



Thermochromic properties of vanadium oxide films prepared by dc reactive magnetron sputtering

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Abstract

A transparent vanadium oxide film has been one of the most studied electrochromic (EC) and Thermochromic (TC) materials. Vanadium oxide films were deposited at different substrate temperatures up to 400 °C and different ratios of the oxygen partial pressure (P_{O_2}). SEM, AFM and X-ray diffraction's results show detail structure data of the films. IR mode assignments of the films measured by IR reflection–absorbance in NGIA (near grazing incidence angle) are given. It is found that the film has V_2O_5 and VO_2 combined structures. The films exhibit clear changes in transmittance when the environment temperature (T_e) is varied, especially in the 3600–4000 cm^{-1} range. Applying a T_e that is higher than a critical temperature (T_c) to the samples, the as-RT (room temperature) deposited film with 9% P_{O_2} has a transmittance variation of 30%, but the films that were deposited on a heated substrate of 400 °C have little variation. There is tendency of bigger variation in transmittance for the sample deposited at a larger P_{O_2} , when it is applied by 200 °C T_e . © 2007 Elsevier B.V. All rights reserved.

Keywords: Vanadium oxide films; Thermochromic property; XRD; IR; dc magnetron sputtering

1. Introduction

A vanadium oxide film has been one of the most studied electrochromic (EC) and Thermochromic (TC) materials [1,2]. TC materials change reversibly color with changes in an environment temperature (T_e). They can be semi-conductor compounds, liquid crystals or metal compounds. TC materials change color by a process that is involved a chemical reaction of thermally inducement or a phase transformation. The change in color happens at a determined temperature, is called a critical temperature (T_c), which can be varied by doping materials. Thermochromism is seen in a large number of organic and certain inorganic compounds. Some of these compounds are Fe_3O_4 , NbO_2 , NiS , Ti_2O_3 , VO_2 and V_2O_5 [2]. Such material can be used to control transmittance and infrared emissivity of a

glazing, and also as thermotropic (TT) material which can cause a significant change in its electronic properties from an insulator to semiconductor transition or from a semiconductor to metallic state when the T_e exceeds the material's T_c .

Vanadium has various valence states and results in a number of oxide forms of vanadium oxides. V_2O_3 , VO_2 and V_2O_5 films have been widely studied for optical, electrical, electrochemical,

Table 1
Deposition conditions, parameters and thermochromic properties of vanadium oxide films

Sample	P_{O_2} (%)	T_s (°C)	T_a (°C)	$IR_{at RT}$ (%)	$IR_{at 200 °C}$ (%)	ΔIR (%)
V1	9	RT	–	79.0	49.0	30.0
V2	15	400	–	26.0	22.5	3.5
V3	20	RT	–	83.0	66.0	17.0
V1a	9	RT	400	27.5	16.0	11.5
V3a	20	RT	400	32	5	15.0
V4a	20	RT	200	53.0	14.0	39.0

ΔIR : transmittance different at the 4000 cm^{-1} (2.5 μm) before and after the sample is put, into 200 °C temperature environment, $\Delta IR = IR_{at 200 °C} - IR_{at RT}$.

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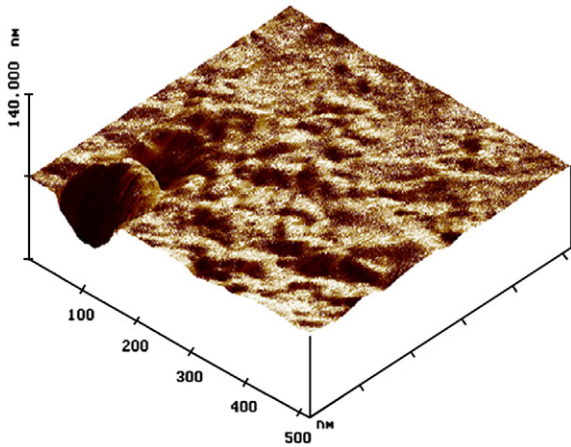


Fig. 1. Three dimensions (3D) AFM image of vanadium oxide film deposited with 9% oxygen partial pressure (P_{O_2}) at room temperature.

thermo-chromic and thermal switching materials. VO_2 and V_2O_5 have been considered for window applications [3–6]. The interest in these materials has been increased in the last few years due to their potential applications in a wide variety of optical modulation devices.

Many research works have been focused on electrochromic coloration of this material, few works can be found on the study of the structure characterizations and thermochromic behaviours of vanadium oxide films. Different techniques have been used to synthesize vanadium oxide films, such as sputtering [7], thermal evaporation [4,5], pulse laser deposition [6], sol–gel [8] etc. Depending on the deposition conditions and techniques, films may present considerably different structural, optical and electrical character, and consequently different electrochromic and thermotropic behaviour. The sputtering is the most widely investigated and large-scale deposition set is available. With direct-current (dc) sputtering from a target Vanadium, thin film properties can be improved by controlling the reactive gas atmosphere and substrate temperature (T_s).

In this work, vanadium oxide films have been deposited onto glass substrates by dc reactive magnetron sputtering at different

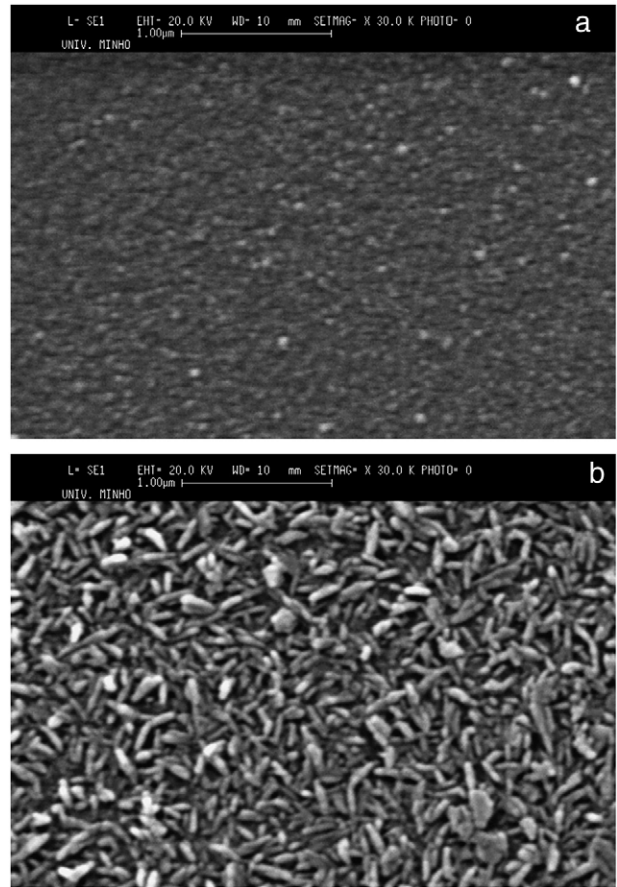


Fig. 3. SEM images of vanadium oxide films prepared at different depositing T_s (a) 100 °C and (b) 200 °C; scale is 1 µm.

T_s and ratio of oxygen partial pressure (P_{O_2}). The structural and thermochromic properties of these films are studied.

2. Experimental details

Vanadium oxide films were deposited by using a home-made dc magnetron sputtering system. The target is a vanadium metal

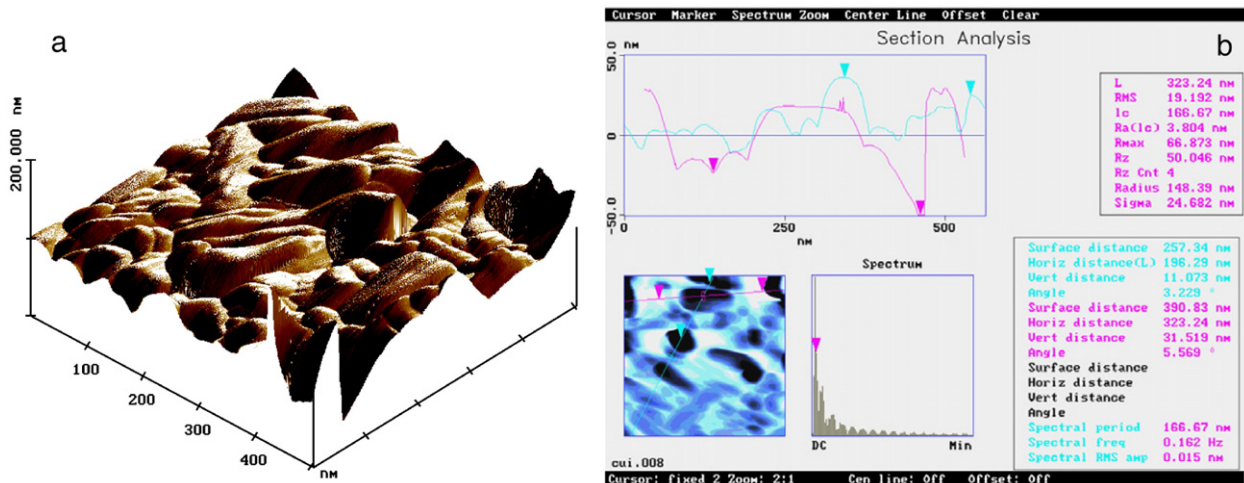


Fig. 2. AFM image (a) and section analysis (b) of vanadium oxide film deposited with 15% P_{O_2} and at 400 °C depositing T_s for 20 min.

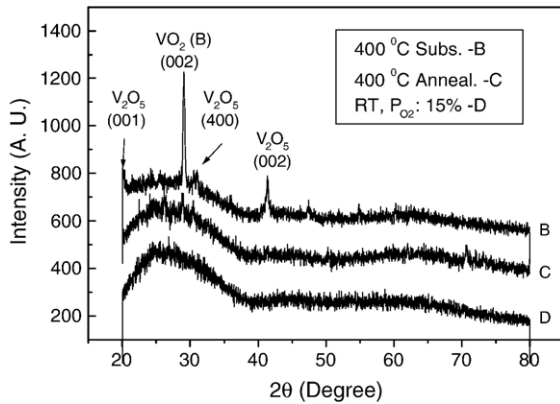


Fig. 4. X-ray diffraction spectra of vanadium oxide films deposited with 15% P_{O_2} at 400 °C depositing T_s (B), after 400 °C annealing (C), and at room temperature deposition (D).

disk (70 mm diameter) with a purity of 99.8%. The vacuum chamber was evacuated down to pressure 1×10^{-3} Pa prior to deposition. The sputtering gas (Ar) and reactive gas (O_2) were introduced into the chamber separately, and were controlled through two gas mass flow rate controllers. The ratio of oxygen partial pressure is defined as $P_{O_2} = P(O_2) / [P(O_2) + P(Ar)]$, where $P(O_2)$ and $P(Ar)$ are the oxygen and argon gas pressures respectively. The P_{O_2} can be adjusted in different experiments. The oxygen reactive gas was introduced into the chamber and the required pressure was set. Argon gas was introduced thereafter till the preset pressure was reached (1 Pa). The dc power during the film deposition was 160 W. The temperature was varied from room temperature (RT) until 400 °C.

The surface topology and cross-sectional structure of the films were observed by means of scanning electron microscopy (SEM, UK Leica-Cambridge S360) and AFM (atomic force microscopy, Multimode TM SPM 3, Digital Instruments Nanoscope). In order to prevent charge build-up, a thin gold film was coated on the sample surface before SEM was carried out. The film X-ray diffractions (XRD) have been made using a Philips PW1710 computer-controlled diffractometer. $Cu K_{\alpha}$ radiation from an X-ray tube with normal focus was used. The film optical transmittance was measured by Shimadzu double-beam spectrophotometer UV-3101PC. The *ex-situ* IR spectra of

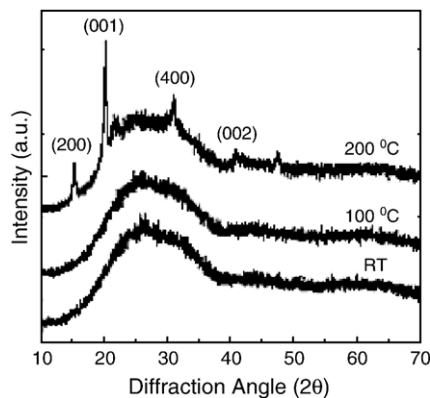


Fig. 5. X-ray diffraction patterns of vanadium oxide films prepared with 9% P_{O_2} at different depositing T_s .

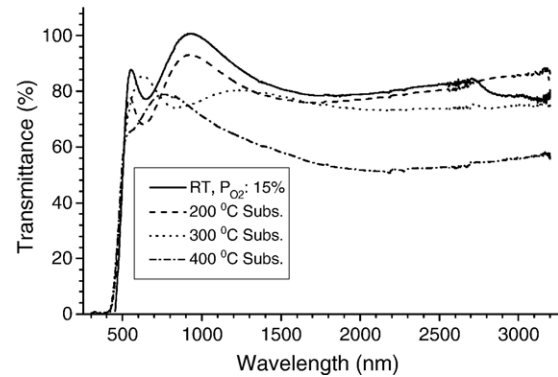


Fig. 6. Spectral transmittance of vanadium oxide films prepared at 15% P_{O_2} (the ratio of oxygen partial pressure), and different depositing T_s .

the films were obtained using a Fourier-transform infrared (FT-IR) Bio-Rad FTS135 spectrometer (spectral range 4000–400 cm^{-1}). Reflective absorption spectra in the mid-infrared were investigated in the films. The IR technique of reflective absorption is chosen in case of near graze incidence angle (NGIA). The background spectra were scanned with an Al (aluminium) mirror as the reference. The resolution in wavenumber is 2 cm^{-1} .

3. Results and discussion

3.1. Structure characterizations of the films

Vanadium oxide films were prepared at different P_{O_2} , depositing T_s , and annealing temperature (T_a). Some of them are listed in the Table 1. The surface and the cross sectional morphologies of these films were analyzed (Figs. 1–3). The three dimensional (3D) AFM image of vanadium oxide films prepared at 9% P_{O_2} and RT (sample: V1) is shown in Fig. 1. The finer morphology and roughness of the films can be clearly seen. The photography and AFM software analysis reveal a uniform growth of the film. The average grain size is less than 60 nm. The films prepared at RT and 100 °C have relative smooth surface and very compact structure (Figs. 1 and 3a).

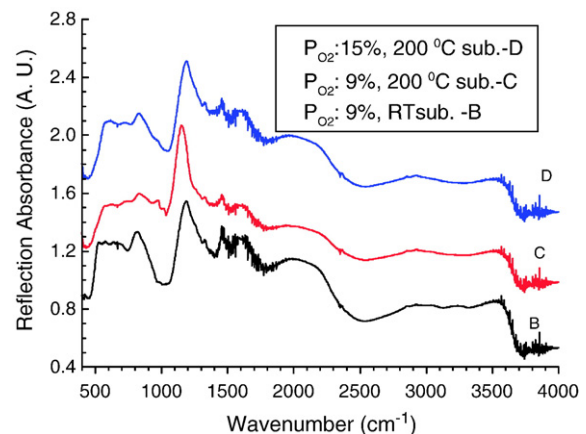


Fig. 7. IR spectra of the vanadium oxide films grown at room temperature and 200 °C depositing T_s with 9% and 15% P_{O_2} respectively.

Table 2
IR vibrational modes of the films (Wavenumbers: cm^{-1})

Exp.	Assi.	V_2O_5 ref.	VO_2	V_2O_3 ref.
418w	$\nu(3\text{V}-\text{O}_\text{C})$	412 [17] 490 [18]		
509m	$\nu(3\text{V}-\text{O}_\text{C})$	507 [19]		508sh [20]
517m		512 [20]		520sh [20]
717m	$\nu(\text{V}-\text{O}_\text{b}-\text{V})$	767 [19] 784 [18]	714sh [20]	
804m	$\nu(3\text{V}-\text{O}_\text{C})$	842 [19]		
816m		828 [20]		
970m		975 [17]		980[20]

Exp.: experiment, ref.: reference, Assi.: assignment, m: medium, sh: shoulder peak, w: weak, Ter.: terminal.

Fig. 2(a) shows the AFM image of the vanadium oxide film deposited with 15% P_{O_2} at 400 °C T_s (sample: V2) for 20 min. It is clearly seen that there are much bigger quasi bar-shape grain formed in the film. Also it has a good uniformity revealing the uniform growth of the films. The average grain dimensions are less than 55×135 nm. Fig. 2(b) presents a section analysis and data determined by the AFM analysis. The maximum roughness and the average RMS (root mean square) roughness are 66.9 and 19.2 nm. The grain size of the V_2O_5 film deposited at 400 °C T_s is much bigger than that of the film annealed at 400 °C. By the theory analysis [9] the bar-shaped grains may come from combining the effects of the direction of flowing field of the sputtering gas and the thermal field of high 400 °C T_s . When the depositing T_s is increased and higher than 200 °C, the films show many small bar-shaped grains with the voids between them in SEM images of vanadium oxide films (Fig. 3). SEM images confirmed the AFM result.

In order to study the film structure, XRD spectra of the samples were measured and their patterns are shown in Figs. 4 and 5. Fig. 4 reveals the effects of post-treating T_a and depositing T_s of the vanadium oxide films deposited at 15% P_{O_2} . For curve (D) only very weak peaks plus a broad background from the glass substrate can be observed, which indicates that the film obtained at RT is amorphous. The films prepared at 400 °C T_a have no sharp peak too; only very weak peaks of V_2O_5 (400), VO_2 (B') (002) and V_2O_5 (002) [10], plus

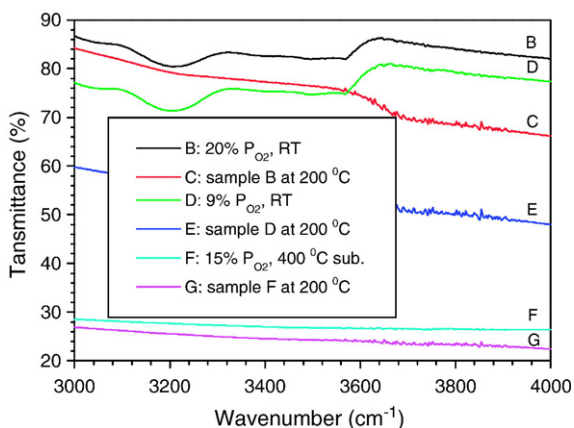


Fig. 8. IR spectra of vanadium oxide films (sample V1=D; V2=F; V3=B) deposited with different P_{O_2} before and after putting them into 200 °C T_c .

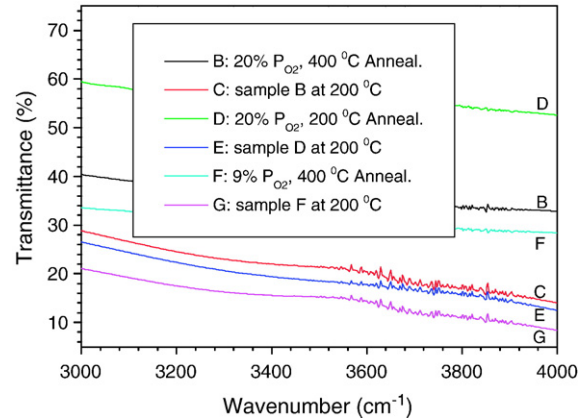


Fig. 9. IR spectra of the annealed vanadium oxide films (sample V1a=F; V3a=B; V4a=D) before and after putting them into 200 °C T_c .

a broad background from the glass substrate are observed for the curve (C), because the films are amorphous and thin. The spectrum (B) shows the peaks that coincide with the VO_2 (B') (001), V_2O_5 (001), V_2O_5 (400), and V_2O_5 (002) [10,11]. VO_2 (B') is a metastable compound which can be converted into stable VO_2 with a rutile or monoclinic structure in some conditions. Its structure is derived from the orthorhombic V_2O_5 by a crystallographic shear belonging to the same series as V_6O_{13} [12]. VO_2 (B') was reported to be an intermediate phase between V_2O_5 and V_2O_3 [11]. Although there are many possible phases of vanadium oxides, the X-ray analysis revealed that the films are VO_2 (B') and V_2O_5 . The following IR result confirms the XRD analysis. All the films were strongly oriented with respect to VO_2 (B') {001}, V_2O_5 {001}, and V_2O_5 {100}. The structure correlates mainly with depositing T_s and little with annealing temperature.

The XRD measurements of Fig. 5 reveals that the films prepared at 9% P_{O_2} and the depositing T_s lower than 200 °C are amorphous; and the film prepared at the T_s (higher than 200 °C) shows a polycrystalline structure [13]. When the T_s is higher than 300 °C, the films show a random orientation. When the argon ions bombard the vanadium target, the pure vanadium atoms are sputtered and the kinetic energy is also transferred to them from the argon ions. Some of the sputtered vanadium atoms will impinge the substrate with some kinetic energy. However, with the power level in our experiments (160 W), the sputtered vanadium atoms can not get enough energy to form a crystalline V_2O_5 thin film on the substrate. Yoon et al. has reported that even 250 W dc power is not enough to grow a crystalline V_2O_5 thin film [14]. With increasing T_s the more energy will be supplied to the adatoms and results in an increasing of their mobility, which favor the recrystallization and increasing order of the microstructure. That is why the films prepared at high T_s have a crystalline structure and the films prepared at low T_s and RT with lower annealing temperature have an amorphous structure.

Fig. 6 shows the UV-VIS transmittance spectra of the films prepared at three different depositing T_s . It could be clearly seen that the transmittance decreases as the depositing T_s is increased. From the Fig. 3 it can be seen that the sample surface become

rough as the T_s is increased. The rough surface could result in a scattering light loss and then a low transmittance.

According to the results of the theoretical analysis, 21 modes of vibration are possible in the Raman and 15 in the IR spectrum of the V_2O_5 . The effect of the deposition P_{O_2} of the film that was grown at RT and 200 °C T_s in 15% P_{O_2} and 9% P_{O_2} is shown in Fig. 7. It is seen that the absorbance peaks 970 and 1020 cm^{-1} of the films become stronger after depositing at 200 °C T_s . The thickness increased a little and the color of the film changed from light yellow to yellow at the higher depositing T_s .

The bands appearing at 970 and 1020 cm^{-1} correspond to the V (vanadium)–O_v (vanadyl oxygen) stretching mode. The band between 700 and 900 cm^{-1} is assigned to the anti-symmetric stretching vibration of the V–O_b–V group (O_b: bridge oxygen). The group of band, which presents at <600 cm^{-1} wavenumber, corresponds to the edge-shearing 3V–O_c stretching and the bridging V–O_b–V deformations [10,15]. The shift of the strong band between 1140 cm^{-1} and 1220 cm^{-1} , which is assigned to $\delta(w-o)$ in the M–OH...H₂O group, was observed as the plane deformational (bending) M–O mode. Detailed assignment of these modes determined from the NGIA IR reflection-absorbance spectra and some data from other references are given in Table 2.

3.2. Thermochromic properties of the films

The IR transmittance spectra of the films are shown from G in the 3000–4000 cm^{-1} (3.3–2.5 μm) range, before and after these samples are put into 200 °C T_c . The films exhibit clear changes in transmittance, especially in the range 3600–4000 cm^{-1} . The variation of the transmittance arises due to the films change from a semiconductor phase to a metallic phase [16]. The data is summarized in the Table 1. Fig. 8 shows that after applying higher T_c ($>T_c$) to the as-deposited films (sample V1; V2; V3) prepared with different P_{O_2} and depositing T_s , the transmittance changes reaching a value up to 30%. The films deposited at 400 °C T_s show little variation. Fig. 9 shows that the 200 °C T_a films (sample V1a; V3a; V4a) have strong transmittance variance, after applying higher T_c ($>T_c$) to these samples that were deposited at different P_{O_2} and were treated at different T_a . The maximum variation of the transmittance reaches 39% between sample D and E at 4000 cm^{-1} wavenumber.

4. Conclusions

AFM and SEM analysis show that vanadium oxide films prepared at RT and 100 °C T_s are amorphous and compact. The film surface gets rough as the depositing T_s is increased. XRD of the sample reveals structural information of the film. An amorphous film was obtained at RT. Only very weak peaks of V_2O_5 plus a broad background from the glass substrate could be observed. The film prepared above 200 °C T_s has a polycrystalline structure with a preferred orientation along the (001) direction. The films treated at 400 °C T_a have no sharp peaks too in their X-ray diffraction spectra.

In the UV-VIS NIR studies it is found that as the depositing T_s increases from RT to 400 °C, the transmittance of the films in the 300–3200 nm region decreases. The IR vibration results show that the absorbance peaks 970 and 1020 cm^{-1} of the films become stronger after depositing at 200 °C T_s comparing with sample deposited at RT. The bands appearing at 970 and 1020 cm^{-1} correspond to the V (vanadium)–O_v (vanadyl oxygen) stretching mode. All detailed assignment of these modes determined from the NGIA of IR reflection-absorbance spectra are given. The both XRD and IR results show a clear V_2O_5 and VO_2 peaks for the vanadium oxide films.

These films were investigated for thermochromic applications. The film exhibits clear changes in transmittance when the T_c ($>T_c$) of the sample is applied. The film deposited at RT and 9% P_{O_2} has a transmittance variation of 30% before and after putting it into 200 °C T_c , but the film that was deposited at 400 °C T_s and 15% P_{O_2} has little variation. The maximum variation of transmittance of the sample reaches 39%. There is tendency of bigger variation in transmittance for the sample with larger P_{O_2} deposition condition, when it was put into 200 °C T_c . All these properties of the films indicate that vanadium oxide films have good thermochromic behaviors and they are ideal TC materials.

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