Journal of the Korean Crystal Growth and Crystal Technology
Vol. 23, No. 5 (2013) 224-229
http://dx.doi.org/10.6111/JKCGCT.2013.23.5.224

p-ISSN 1225-1429
e-ISSN 2234-5078

Optical properties of vanadium dioxide thin films on c-Al_2O_3 (001) substrates by *in-situ* RF magnetron sputtering

Seung Ho Han*, So Hee Kang*,**, Hyeongkeun Kim*, Dae Ho Yoon** and Woo Seok Yang*,†

**Electronic Materials & Device Research Center, Korea Electronics Technology Institute, Seongnam, Gyeonggi 463-816, Korea*
***School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Korea*

(Received September 2, 2013)
(Revised October 8, 2013)
(Accepted October 18, 2013)

Abstract Vanadium oxide thin films were deposited on c-Al_2O_3 (001) substrate by *in-situ* RF magnetron sputtering. Oxygen partial pressure was adjusted to prepare thermochromic VO_2 phase. X-ray diffraction patterns and scanning electron microscopy convincingly showed that plate-like V_2O_5 grains were changed into round-shape VO_2 grains as oxygen partial pressure decreased. After the optimized deposition conditions were fixed, the effect of substrate temperature and orientation on the optical properties of VO_2 thin films was analyzed.

Key words VO_2, Thermochromic, Optical properties, Crystal structure, Microstructure, Thin Films

1. Introduction

Thermochromic materials are capable of reversible change of their optical properties in response to temperature [1]. Such materials have been attracting great attention in applications including smart window coatings for buildings and vehicles to control the solar irradiance automatically. Vanadium oxide (VO_2) is a promising candidate for thermochromic application. The crystal exhibits an abrupt metal-insulator transition at a critical temperature $T_C = 68^\circ C$ [2,3]. The metal-insulator transition of VO_2 is attributed to crystallographic structure change, which is from monoclinic to tetragonal. Below T_C, the material is semiconducting and IR transparent; above T_C, it is metallic and IR reflecting.

There have been many reports for the fabrication of VO_2 by pulsed laser deposition [4-6], sol-gel process [7, 8], atmospheric pressure chemical vapor deposition [9, 10], and magnetron sputtering [11-13]. Among them, magnetron sputtering method has advantages for high deposition rate and large area deposition. However, deposition of VO_2 thin films by magnetron sputtering has been quite difficult due to the very narrow phase existence in the complex V-O system [14, 15]. To form a single phase VO_2 thin film by reactive magnetron sputtering, oxygen partial pressure should be precisely controlled. While many studies have reported VO_2 films by magnetron sputtering methods, few studies have been focused on the effect of crystal structure and microstructure change on the optical properties of VO_2 thin films [15, 16]. In particular, optical properties of VO_2 thin films on c-Al_2O_3 (001) substrate have been scarcely reported [11].

In the current study, thermochromic vanadium oxide thin films were deposited on c-Al_2O_3 (001) substrates by *in-situ* RF magnetron sputtering. Optimum deposition conditions to prepare highly oriented VO_2 thin film were found with changing oxygen partial pressure (P_O). The effect of substrate temperature (T_S) and orientation on the crystal structure, microstructure, optical transmittance, and transition behavior of VO_2 thin films was analyzed.

2. Research Procedure

2.1. Films Preparation

The c-Al_2O_3 (001) single crystal substrates were ultrasonically cleaned with acetone, absolute methyl alcohol, and de-ionized water for 5 minutes, respectively. The VO_2 thin films were deposited on c-cut sapphire substrates by reactive radio frequency (RF) magnetron sputtering using a V metal target of 2 inch in diameter with 99.9 % purity. The RF power, total flow rate, and working pressure were maintained at 150 W, 50 sccm, and 30 mTorr, respectively during the deposition. The P_O was changed from 0.8 to 1.1 sccm (1.6 to 2.2 %) to find the optimum condition for obtaining VO_2 thin film.

[†] Corresponding author
Tel: +82-31-789-7256
Fax: +82-31-789-7249
E-mail: wsyang@keti.re.kr

The mass flow controller was applied for the fine control of O_2 flow ratio. The T_S was varied from 300°C to 400°C. The lowest T_S to obtain crystalline VO_2 was found to be 300°C.

2.2. Characterizations

The crystal structure and phase composition of the vanadium oxide film was determined using X-ray diffractometry (XRD) in the θ-2θ mode with CuKα radiation operated at 30 kV and 20 mA in a 2θ range of 15~60°. To observe the surface microstructure of VO_2 thin films, scanning electron microscopy (SEM) was used. Spectral transmittance was measured using UV-Vis spectrometer at wavelengths between 400 to 2500 nm with a step width of 2 nm. Temperature-dependent transmittance curve (hysteresis curve) was also obtained using UV-Vis spectrometer at wavelength of 2500 nm. From the hysteresis curve, the midpoint of heating curve (T1), midpoint of cooling curve (T2), hysteresis width (T: difference between the T1 and T2), and transmittance difference ($\Delta Tr = Tr(30^{o}) - Tr(90^{o}C)$) were evaluated. The T_C (minimum of the derivative of the heating curve) was also evaluated.

3. Results and Discussion

The XRD patterns of the vanadium oxide thin films deposited with oxygen partial pressures of 2.2, 2.0, 1.8, and 1.6 % are presented in Fig. 1. The thin films were *in-situ* heated at T_S of 400°C. It can be seen that the intensity of the VO_2 (020) is gradually increased whereas the intensity of the V_2O_5 (410) phase is gradually decreased as the P_O decreased from 2.2 to 1.6 %. Although V_2O_5 second phase and VO_2 (012) plane was found in the vanadium oxide film deposited with the P_O of 1.6 %, VO_2 phase was highly oriented with (010) planes parallel to the surface of the substrate. For the VO_2 (020) peak, the full width half maximum (FWHM) value is found to be about 0.19°, which corresponds to high crystallinity thin film. The $VO_2(010)_m//Al_2O_3(001)$ relationship is consistent with previous reports [6, 17].

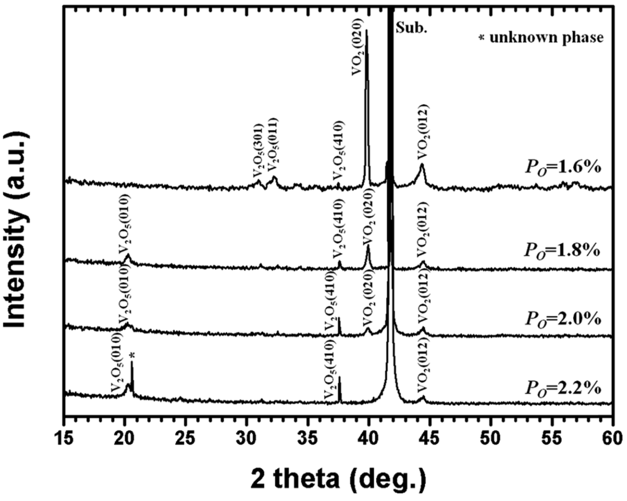

Fig. 1. XRD patterns of the vanadium oxide thin films deposited with oxygen partial pressures of 2.2, 2.0, 1.8, and 1.6 %.

Fig. 2 shows SEM images of the vanadium oxide thin films deposited with oxygen partial pressures of 2.2 (a), 1.8 (b), 2.0 (c) and 2.2 % (d). The insets are corresponding spectral transmittance. As the oxygen partial pressure decreased the fraction of plate-like grains were reduced and round-shape grains were increased. According to Figs. 1 and 2, it might be concluded that plate-like grains correspond to V_2O_5 phase and round-shape grains correspond to VO_2 phase. Spectral transmittances confirm that the thermochromic properties are enhanced as VO_2 phase increases. As the V_2O_5 phase is the most stable oxide in the V-O system [18-20], oxygen partial pressure should be precisely adjusted to form VO_2 phase.

XRD patterns and SEM images obtained from VO_2 thin films deposited at the T_S of 300 and 350°C with oxygen partial pressure of 1.6 % are shown in Fig. 3(a). It can be seen that the intensity of the VO_2 (020) peak decreases as the T_S decreases from 350 to 300°C. Average grain size of the thin films was calculated using Scherrer’s formula [21]:

$$b = \frac{0.9\lambda}{\beta\cos\theta}$$

where b is the average grain size, $\lambda = 1.541$ Å (X-ray wavelength), and β is the FWHM for the diffraction angle 2θ. The calculated grain sizes of the VO_2 thin films deposited at the T_S of 300 and 350°C are 5.8 and 6.8 nm, respectively. SEM images also follow a similar trend to the calculated grain sizes. Both images show uniform-sized nano-grain but the VO_2 thin films deposited at 350°C have relatively large grain sizes than the VO_2 thin films deposited at 300°C. In order to investigate the influence of T_S on the crystal structure, we obtained subtle XRD patterns of 2θ near 39.8, as shown in Fig. 3(b). As T_S increases from 300 to 350°C, the diffraction peak of VO_2 (020) shift to higher position from 39.84 to 39.92, which correspond to (010) lattice spacing of 4.523 Å and 4.514 Å, respectively. Epitaxial VO_2 thin film deposited on *c*-Al_2O_3 (001) substrate with T_S of 400°C showed VO_2 (020) position of $2\theta = 39.98$ –

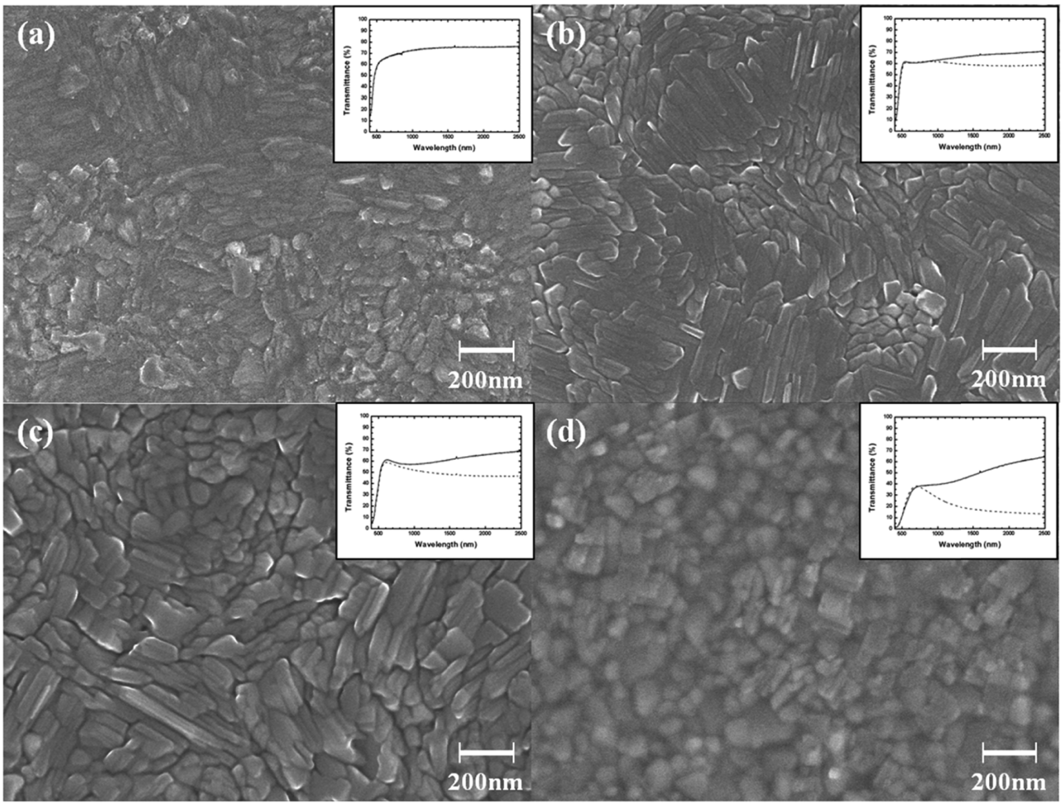

Fig. 2. SEM images of the vanadium oxide thin films deposited with oxygen partial pressures of 2.2 (a), 2.0 (b), 1.8 (c), and 1.6 % (d). The insets are corresponding spectral transmittance.

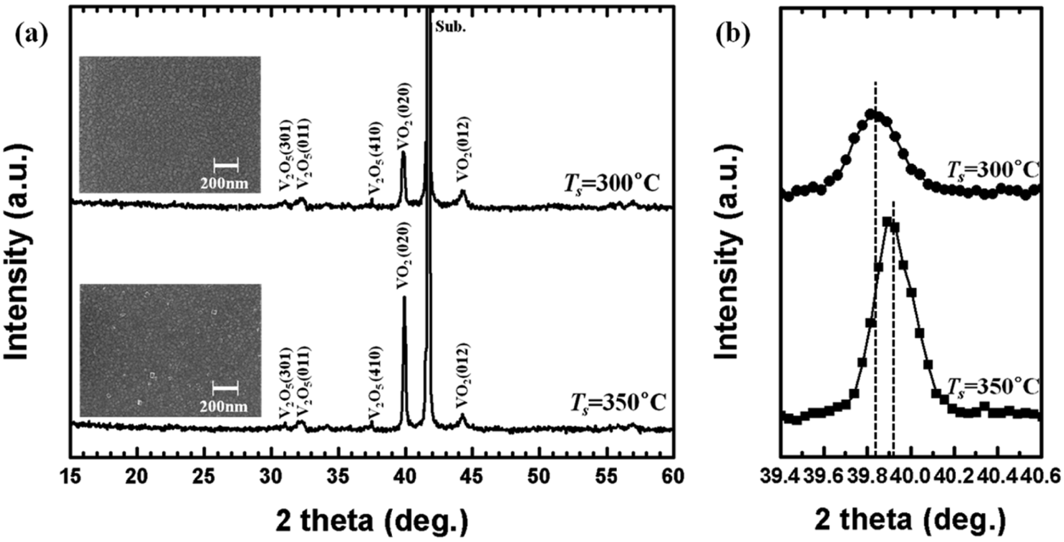

Fig. 3. (a) XRD patterns and SEM images of VO_2 thin films deposited at the TS of 300 and 350°C with oxygen partial pressure of 1.6 % and (b) subtle XRD patterns of 2θ near 39.8°.

40.0 [6, 17], indicating that our VO_2 thin film deposited at the T_S of 350°C have similar crystal structure with epitaxial thin film with good crystallinity but the VO_2 thin film deposited at the T_S of 300°C is not fully crystallized and have relatively open structures.

Fig. 4 shows the spectral transmittance of the VO_2 thin films deposited at 300°C (a) and 350°C (b) at $T < T_C$ (30°C) and $T > T_C$ (90°C). The film deposited at 350°C shows higher visible region transmittance and Tr than the film deposited at 300°C due to larger grain size and better crystallinity. However, both films show large transmittance difference between the semiconductor state of

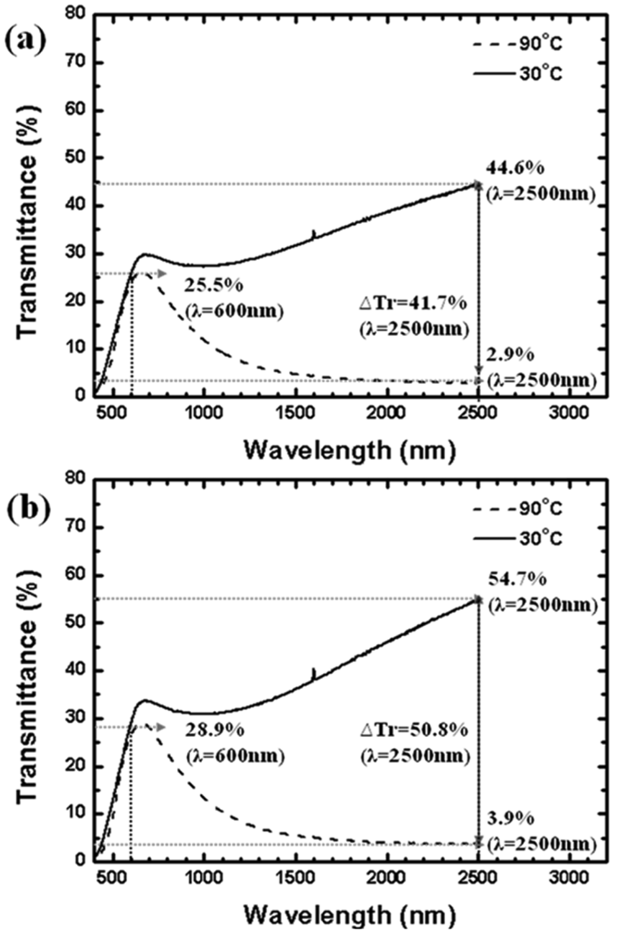

Fig. 4. Spectral transmittance of the VO_2 thin films deposited at 300°C (a) and 350°C (b) at $T < T_C$ (30°C) and $T > T_C$ (90°C).

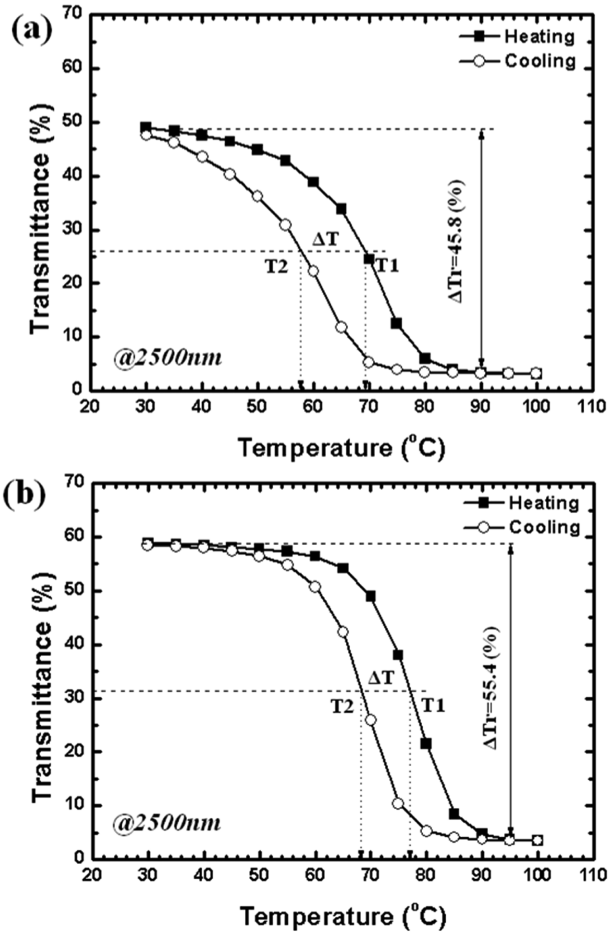

Fig. 5. Temperature-dependent transmittance curve (hysteresis curve) of the VO_2 thin films deposited at (a) 300°C and (b) 350°C.

$T < T_C$ (30°C) and metal state of $T > T_C$ (90°C) in the infrared region, which means good thermochromic property.

Hysteresis curves of the VO_2 thin films deposited at 300°C (a) and 350°C (b) are shown in Fig. 5. Table 1 shows the T1, T2, T, Tr, and the T_C of the VO_2 thin films deposited at 300°C and 350°C in which obtained from Fig. 5. While the VO_2 thin film deposited at 350°C have relatively sharp decrease of transmittance with Tr of 55.4 %, the film deposited at 300°C have broad change of transmittance with decreased Tr of 45.8 %. The T is increased from 9.6 to 11.4°C and the T_C is decreased from 77.5 to 70.3°C with decreasing T_S. The VO_2 films deposited at low temperature can lead to the destabilization of low-temperature semiconductor phase and thereby causing reduced T_C and transition sharpness [15, 22], which is consistent with our results. However, considering the reduced T_C by the crystalline imperfection, the T_C of the both films are still larger than the bulk value of ~68°C.

The lattice parameters and thermal expansion coefficients for the rhombohedral Al_2O_3 substrate and monoclinic VO_2 film are shown in Table 2. The lattice parameter a of rhombohedral Al_2O_3 is 4.758 and the lattice parameters a, b and c of monoclinic VO_2 are 5.753, 4.526, and 5.382, respectively. The epitaxial $VO_2(010)//Al_2O_3(001)$ can induce the epitaxial relationship of $VO_2(010)//Al_2O_3(001)$,

Table 1
The T1, T2, ΔTr, ΔT, and the T_C of the VO_2 thin films deposited at 300 and 350°C

TS	ΔTr (%)	T1 (°C)	T2 (°C)	ΔT (°C)	T_C (°C)
300°C	45.8	69.2	57.8	11.4	70.3
350°C	55.4	72.0	63.2	8.8	72.5

Table 2
Lattice parameters of rhombohedral Al_2O_3 substrate and monoclinic VO_2 film

Materials	Lattice parameters (Å)	
	a	c
Al_2O_3	4.758	12.992
VO_2	a = 5.753, b = 4.526	5.382

(100)//(100). As a result, in-plane compressive stress and corresponding out of plane tensile stress can be induced. In the form of thin film, the T_C of VO_2 can be modified by the control of *c*-axis stress induced by the lattice mismatch between the film and substrate [5,23]. The *c*-axis compressive stress decreases the T_C, whereas the *c*-axis tensile stress increases the T_C. The increased T_C of our VO_2 thin film deposited on *c*-Al_2O_3 (001) might be originated from increased *c*-axis tensile stress.

As mentioned earlier, the lattice spacing was decreased from 4.523 Å to 4.514 Å with increasing T_S from 300 to 350°C. The decrease in *c*-axis lattice spacing means *c*-axis compressive stress, and hence the T_C should be decreased. However, the T_C was increased with great extent of ~7.2°C with increasing T_S from 300 to 350°C, that is opposite tendency compared with previous reports [5, 23]. A more detailed research concerning the correlation between the T_S and the T_C of the VO_2 films deposited on *c*-Al_2O_3 (001) substrate is under investigation.

4. Conclusions

Vanadium oxide thin films were deposited on *c*-Al_2O_3 (001) substrate by *in-situ* RF magnetron sputtering. As the oxygen partial pressure decreased, rod-like V_2O_5 grains were reduced and plate-like VO_2 grains were increased. With increasing substrate temperature, grain size increased and (010) lattice spacing decreased from 4.52 to 4.514 Å. The VO_2 thin films deposited at 300 and 350°C showed large transmittance difference between the semiconductor state and metal state in the infrared region, which implies good thermochromic property. While the VO_2 thin film deposited at 350°C had relatively sharp decrease of transmittance, the film deposited at 300°C had broad change of transmittance with decreased Tr due to the crystalline imperfection. The increase in T_C of VO_2 thin film deposited on *c*-Al_2O_3 (001) substrate compared with bulk VO_2 might be originated from *c*-axis tensile stress induced by lattice mismatch.

Acknowledgement

This work was supported by Technology Innovation Program (No. 10044410, Commercialization of flexible touch panels based on 900x1600 mm^2 large, less than 1 nm thick graphene film synthesis technique) funded by the Ministry of Trade, Industry.

References

[1] C.G. Granqvist, “Materials science for solar energy conversion systems”, (Pergamon Press, Oxford, 1991) Chap. 5.
[2] F.J. Morin, “Oxides which show a metal-to-insulator transition at the Neel temperature”, Phys. Rev. Lett. 3 (1959) 34.
[3] J.B. Goodenough, “The two compounds of the crystallographic transition in VO_2”, J. Solid State Chem. 3 (1971) 490.
[4] D.H. Kim and H.S. Kwok, “Pulsed laser deposition of VO_2 thin films”, Appl. Phys. Lett. 65 (1994) 3188.
[5] Y. Muraoka and Z. Hiroi, “Metal-insulator transition of VO_2 thin films grown on TiO_2 (001) and (110) substrates”, Appl. Phys. Lett. 80 (2002) 583.
[6] K. Okimura, J. Sakai and S. Ramanathan, “In situ x-ray diffraction studies on epitaxial VO_2 films grown on *c*-Al_2O_3 during thermally induced insulator-metal transition”, J. Appl. Phys. 107 (2010) 063503.
[7] H.-T. Kim, Y.W. Lee, B.-J. Kim, B.-G. Chae, S.J. Yun, K.-Y. Kang, K.-J. Han, K.-J. Yee and Y.-S. Lim, “Monoclinic and correlated metal phase in VO_2 as evidence of the Mott transition: coherent phonon analysis”, Phys. Rev. Lett. 97 (2006) 266401.
[8] B.-J. Kim, Y.W. Lee, B.-G. Chae, S.J. Yun, S.-Y. Oh and H.-T. Kim, “Temperature dependence of the first-order metal-insulator transition in VO_2 and programmable critical temperature sensor”, Appl. Phys. Lett. 90 (2007) 023515.
[9] U. Qureshi, T.D. Manning and I.P. Parkin, “Atmospheric pressure chemical vapour deposition of VO_2 and VO_2/TiO_2 films from the reaction of $VOCl_3$, $TiCl_4$ and water”, J. Mater. Chem. 14 (2004) 1190.
[10] R. Binions, G. Hyett, C. Piccirillo and I.P. Parkin, “Synthesis and terahertz transmission properties of nanoporous vanadium dioxide films”, J. Mater. Chem. 17 (2007) 4652.
[11] G. Xu, P. Jin, M. Tazawa and K. Yoshimura, “VO_2-Sb:SnO_2 composite thermochromic smart glass foil”, Appl. Surf. Sci. 244 (2005) 449.
[12] H. Kakiuchida, P. Jin, S. Nakao and M. Tazawa, “Optical properties of vanadium dioxide film during semiconductive-metallic phase transition”, Jpn. J. Appl. Phys. 46 (2007) L113.
[13] Z. Yang and S. Ramanathan, “Direct measurement of compositional complexity-induced electronic inhomogeneity in VO_2 thin films grown on gate dielectrics”, Appl. Phys. Lett. 98 (2011) 192113.
[14] C.H. Griffiths and H.K. Eastwood, “Influence on stoichiometry on the metal-semiconductor transition in vanadium dioxide”, J. Appl. Phys. 45 (1974) 2201.
[15] P. Jin, K. Yoshimura and S. Tanemura, “Dependence of microstructure and thermochromism on substrate temperature for sputter-deposited VO_2 epitaxial films”, J. Vac. Sci. Technol. A. 15 [3] (1997) 1113.
[16] J. Lappalainen, S. Heinilehto, S. Saukko, V. Lantto and H. Jantunen, “Microstructure dependent switching properties of VO_2 thin films”, Sens. Actuators A 142 (2008) 250.
[17] K. Okimura and Y. Suzuki, “Epitaxial growth of V_2O_3

thin films on c-plane Al_2O_3 in reactive sputtering and its transformation to VO_2 films by post annealing", Jpn. J. Appl. Phys. 50 (2011) 065803.

[18] C.W. Zou, X.D. Yan, D.A. Patterson, E.A.C. Emanuelsson, J.M. Bian and W. Gao, "Temperature sensitive crystallization of V_2O_5: from amorphous film to β-V_2O_5 nanorods", Cryst. Eng. Comm. 12 (2010) 691.

[19] N. Fateh, G.A. Fontalvo, L. Cha, T. Klünsner, G. Hlawacek, C. Teichert and C. Mitterer, "Synthesis-structure relations for reactive magnetron sputtered V_2O_5 films", Surf. Coat. Technol. 202 (2008) 1551.

[20] P. Singh and D. Kaur, "Influence of film thickness on texture and electrical and optical properties of room temperature deposited nanocrystalline V_2O_5 thin films", J. Appl. Phys. 103 (2008) 043507.

[21] B.D. Cullity, "Elements of X-ray diffraction" (Addison-Wesley, Reading, MA, 1978).

[22] Y. Muraoka, Y. Ueda and Z. Hiroi, "Large modification of the metal-insulator transition temperature in strained VO_2 films grown on TiO_2 substrates", J. Phys. Chem. Solids 63 (2002) 965.

[23] L.A. Ladd and W. Paul, "Optical and transport properties of high quality crystals of V_2O_4 near the metallic transition temperature", Solid State Commun. 7 (1969) 425.