

Surface oxidation of vanadium dioxide films prepared by radio frequency magnetron sputtering*

Wang Xue-Jin(王学进)^{a)}, Liang Chun-Jun(梁春军)^{b)}, Guan Kang-Ping(管康萍)^{b)},
Li De-Hua(李德华)^{c)}, Nie Yu-Xin(聂玉昕)^{c)}, Zhu Shi-Oiu(朱世秋)^{a)},
Huang Feng(黄峰)^{a)}, Zhang Wei-Wei(张葳葳)^{a)}, and Cheng Zheng-Wei(成正维)^{b)}

^{a)} College of Science, China Agricultural University, Beijing 100083, China

^{b)} School of Science, Beijing Jiaotong University, Beijing 100044, China

^{c)} Laboratory of Optical Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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This paper reports that the thermochromic vanadium dioxide films were deposited on various transparent substrates by radio frequency magnetron sputtering, and then aged under circumstance for years. Samples were characterized with several different techniques such as x-ray diffraction, x-ray photoelectron spectroscopy, and Raman, when they were fresh from sputter chamber and aged after years, respectively, in order to determine their structure and composition. It finds that a small amount of sodium occurred on the surface of vanadium dioxide films, which was probably due to sodium ion diffusion from soda-lime glass when sputtering was performed at high substrate temperature. It also finds that aging for years significantly affected the nonstoichiometry of vanadium dioxide films, thus inducing much change in Raman modes.

Keywords: surface oxidation, vanadium dioxide, films, magnetron sputtering

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1. Introduction

Vanadium dioxide (VO_2) has attracted much attention in recent years because of its particular properties. VO_2 exhibits a semiconductor phase when its temperature is below 68°C and a metal phase when its temperature is above 68°C , accompanied by dramatic change in electric resistance and optical transmittance, which makes it very suitable to fabricate ‘smart windows’,^[1] uncooled bolometer,^[2,3] and recording materials,^[4] etc.

VO_2 thin films have been deposited on various substrates using several methods, such as sol-gel,^[5,6] pulse laser deposition,^[7] vacuum evaporation,^[8] chemical vapour deposition^[9], and magnetron sputtering,^[10] etc. However, it was found that magnetron sputtering was one of the most effective methods to deposit high quality VO_2 films by controlling oxygen concentration in oxygen/argon gas and substrate temperature.

In our previous papers, vanadium oxide films, including VO_2 , were deposited on various substrates by radio frequency (RF) magnetron sputtering.^[11–14]

High quality VO_2 films with main (011) orientation were fabricated by controlling the parameters carefully. Nonstoichiometry of VO_2 determined by deposition parameters was characterized by Raman study. Raman spectra is an useful tool to investigate the vibrated modes, introduced by Parker,^[15] to study the oxidation of single crystal VO_2 . In recent years, Raman spectra was also introduced to determine oxidation state of VO_2 thin films. In this paper, we studied the aging properties of VO_2 thin films using x-ray photoelectron spectroscopy (XPS) and Raman spectra for the first time. We concluded that aging for years significantly affected the nonstoichiometry of VO_2 thin films and degraded the electro-optical properties of the films.

2. Experimental details

Thin films of high quality VO_2 were deposited in an argon/oxygen atmosphere by RF magnetron sputtering. Previous to film deposition, the sputtering chamber was evacuated to about 1×10^{-3} Pa by turbo-

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molecular pump. Then the argon/oxygen gases, which had a typical purity of 99.999%, were introduced to the sputtering chamber. The vanadium had a purity of 99.9% using as a target. The soda-lime glasses and fused silica were used as substrates. The temperature of substrates was about 580°C, typical deposition parameters were as follows: the ratio of oxygen to argon, 0.8%–1.2%; total sputter gas pressure, 1.0 Pa; RF power, 120 W.

All the samples were loaded into an ultrahigh vacuum (UHV) chamber for XPS characterization. The UHV system was equipped with a monochromatized Al K α source and a hemisphere analyser for XPS. The base pressure of the UHV system was 1.33×10^{-7} Pa and XPS energy resolution ~ 0.6 eV. The binding energy scale was calibrated against the C1s line centred at 285.0 eV. The Raman spectra were acquired at room temperature using RENISHAW 1000 system. The 514.5 nm line of argon ion laser was used as exciting light. The spectra were measured in backscattering geometry. The resolution was about 1 cm^{-1} , a $50\times$ objective was used to focus the laser light on sample surface to a spot size of $2 \mu\text{m}$.

3. Results and discussion

The x-ray diffraction (XRD) patterns of the fresh VO₂ film and aged one were not obviously different, which were also in agreement with those of VO₂ film we had published before.^[12,13]

XPS was used in an attempt to determine the surface difference of both films above. The survey scans of both the fresh VO₂ film and the aged one deposited on soda-lime glasses were nearly the same (Fig.1(a)), which were due to lower energy resolution when scanned in a whole region, not identifying the surface difference of both films. From the Fig.1(a), the XPS peaks of V2p, O1s were observed and assigned to VO₂. The C1s peak centred at 285 eV probably originated from carbon contamination. Particularly, two novel peaks centred at 497 eV and 1072 eV were observed, respectively, which originated from soda-lime glass substrate. For comparison, the survey scan of VO₂ film deposited on fused silica was provided in Fig.1(b). From Fig.1(b), the above two peaks assigned to sodium did not appear any more because of fused silica substrate not including any sodium ions. We strongly concluded that sodium ions would diffuse from soda-lime substrate to film surface when sputter

performed at high substrate temperature, which was not in agreement with other authors who claimed that VO₂ film could not deposit on soda-lime glass because of sodium contamination.^[16]

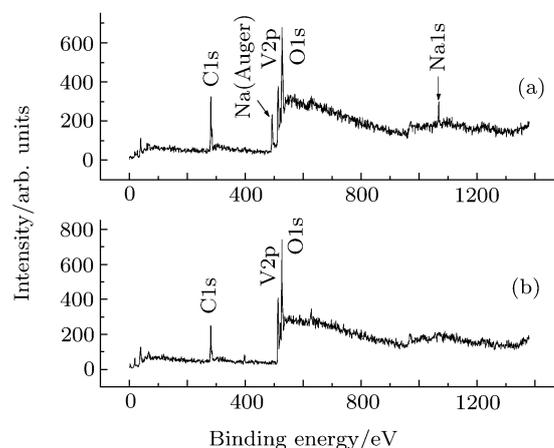


Fig.1. XPS survey scan of VO₂ films deposited on (a) soda-lime glass, (b) fused silica.

Figures 2(a) and 2(b) showed the V2p and O1s core lines for fresh VO₂ film and aged one deposited on soda-lime glasses, respectively. These lines had been fitted with partial Lorentzian and Gaussian line shapes by software XPSpeak41. The intensity ratio of V2p_{3/2} to V2p_{1/2} was constrained to about 2:1. The peak positions of some of the core lines for above films were given in Table 1.

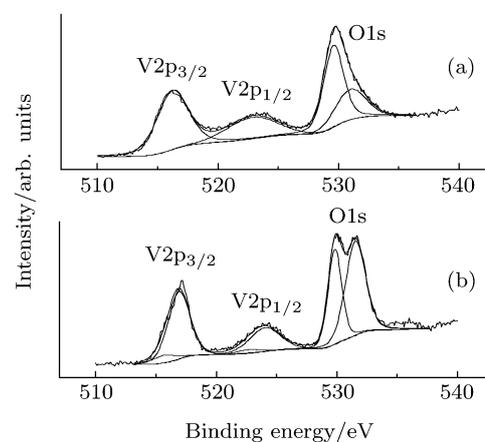


Fig.2. XPS spectra of the V2p and O1s region for (a) fresh VO₂ film, (b) aged VO₂ film.

Table 1. Binding energies of core lines of stoichiometric and oxygen rich VO₂ films.

materials (VO ₂ films)	binding energy/eV			
	V2p _{3/2}	V2p _{1/2}	O1s	O1s
stoichiometric	516.3	523.5	529.6	531.1
oxygen rich	516.9	524.3	529.9	531.6

From Figs.2(a) and 2(b), it was found that the features of O1s lines of VO₂ film and aged one were quite different. In case of aged VO₂ film for years, the intensity ratio of higher binding energy peak to lower one of O1s doublet increased, as compared with that of fresh VO₂ films. In order to prevent samples from absorption effect, we heated the sample in nitrogen filled glove box at 100°C and subsequently measured in XPS system. We could not reduce the relevant intensity ratio of O1s doublet for aged VO₂ film yet. This showed that surface oxidation, not surface absorption played an important role in line shape of O1s doublet in our case. Surface oxidation occurred perhaps due to irreversibly deteriorative VO₂ by aging under circumstance for years.

To further explore the different properties of both the fresh VO₂ film and aged one deposited on soda-lime glass, Raman spectra was carried out to detect the mode change of both films mentioned above, because it is an effective and sensitive tool to determine stoichiometric and nonstoichiometric VO₂. Figures 3(a) and 3(b) showed the Raman spectra of fresh VO₂ film and aged one. The major peak positions of both films were given in Table 2. As can be seen, the two spectra are quite different. For fresh VO₂ film, Raman spectrum is in agreement with that of stoichiometric VO₂ reported elsewhere. The major peaks of the spectrum were centred at 193, 224, and 613 cm⁻¹, respectively. However, for aged VO₂ film, the major peaks are shifted to higher frequencies of 201, 226, and 640 cm⁻¹ accordingly, as compared with those of fresh one. This is in agreement with a result of surface oxidation of VO₂ reported by Parker. Therefore we confirmed further that surface oxidation occurred when fresh VO₂ films exposed in air for years.

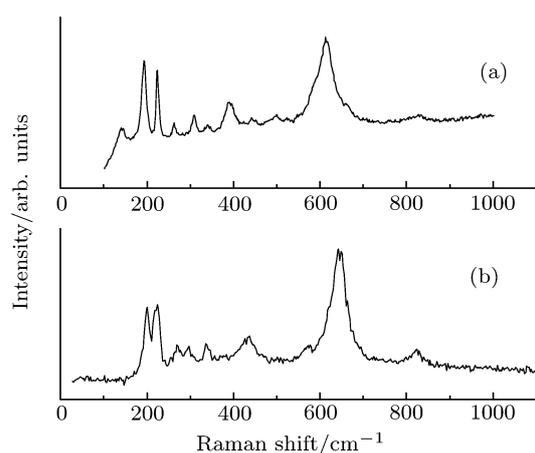


Fig.3. Raman spectra of (a) fresh VO₂ film, (b) aged VO₂ film.

Table 2. Comparison of Raman peak positions measured in this work with the results provided in Parker's report. All values are in cm⁻¹.

Present work (VO ₂ films)		Parker J C ^[15]	
stoichiometric	oxygen rich	stoichiometric	oxygen rich
142		142	
193	201	191	202
224	226	223	232
263	272	262	266
309	295	310	305
392		392	382
	430	443	455
500		500	580
613	644	613	640
	822		

4. Conclusion

XPS was used to study the electronic structure of fresh VO₂ film and aged one prepared by RF magnetron sputtering. We found that sodium ions diffused from substrate to film surface when a VO₂ film was deposited on soda-lime glass at high substrate temperature. There were obvious changes in O1s doublet for VO₂ film and aged one described above. Raman was performed to further detect surface difference of the films. We found that major peak positions of fresh VO₂ were in agreement with those of stoichiometric VO₂, however, major peak position of aged VO₂ were shifted to higher frequencies, indicating occurrence of surface oxidation of aged VO₂ in air for years.

The optical and electrical properties of VO₂ were affected by the stoichiometry of the films. The change of stoichiometry VO₂ occurred when they were exposed in natural circumstance because of the effect of oxygen and humidity. This showed that aging of the stoichiometric VO₂ would probably degrade the properties of the films, therefore not benefit the applications such as smart windows, bolometer, and recording materials. We suggested that a protected layer deposited on the relevant VO₂ films were necessary especially when they would be used under a hot and damp circumstance.

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