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Coexistent structures and film growth in vanadium oxides films

Jiaqi Luo [a], Fen Long [a], Hangyu Long [a], Yijia Wang [a], Dengfeng Yin [a], Qiuping Wei [a,b,*], Z.M. Yu [a,b,*]

[a] School of Materials Science and Engineering, Central South University, Changsha 410083, PR China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China

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ABSTRACT

We report on the coexistent structures of vanadium oxides films prepared by reactive magnetron sputtering. Various tests combined with sputter etching were performed. Coexistence of amorphous, textured and homogeneous polycrystalline structures was discovered in these films. These coexistent structures were discussed and a three-step growth model was proposed which drew a precise picture of the sputtering process.

1. Introduction

Vanadium dioxide (VO_2), a remarkable material which has a thermochromic metal-to-insulator phase transition around 68 °C [1], has been commonly fabricated by reactive magnetron sputtering [2–4]. Although VO_2 film prepared through physical vapor deposition has been widely studied as application for smart window [5], smart radiation devices [6] and laser protection devices [7], few attentions were drawn to the film structure. However, the different structure parameters were proved to have a great impact on the performance of VO_2 films [8]. Investigation of the structure is helpful to understand the correlations of them and lead to better control of these films. Regarding film structure, vanadium oxides films were mostly found in homogeneous form [3] or textured form [4]. Classical structure-zone model (SZM) [9] describes the most regular growth process for sputtered film, and competitive growth model [10] tells how texture grows in thin films, however, none of them predicted a film with rather complicated structures of various phases.

In this study, we found out how VO_2 and vanadium monoxide (VO) existed in the vanadium oxides films and what the film structure was like. Coexistence of amorphous structure, textured crystalline and homogeneous crystalline was observed and confirmed in these films. Furthermore, a new model of film growth was proposed, which gave insights for complexity of vanadium oxides films and even the general film growth during sputtering.

2. Experimental details

The deposition process was performed by DC reactive magnetron sputtering. Cover glass was used as substrate heated at 400 °C during deposition. The sputtering time was 30 min, while the sputtering power was kept on 200 W. Pure vanadium target (99.999%) which has a diameter of 60 mm was used. The oxygen partial pressure was maintained at 5% in a total pressure at 2 Pa. After deposition, samples were annealed at 450 °C for 60 min in nitrogen ambient of 1 kPa. Sputter etching of the films was done by Kaufman ion source in fixed parameters (See Table S1, Supplementary data).

Crystalline structure and phases of the films were confirmed by X-ray diffraction (XRD) experiments, which were completed on Dmax-2500VBX with a Cu Kα radiation at a wavelength of 1.540 Å. Phases were further characterized by Raman spectroscopy (Raman, LabRAM ARAMIS) at an excitation wavelength of 532 nm. The chemical composition and the oxidation state of vanadium of the as-deposited film were examined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Al Kα was used) with an argon gun for depth profiling.

3. Results and discussion

XRD experiments were firstly utilized for investigating phases and transformation among them. In Fig. 1A, the pattern (a) only

* Corresponding authors at: School of Materials Science and Engineering, Central South University, Changsha 410083, PR China. Tel.: +86 73188830335; fax: +86 73188876692.
E-mail addresses: qiupwei@csu.edu.cn (Q. Wei), zhiming@csu.edu.cn (Z.M. Yu).

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shows that the as-deposited film is composed by VO with (111) preferred orientation. The broad background hump which centered at 25° is mainly due to the amorphous substrate made of glass. For the annealed sample, new peaks at 2θ=27.7° and 36.9° appear, which are corresponding to (011) plane and (211) plane of VO_2 respectively. However, for the peaks of VO, no

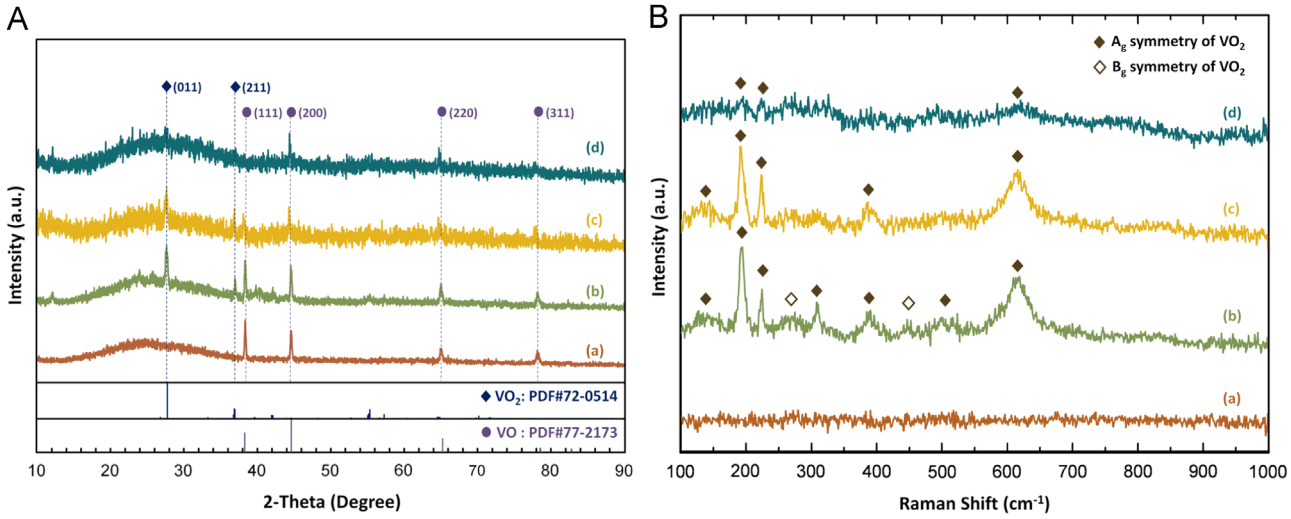

Fig. 1. (A) XRD patterns and (B) Raman spectra of vanadium oxides films which was deposited for 30 min in different states including (a) as-deposited film, (b) annealed film, (c) annealed film after 20 min etching, (d) annealed film after 40 min etching.

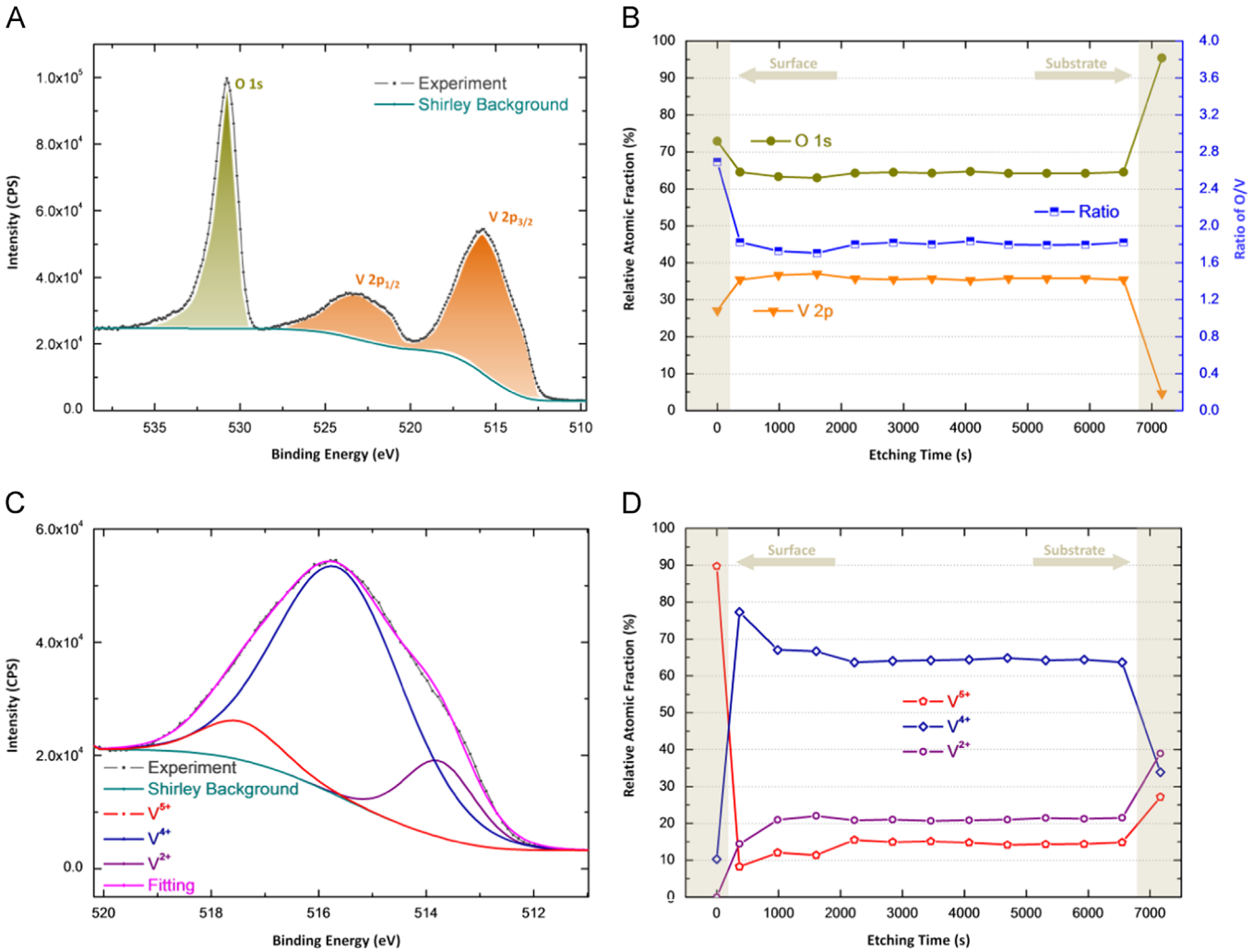

Fig. 2. XPS characterization of the as-deposited film: (A) high resolution scan for O1s and V2p at the first etch level, (B) compositional depth profile calculated by Wagner atomic sensitivity factors, (C) de-convolution of $V2p_{3/2}$ peak at the first etch level, (D) vanadium oxidation values depth profile.