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Effect of nonstoichiometry on Raman scattering of VO_2 films*

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We report on Raman scattering of VO_2 films prepared by radio frequency magnetron sputtering under different conditions. Our investigations revealed that the dominated Raman peaks shift towards high frequency for both V-rich and O-rich VO_2 films, compared with the stoichiometry VO_2 films. The experimental evidence is presented and the cause for nonstoichiometry dependence of Raman spectra of VO_2 films is discussed.

Keywords: vanadium dioxide thin films, Raman spectra, nonstoichiometry, RF magnetron sputtering
PACC: 6480, 7830, 8115C

1. Introduction

Vanadium dioxide (VO_2) undergoes a semiconductor-to-metal (SM) structure transformation from low-temperature monoclinic phase to high-temperature tetragonal phase at 68°, and accompanied by a dramatic change in electrical and optical properties.[1] This makes VO_2 a strong candidate in the applications to making electrical and optical devices and "smart" windows.[2,3]

Raman scattering is a useful tool to study the electron–phonon interactions of VO_2 for it is believed that these interactions seem to be the important mechanism in the SM transformation. Unfortunately, although researches on Raman scattering of VO_2 have not been very many, different authors gave different results, including the different spectral feature, peak position, and mode symmetry assignment. Parker [4] first gave a systematic research, trying to explain these difference by annealing stoichiometry VO_2 or studying natural aging, then comparing the Raman spectra of the above samples with those of the stoichiometric one. He found that surface oxidation plays an important role in the spectral feature and peak position. However, he did not present an oxygen deficiency dependence of the Raman spectra of VO_2. Therefore, it is necessary to further study the Raman spectra of V-rich VO_2.

In this article, we present a series of Raman measurements carried out on VO_2 thin films. We propose a physical mechanism that is responsible for the cause of difference between previously reported Raman spectra of VO_2 and the correct Raman signature for VO_2.

2. Experimental details

Vanadium dioxide thin films were deposited on soda-lime glass by radio frequency (RF) magnetron sputtering. The target was a vanadium metal plate (purity 99.9%), and the substrates were slides of size 9mm×9mm. The deposition conditions were as follows: initial pressure was $< 1.3 \times 10^{-3}$Pa; pressure during sputtering, 1.0Pa; distance of target to substrate, 60mm; RF power, 120W. First the substrates were heated to 580°C. All the films were deposited for 60min, and after the deposition, the samples were cooled to room temperature in vacuum without post-annealing. X-ray diffraction (XRD) measurement was performed by means of a RINT 2400 diffractometer with a monochromatized Cu$K\alpha$ radiation. The Raman spectra were acquired at room temperature using RENISHAW 1000 system and SPEX 1403. The 514.5nm line of argon ion laser was used as exciting

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light. The spectra were measured in backscattering geometry.

3. Results and discussion

Figure 1 shows the XRD patterns of VO_2 thin film prepared at oxygen content of 1.0%. Only one distinguished peak at 2θ=27.76° is observed in the diffraction curve, corresponding to the (011) diffraction of the monoclinic VO_2. This is in good agreement with previous result [5] of our group. The intensity of the XRD peak indicates a preferred orientation.

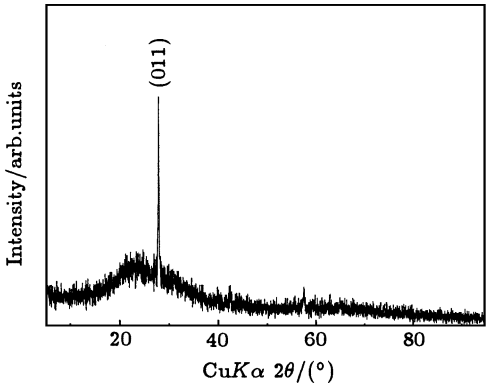


Fig.1. XRD pattern of VO_2 thin film prepared at oxygen content of 1.0%.

Figure 2 shows the room temperature Raman spectra of the same VO_2 film as for the XRD measurement. As can be seen, the spectra are dominated by two sharp peaks at 192 and 224 cm^{-1} and a boarder peak at 614cm^{-1}. The weaker peaks are identified in Table 1. The spectral feature, peak positions and symmetry assignments agree quite well with the results of Aronov *et al*,[6] indicating that the VO_2 thin film is a stoichiometric one. On the basis of this result, we can further study the Raman spectra of both vanadium-rich and oxygen-rich VO_2 thin films.

In this study, stoichiometric V-rich and O-rich VO_2 films were obtained by controlling the oxygen content. The as-prepared stoichiometric VO_2 film was obtained at an oxygen content of 1.0%. Although VO_2 lattice was still formed as the only stable phase at oxygen content down to 0.8%, it should be assumed that this material was chemically VO_{2-x}. In contrast, the VO_2 lattice was still formed as the only stable phase at oxygen up to 1.2%, and it must be assumed that this material was chemically VO_{2+x}.

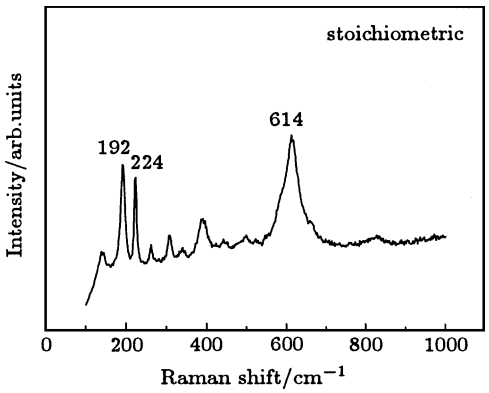


Fig.2. The Raman spectra of VO_2 thin film prepared at oxygen content of 1.0%.

Table 1. Comparison of Raman peak positions measured in this work and the results of Aronov *et al.*[6] All the data are in cm^{-1} units.

Aronov	142	191	222	259	308	335	389		497	611
This work	141	192	224	263	308	339	391	443	497	614

Figure 3 shows Raman spectra of VO_2 films prepared under different oxygen contents at room temperature. The thickness of all the films is about 120nm. For stoichiometric VO_2 film, three dominant peaks are observed at 192, 224, and 614 cm^{-1}. For O-rich VO_2 films, with the decrease of the ratio of vanadium to oxygen, the above three peaks shift to higher frequencies. In the end, the first two sharp peaks become very weak, and the broader peak shifts to 642cm^{-1}. In Parker's paper [4], the trend of oxidation tends to shift the major spectral peaks at 191, 223, and 613cm^{-1} to higher frequencies of 202, 232 and 640cm^{-1}, respectively. Our trend is almost the same as his. For this, his explanation is that surface oxidation makes stoichiometry VO_2 films become O-rich, which leads the Raman spectral peaks shifting to higher frequencies. But he did not further explicate this result. For V-rich VO_2 films, with the increase of the ratio of vanadium to oxygen, the major spectral peaks at 192, 224 and 614cm^{-1} shift to higher frequencies. In the end, the first two sharp peaks become very weak, and the broader peak shift to 644cm^{-1}.

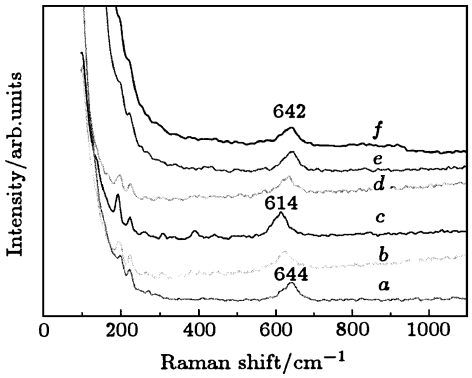


Fig.3. The Raman spectra of VO_2 thin films prepared by RF magnetron sputtering under different oxygen contents of *a*: 0.8%, *b*: 0.9%, *c*: 1.0%, *d*: 1.1%, *e*: 1.2%, *f*: 1.3%.

Previous studies [7] on VO_2 films suggested that in the lattice with very small amount of cations V^{3+}, oxygen deficiency can be accommodated by the introduction of interstitial cations rather than anion O^{2-} vacancies. This situation may result in the presence of sufficient V^{3+} ions in the lattice to preserve electrical neutrality and cause the lattice expansion which is observed in oxygen-deficient films. Excess oxygen cannot go into the lattice interstitially due to the large size of O^{2-} ions, and this condition is therefore accommodated by cation vacancies. The decreasing screening of the O^{2-} ions results in the increase of Coulomb repulsion and a corresponding increase in cell volume. Although the cell volume of nonstoichiometry became larger than that of stoichiometric VO_2, the interaction between atoms increases as seen from Raman spectra analysis of the above samples. We know that a large amount of V^{3+} in the lattice will result in noncrystalline VO_2 and the dramatic decrease of its resistivity,[8] but fewer V^{3+} ions in the lattice will produce compressive stress. Therefore, it is reasonable that the Raman spectra of V-rich VO_2 will shift to higher frequency due to the compressive stress. As for O-rich VO_2, we consider that the Coulomb repulsion many generate internal stress/strain or simply alter the interatomic force constant, both of which will cause the present observations.

4. Conclusion

In summary, we have described the Raman signature for both stoichiometric and nonstoichiometric VO_2 films and demonstrated the influence of nonstoichiometry on the feature of Raman spectra of these materials. From these results we suggest that the nonstoichiometry influence has been an important contribution to the difference we have seen in previously reported Raman spectra of VO_2.

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