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Structural and optical properties of reactive-sputtered films of V_2O_5: Measurement of optical bandgap and roughness correction

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ABSTRACT：Films of vanadium oxide were prepared by reactive DC magnetron sputtering. Crystalline films of α-V_2O_5 could be obtained at 500°C for an hour in oxygen atmosphere. Further annealing made rod-like crystallites to grow, and optical spectra of transmittance and reflectance changed with annealing, but the change after the crystallization could be explained by the increase in the surface roughness and the corrected absorption coefficients yielded a value of 2.25 eV for the bandgap energy.
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1. Introduction

Vanadium pentoxide (V_2O_5) is a well-known catalyst for oxidation, but in the last two decades investigation about V_2O_5 has opened new application areas such as lubricants[1], electrochromic devices and optoelectronic switches[2,3] along with the development of thin film technologies. Recently Kang *et al*.[4] have reported the observation of the metal-insulator transition (MIT) in V_2O_5, while a great number of related research works have been dedicated to vanadium dioxide (VO_2) because MIT in VO_2 occurs at near-ambient temperature about 68°C[5] and it is not believed to occur in V_2O_5. Kang *et al*. reported that the V_2O_5 film underwent a MIT by a factor of 100 in the electrical resistance at temperatures between 280 and 310°C. They prepared polycrystalline α-V_2O_5 films on the sapphire (0001) substrate at 500°C and investigated the film with spectroscopic ellipsometry and x-ray diffraction. The film showed a well-oriented crystallographic nature, while the surface was slightly rough. They employed an optical model based on the effective media approximation with new data for respective oscillators[6] so as to generate the observed data over the photon energy range between 0.75 to 4.0 eV

It has been reported that the morphology of V_2O_5 films becomes rough showing microcrystallites of rods and platelets after oxidation of amorphous films. For various electro-optical applications, a smooth film surface is preferable and we have started studying to obtain smooth crystalline films of V_2O_5. In this letter, we would like to report on the roughness development in the film and the effect on the optical properties.

2. Experiments

Films of vanadium oxide were deposited at room temperature by reactive DC magnetron sputtering. A vanadium metal target of 5 cm in diameter was sputtered in a mixture gas of argon and oxygen in a vacuum system (Vacuum Products, VPSD), whose base pressure was lower than 8×10^{-5} Pa. After baking the chamber at 150°C for 2 hours, Ar gas was introduced at a rate of 10.5 sccm, where the pressure was controlled to be 0.80 Pa with a capacitance manometer (MKS, Type 626). The target was pre-sputtered for 20 minutes at a power of 50 W with a power supply (Advanced Energy, MDX-1.5K). Then the total pressure was raised to 1.0 Pa by adding 2.1 sccm O_2. The discharge voltage, which was 290 V in pure Ar, rose up to 450 V at a flow of 1.0 sccm of O_2, which meant that the sputtering was operated under the oxide mode. After the target surface was conditioned for 10 minutes, oxide films were deposited for 1.0~2.8 hours on the substrate

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of polished silicon and quartz. Substrates were placed facing the target at a distance of 7 cm. Thickness of as-deposited films ranged from 300 to 740 nm. Then the specimen was annealed at 500±2 °C for 15, 60 and 120 minutes in an open quartz tube, where the dry O_2 was fed at a rate of 1.0 L/min. The morphology and the optical transmission spectra were studied using a scanning electron microscope (SEM: JEOL, JSM-6510) and a uv/vis spectrometer (Hitachi, U-3210). The crystalline structure was studied by out-of-plane measurement using an x-ray diffractometer (X'Pert Pro MRD).

3. Results and Discussion

3. 1 Crystallographic structure

The surface of as-deposited films of vanadium oxide was smooth and any trace of diffraction peak could not be observed. After the heat treatment at 500 °C for 1 hour, facetted surface appeared as shown in Fig. 1. Crystallites were found to grow with increasing film thickness. After another annealing of 1 hour, rod-like crystallites grew up to be several micrometers in length.

Figure 2 shows the XRD pattern of films annealed for 2 hours. The orthorhombic crystallites of α-V_2O_5 were grown

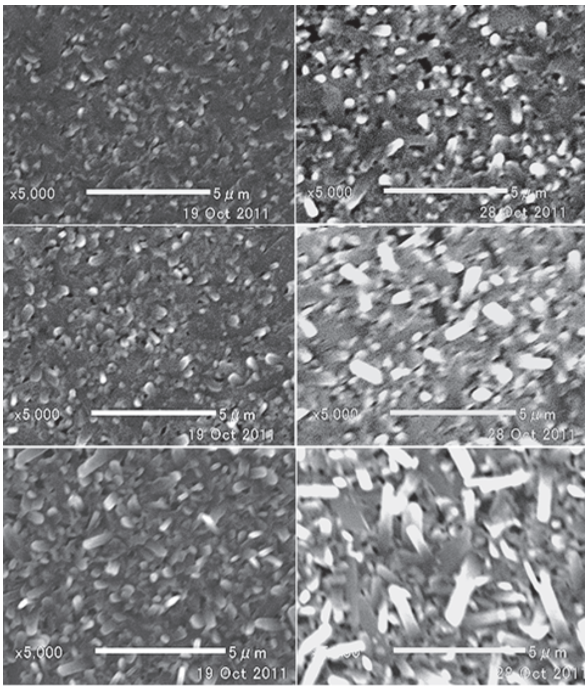

Fig. 1 SEM images of V_2O_5 films annealed at 500℃ for 1 hour (left) and for 2 hours (right). No structure could be seen before annealing. The thickness of as-sputtered films was (a) 390 nm, (b) 590 nm, and (c) 740 nm. The scale bar indicates 5 μm.

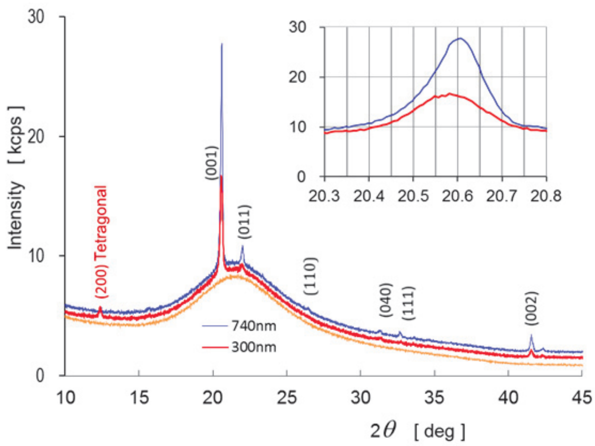

Fig. 2 XRD pattern of α-V_2O_5 films (Cu Kα). Insert shows magnified plots of (001) peaks. As-deposited film of 740 nm thickness was amorphous (the lowest orange curve).

preferentially in parallel to the substrate surface, while a trace of tetragonal structure of β-V_2O_5 was observed in 300 nm-thick film. This thickness effect on the annealing behavior is the same as that reported by Singh and Kaur[7]. Full width of half maximum of the (001) peak given in the insert in Fig. 2 yields a crystallite size of 50 nm for 300 nm-thick film and 80 nm for 740 nm-thick film, respectively.

3. 2 Optical properties and bandgap

The color of as-deposited films was yellowish and transparent. The optical transmission spectra $T(\lambda)$ are shown in Fig. 3, where wavy patterns due to the interference can be seen in the longer wavelength region. The absorbance in the low transmittance region did not show any specific structure even if it was magnified.

After heat treatment at 500 °C for 15 minutes the color turned brownish, and some structure of absorption appeared in the wavelength region of 200−500 nm. The optical spectra changed gradually after the first annealing, but the change was not so drastic compared to the first annealing (Fig. 4). In order to study the optical bandgap of the crystalline V_2O_5, the reflectance spectra of the film from the film side (Fig. 5) and those taken from the substrate side were measured. The absorption coefficient α can be calculated from the formula[8]:

$$\alpha d = -\ln T_o + \ln(1 - R_o) + \ln\left(1 - R_o' + \tfrac{1}{2}R_{So}\right) + \ln\left(1 - \tfrac{1}{2}R_{So}\right), \quad (1)$$

where d is the film thickness, T_o: observed transmittance,

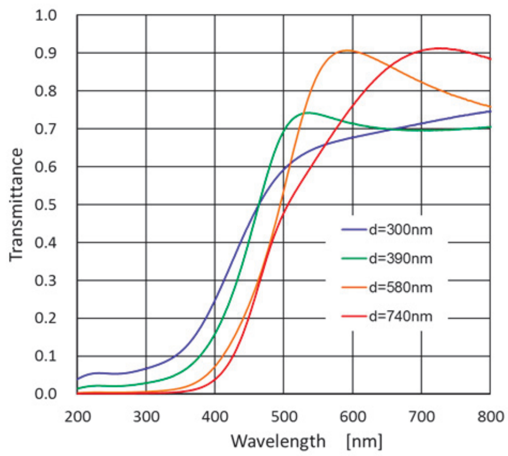

Fig. 3　Observed transmittance spectra of as-deposited VO_x films on quartz substrate.

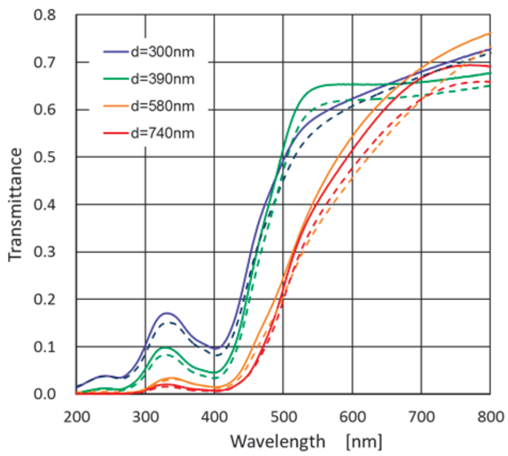

Fig. 4　Transmittance spectra of annealed V_2O_5 films on quartz substrate. Solid curves were obtained after annealing for 1 hour, and dashed curves for 2 hours.

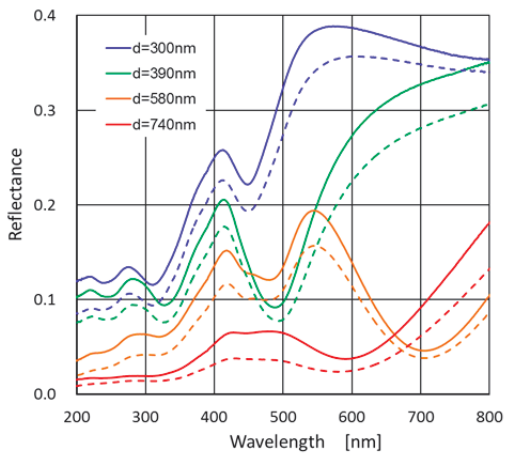

Fig. 5　Reflectance spectra of annealed V_2O_5 films on quartz substrate. Solid curves were obtained after annealing for 1 hour, and dashed curves for 2 hours.

R_o: observed reflectance from the film, R'_o: reflectance observed from the substrate side, and R_{So}: reflectance of the substrate, respectively. The data of α were plotted as $\sqrt{\alpha h\nu}$ against the photon energy $h\nu$ (known as Tauc plots[9,10]) to obtain the bandgap. Plotted curves, however, moved bit by bit after every annealing. Here, we took the surface roughness of the V_2O_5 film into account. Though Kang *et al.*[4] calculated the optical response with an effective media approximation, we tried to consider the roughness as the light loss based on the Beckmann model[11] which was not only simple but appropriate for films having a slightly rough surface.

The equation (1) is derived from the assumption that the observed quantities are described as

$$T_o \approx (1-R_{01})\cdot\exp(-\alpha d)\cdot(1-R_{12})(1-R_{20}) \ , \qquad (2a)$$

$$R_o \approx R_{01} \ , \qquad (2b)$$

$$R'_o \approx R_{20} + R_{12}(1-R_{20})^2 \ , \text{and} \qquad (2c)$$

$$R_{So} \approx 2R_{20} \ , \qquad (2d)$$

where the light goes from air (medium 0) through the film (medium 1) to the substrate (s), and the notation R_{ij} is the intensity reflection coefficient at the interface between media i and j. The Beckmann model can be summarized that the coefficients of reflection and transmission are reduced by the factors of B_R and B_T, respectively, as

$$\langle R_{01}\rangle = R_{01}\cdot B_R \, , \qquad B_R = \exp\left[-\left(\frac{4\pi\sigma}{\lambda}n_0\right)^2\right] \qquad (3a)$$

$$\langle T_{01}\rangle = T_{01}\cdot B_T \, , \quad B_T = \exp\left[-\left(\frac{2\pi\sigma}{\lambda}|n_0-n_1|\right)^2\right] \qquad (3b)$$

where the surface roughness is given by σ and the refractive indices of media 0 and 1 are denoted by n_0 and n_1. Then the formula of Eq. (1) can be modified as

$$\alpha d = -\ln\left(\frac{T_o}{B_T}\right) + \ln\left(1-\frac{R_o}{B_R}\right) + \ln\left(1-R'_o+\tfrac{1}{2}R_{So}\right) + \ln\left(1-\tfrac{1}{2}R_{So}\right) \ . \qquad (4)$$

To perform the correction, the information about the wavelength dispersion of the refractive index, $n_1(\lambda)$, is necessary. We employed a model dielectric function[12] (MDF), where the parameters were chosen, as listed in Table I, to give a good fit to the observed spectra in the transparent region ($\lambda \gtrsim 500$ nm). Calculated dispersion of complex refractive index $n-ik$ is shown in Fig. 6. The employment of the MDF is only partial, and the extension will be limited probably down to $\lambda = 400$ nm.

Table I Parameters of MDF for V_2O_5, which can give the refractive index in the transparent wavelength region. The notations are in accordance with the reference [12]. The energy values are given in eV.

E_1	B_1	B_{1X}	E_2	Γ_2	F	C_4	γ_4	E'_0	C_5	γ_5	E'_1	C_6	γ_6
2.2	0.3	0.4	2.9	1.0	0.5	0.8	0.2	1.9	0.1	0.8	4.6	0.9	0.4

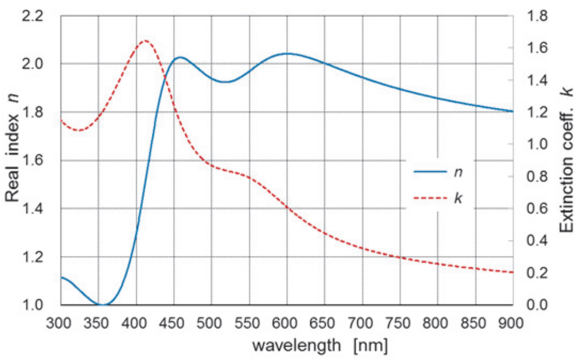

Fig. 6 Complex refractive index of V_2O_5 calculated from a model dielectric function. Employed parameters are given in Table I.

It was found that this modification worked well in the Tauc plots. Apparent deviation in the plots could be corrected with an addition of σ. An example for 300 nm-thick film is shown in Fig. 7. The linear portion of the plot of 2h-annealed sample calculated from Eq. (1) shifted to that of the 1-h annealed sample by using Eq. (4) with the roughness of 19 nm. The extrapolation of the line gives a value of 2.25 eV for the bandgap. The disagreement in the low absorption range is considered to come from the limitation of the formula (2a). The success in the correction suggests that the roughness affects the Tauc-plot analysis, and that the crystallization to α-V_2O_5 films from amorphous VO_x would be completed by the annealing at 500°C for 1hour.

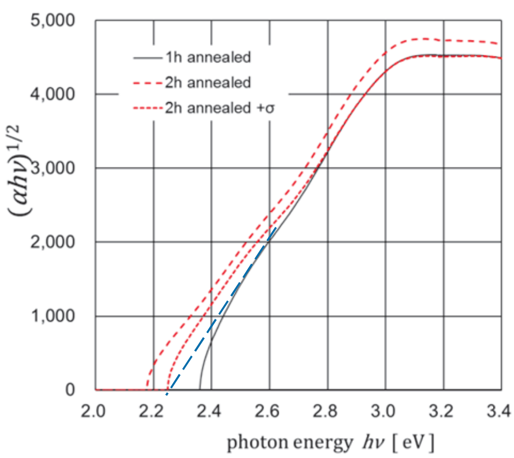

Fig. 7 The linear portion of the Tauc plot of 2-hour annealed sample moved on that of 1-hour annealed sample after the correction of the surface roughness.

4. Conclusion

Crystalline films of α-V_2O_5 could be prepared after a short period of annealing at 500°C. The roughness developed with the annealing time. Transmission and reflectance spectra changed with the annealing, but the same value of optical bandgap in Tauc plots could be obtained after the correction due to surface roughness.

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References

1) N. Fateh, G.A. Fontalvo, C. Mitterer, Tribol. Lett. **30**, 21-26 (2008).
2) C.W. Zou, L. Fan, R. Chen, X.D. Yan, W.S. Yan, G.Q. Pan, Z. Wu, W. Gao, CrystEngComm **14**, 626-631 (2012).
3) X.C. Wu, F.C. Lai, L.M. Lin, L.G. Lin, Y. Qu, Z.G. Huang, Appl. Surf. Sci. **255**, 2840-2844 (2008).
4) M. Kang, I. Kim, S.W. Kim, J-W. Ryu, H.Y. Park, Appl. Phys. Lett. **98**, 131907-3 (2011).
5) K. Okimura, Y. Nihei, Y. Sasakawa, Solid State Phenomena **124-126**, 703-706 (2007).
6) M. Losurdo, G. Bruno, D. Barreca, E. Tondello, Appl. Phys. Lett. 77**,** 1129-1131 (2000).
7) P. Singh, D. Kaur, J. Appl. Phys. **103**, 043507-7 (2008).
8) S. Yoshida and H. Yajima, *Optical Thin Films and Devices* (Univ. of Tokyo Press, Tokyo, 1994) p. 73, in Japanese.
9) J. Tauc, *Optical Properties of Solids*, ed. F. Abeles (North-Holland, Amsterdam, 1972) p. 277.
10) R. Lopez, R. Gomez, J. Sol-Gel Sci. Technol. **61**, 1-7 (2012).
11) P. Beckmann, A. Spizzichino, *The Scattering of Electromagnetic Waves from Rough Surfaces*, (Pergamon, New York, 1963).
12) Z-T. Jiang, T. Yamaguchi, M. Aoyama, T. Hayashi, Jpn. J. Appl. Phys. **37**, 479-483 (1998).