms into V_2O_5 structure matrix benefits the formation of layer structure. However, X-ray diffraction measurements (not shown here) show that the as-deposited V_2O_5 films are non-crystal.

The layer-type structure of V_2O_5 is stacked up from distorted trigonal bipyramidal coordination polyhedra of oxygen atoms around vanadium atoms. The share edges form $(V_2O_4)_n$ zigzag double chains along the (001) direction and are cross-linked along (100) through the shared corners [11]. The skeleton bent mode observed at 146 cm^{-1} is evidence for the layer-type structure of V_2O_5 films. Moreover, the peak at 994 cm^{-1}, which is associated with the vanadyl mode corresponding to the stretching of vanadium atoms connected to oxygen atoms by double

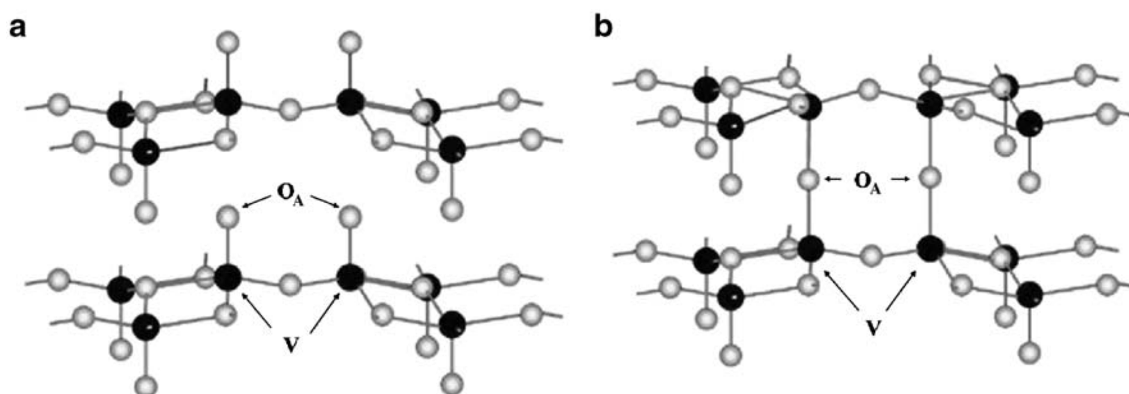

Fig. 4 The perfect structure of V_2O_5 (001) surface (**a**) and a possible deficient structure of V_2O_5(001) surface with oxygen vacancies (**b**) [8]; vanadium atoms are depicted as the *black circles* and oxygen atoms are depicted as the *gray circles*

bonds [11], is also a significant clue to the structure of V_2O_5 film. The vanadyl O_A is easily removed from the surface as a result of the cleavage of (001) planes, and vacancies are left behind in a nonrandom distribution [8].

In order to further investigate the effect of thermal annealing on microstructure of V_2O_5 films, as-deposited samples were annealed at various temperatures in air. Fig. 3a shows the Raman scattering spectra of sputtered V_2O_5 films annealed at different temperatures. A detailed change of the peak at 146 cm^{-1} can be seen as those replotted in Fig. 3b, where the shift in the peak position may be attributed to the strain between film and substrate. The intensity of all the peaks increases with the post-annealing temperature but obviously decreases when the post-annealing temperature reaches 550 °C. It is evident from the Raman scattering spectra that the microstructures of V_2O_5 films are changed with various post-annealing temperatures. As skeleton bent vibration at 146 cm^{-1} and the stretching vibration of vanadyl $V{=}O_A$ at 994 cm^{-1} are the evidences for the perfect layer-type structure of V_2O_5 films, reducing of these two peaks signifies that the structure of V_2O_5 film is distorted at the post-annealing temperature of 550°C and the oxygen vacancies are formed. It is possible that vanadyl O_A is removed from the surface as a result of the cleavage of (001) planes at a high temperature. Resulting from removing of the vanadyl O_A, the defect Vanadium atoms relax inwards and the real V-O_A-V bonds are formed between the layers (shown in Fig. 4).

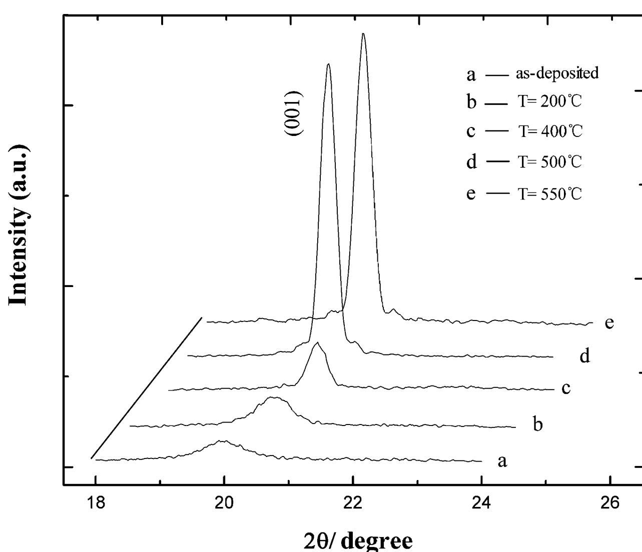

Fig. 5 XRD patterns of sputtered V_2O_5 films annealed at different temperatures

The formation of the V-O_A-V bonds is believed to lead to the decrease of the plane distance of V_2O_5 (001). To confirm this assumption, XRD measurements were performed. In Fig. 5, the peak at $2\theta=20°$ can be attributed to the reflections from V_2O_5 (001) planes and V_2O_5 films have preferred growth orientation along (001) planes and the c-axis is perpendicular to the silicon substrate surface. The crystallinity of V_2O_5 films becomes better with the increasing post-annealing temperature, but it changes unobviously between 500 °C and 550 °C. Table 1 shows the distance values of V_2O_5 (001) planes at different post-annealing temperatures and Fig. 6 shows the variation of plane distance of V_2O_5 (001) planes with post-annealing temperature. It is apparent that plane distance decreases

Table 1 Distance values of V_2O_5 (001) planes at different post-annealing temperatures

Post-annealing temperature	Distance value (Å)
as-deposited	4.4403±0.0010
200 °C	4.3795±0.0010
400 °C	4.3667±0.0010
500 °C	4.3667±0.0010
550 °C	4.3414±0.0010

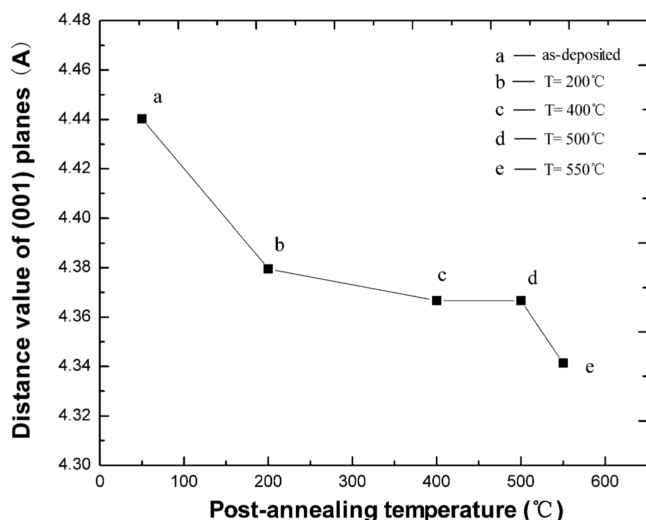

Fig. 6 Variation of distance value of V_2O_5 (001) planes with post-annealing temperature

with the increase of post-annealing temperature. The distance values (4.3669±0.0010 Å) of V_2O_5 (001) planes from XRD measurements at the post-annealing temperature between 400 °C and 500 °C approximately match the lattices parameter (4.3690 Å) according to L. Abello [10]. The decrease of the plane distance at the low temperature of post-annealing can be attributed to the crystallization of V_2O_5 film. However, the corresponding value decreases to 4.3414 Å (±0.0010 Å) when the post-annealing temperature is as high as 550 °C. It signifies that vanadyl V=O_A bonds are breaking and the V-O_A-V bonds are formed between the layers. The result of Raman scattering spectra are in accord with that from XRD measurements. Thus, it can be concluded that oxygen vacancies are induced with the breaking of vanadyl V=O_A bonds and the V-O_A-V bonds between V_2O_5 (001) planes begin to form for the case of what the annealing temperature is beyond 500 °C and the number of the V-O_A-V bond will increase with the vacancy concentration. These results properly match the models according to Ganduglia-Pirovano [8].

Conclusion

In summary, V_2O_5 films were deposited by DC magnetron sputtering at different preparing conditions. Utilizing the Raman scattering spectra, it was found that a mere desirable layer-like structure of V_2O_5 films can be prepared at a higher O_2–Ar gas flow ratio. A proper post-annealing temperature was of advantage to crystallization and formation of the integrated structure of V_2O_5 film. However, the peak intensity at 146 cm^{-1} due to skeleton bent vibration and the peak at 994 cm^{-1} due to the stretching vibration of vanadyl V=O_A bond decreased at the post-annealing temperature of 550 °C; it showed that the structure of V_2O_5 film was distorted and the oxygen vacancies were induced, which led to the V-O_A-V bonds between layers. The reduction of the distance values on V_2O_5 (001) planes from XRD measurements supported this conclusion.

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