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Vanadium oxide thin films deposited on indium tin oxide glass by radio-frequency magnetron sputtering*

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Highly oriented VO_2(B), VO_2(B) + V_6O_{13} films were grown on indium tin oxide glass by radio-frequency magnetron sputtering. Single phase V_6O_{13} films were obtained from VO_2(B) + V_6O_{13} films by annealing at 480°C in vacuum. The vanadium oxide films were characterized by x-ray diffraction and x-ray photoelectron spectra (XPS). It was found that the formation of vanadium oxide films was affected by substrate temperature and annealing time, because high substrate temperature and annealing were favourable to further oxidation. Therefore, the formation of high valance vanadium oxide films was realized. The V_6O_{13} crystalline sizes become smaller with the increase of annealing time. XPS analysis revealed that the energy position for all the samples was almost constant, but the broadening of the $V_{2p3/2}$ line of the annealed sample was due to the smaller crystal size of V_6O_{13}.

Keywords: vanadium oxide, x-ray photoelectron spectroscopy, annealing, sputtering
PACC: 8115C, 6110, 3365F

1. Introduction

Many oxides of vanadium, such as V_2O_5, V_6O_{13} and VO_2(B), which have three-dimensional framework tunnel structures,[1−4] are well known to be suitable for manufacturing cathode materials in secondary lithium batteries. Murphy and Christian[1] first demonstrated that vanadium oxides, particularly non-stoichiometric V_6O_{13}, have a large reversible insertion capacity and high theoretical energy density, making vanadium oxides attractive cathode materials in secondary lithium batteries. Spurdens and Steele[5] reported the lithium transport properties in the (010) and (001) directions of V_6O_{13} single crystal. Recently, much research has been focused on thin-film rechargeable batteries in order to reduce size and cost. Most important of all, thin-film rechargeable batteries are favourable to large-scale integrated circuits. Zhang *et al*[6] reported on cathode materials of vanadium oxide thin films and pointed out that the best film obtained in their work displayed an oxygen-to-vanadium atomic ratio close to that of V_6O_{13}, and that the film exhibited good discharge capacity (∼408mAh/g) and negligible capacity fade (more than 5800 cycles). However, tight control of the deposition parameters is critical to obtain the correct V_6O_{13} stoichiometry, and therefore research has seldom been reported in the literature. In contrast, much research on V_2O_5 films has been reported. For example, Talledo and Granqvist,[7] reported on the structural, electrochemical and optical properties of V_2O_5 films deposited on indium tin oxide (ITO) glass. Miyazaki *et al*[8] reported on the lithium transport properties in the (100) and (010) directions of V_2O_5 films deposited on ITO glass.

In this paper, we first report on V_6O_{13} films deposited on ITO glass (ITO being amorphous) and obtain non-stoichiometric V_6O_{13} films by annealing. The deposited V_6O_{13} films were characterized by x-ray diffraction (XRD) and x-ray photoelectron spectra (XPS).

2. Experimental details

The vanadium oxide samples were grown on ITO films with a sheet resistance of 80 Ω/cm^2 by rf magnetron sputtering. The target was a vanadium metal plate (purity 99.65%). The ITO substrates put into the sample holder above the target were slides 9 × 9mm^2 and the vanadium oxide films on ITO were slides 8.5 × 8.5mm^2. The deposition parameters have

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been described in detail in a previous paper.[9] In this work, all the samples were deposited for 60min. After the deposition, some samples were annealed under the same temperature in vacuum (about 9×10^{-4}Pa). After annealing, the substrate heater was turned off and the film allowed to cool.

The XRD data were obtained using a RINT 2400 spectrometer with monochromatized Cu $K\alpha$ radiation. The XPS were obtained using Mg $K\alpha(h\nu$=1253.6eV) non-monochromatized radiation with a VG-ESCALAB5 spectrometer. The spectra were analysed in terms of relative peak area intensity and chemical shifts of O_{1s} and V_{2p}. The charging effects were corrected by using the C_{1s} peak, as a reference for all samples at a binding energy (BE) of 284.5eV.

3. Results and discussion

The XRD patterns of vanadium oxides grown on ITO substrates under various temperatures and annealing times are shown in Fig.1. The film deposited at 450°C showed a highly oriented VO_2(B) structure (see Fig.1(a)). Vanadium oxide films deposited at 480°C without annealing showed a mixed structure of highly oriented V_6O_{13} and VO_2(B) (see Fig.1(b)), indicating that a higher temperature was favourable for the formation of high valence vanadium oxides. When vanadium oxide was deposited at 480°C and annealed for several hours, single phase V_6O_{13} films were obtained, indicating that annealing in vacuum at 480°C was favourable to oxidation of the above mixture film due to the presence of a little oxygen in the chamber.[9] We also found that the intensity of the V_6O_{13} (003) peaks decreases, but the full width at half maximum (FWHM) of the V_6O_{13} (003) peaks increases with the increase of annealing time, indicating that oxygen-rich V_6O_{13} films result in amorphous and small grain sized V_6O_{13} crystals, due to oxidation distorting the lattice.[10]

In order to describe the dependence of the change of the intensity and FWHM of the V_6O_{13} (003) peaks on annealing time, we list the corresponding parameters and calculated value of crystal size using the Scherrer formula in Table 1. From this table, it is obvious that the V_6O_{13} crystal size becomes smaller with annealing. An increase of the annealing time causes the film to become oxygen rich, consequently distorting the lattice.

The samples were also characterized by XPS analysis. All the data reported in the following have been normalized by assuming the energy position of the carbon peak (C_{1s}) to be at 284.5eV. For better comparison of the shape of the peaks from sample to sample, the peak heights in the figures were adjusted (not normalized).

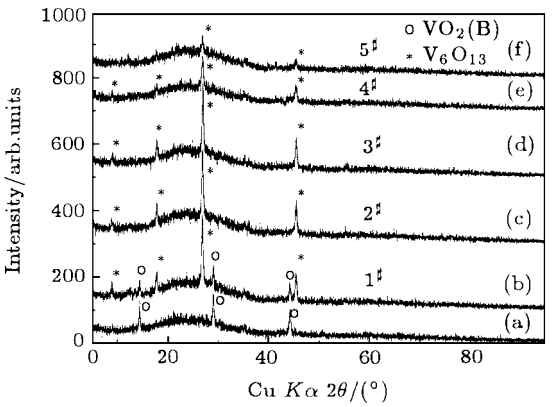


Fig.1. XRD patterns for vanadium oxide films deposited on ITO glass under different conditions: (a) at 450°C for 1 h; (b) at 480°C for 1 h; (c) at 480°C for 1 h and annealing in vacuum at 480°C for 1 h; (d) at 480°C for 1 h and annealing in vacuum at 480°C for 2 h; (e) at 480°C for 1 h and annealing in vacuum at 480°C for 3 h; (f) at 480°C for 1 h and annealing in vacuum at 480°C for 4 h.

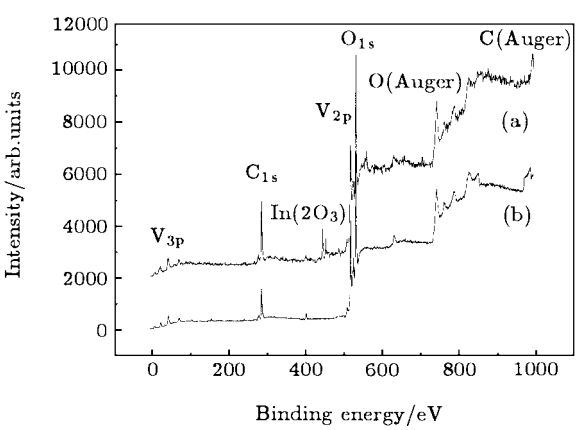


Fig.2. XPS survey spectra for the surface of V_6O_{13} films deposited on (a) ITO glass and (b) fused silica.

Figure 2 shows the XPS spectra of V_6O_{13} films deposited on ITO (a) and fused silica (b) substrates between 0–1000 eV. It can be seen from Fig.2(a) that the V_6O_{13} film deposited on ITO contains elements V, O, C and In. The photoelectron peak for V_{2p} appears clearly at a binding energy E_b of 516 eV, O_{1s} at E_b=530 eV and C_{1s} at E_b=284.5 eV. The In photoelectron peaks are at a binding energy of 444.5 eV. The XPS peaks for In observed in the spectra are due to the existence of ITO not covered by V_6O_{13} films.

The element C in the films is attributed to residual carbon. As can be seen from Fig.2(b), the V_6O_{13} film deposited on fused silica contains only V, O and C.

Figure 3 shows the XPS spectra of vanadium oxide films on ITO substrates in the vanadium–oxygen region (510–540 eV). Such a result indicates that the oxidation state of vanadium remains almost constant upon annealing. The energy position differences between the VO_2(B) and V_6O_{13} films were very slight; as Werfel *et al.*[11] reported, the difference was 0.3 eV. These slight differences are hard for our XPS equipment to detect. Therefore, the energy position for all the samples is found to be almost constant. In contrast, the FWHM of $V_{2p3/2}$ line is seen to change clearly. In VO_2 (B) films, the $V_{2p3/2}$ line is narrow, and is located at 516.7 eV. For the V_6O_{13} system, this line becomes broader. The broad structures of the $V_{2p3/2}$ lines in V_6O_{13} are due to the mixed valance character of the vanadium ions.[12] In the V_6O_{13} system, it is also found that the dependence of the widths of the $V_{2p3/2}$ line on annealing time is interesting (Fig.3(c)–(f)). The $V_{2p3/2}$ line becomes broader with the increase of the annealing time. From Table 1, it can be seen that the increase of the annealing time results in smaller crystal size. In general, the XPS core line is broader for small crystals. The larger number of atoms residing on the surface of small crystals leads to wider peaks. Moreover, core line broadening can be also due to adsorbed oxygen.[13,14] Therefore, we can conclude that the decreasing size of nanoparticles in V_6O_{13} films leads to the broadening of the $V_{2p3/2}$ lines.

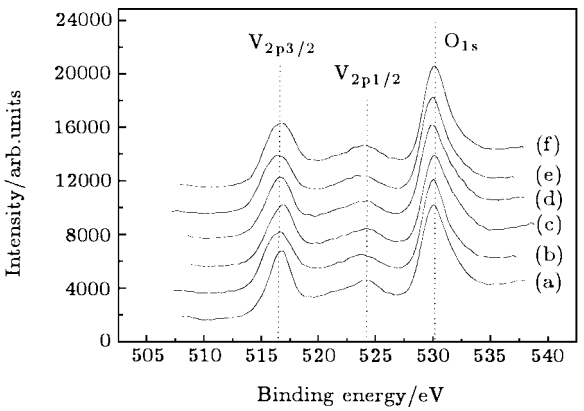


Fig.3. XPS spectra for vanadium oxide film deposited on ITO glass under different conditions: (a) at 450°C for 1 h; (b) at 480°C for 1 h; (c) at 480°C for 1 h and annealing in vacuum at 480°C for 1 h; (d) at 480°C for 1 h and annealing in vacuum at 480°C for 2 h; (e) at 480°C for 1 h and annealing in vacuum at 480°C for 3 h; (f) at 480°C for 1 h and annealing in vacuum at 480°C for 4 h.

Table 1. Structure parameters of thin films measured by XRD.

sample	2θ/(°)	FWHM of V_6O_{13} (003) peak/(°)	crystal size in V_6O_{13} films/nm
1# (Fig.1(b))	26.78	0.282	29.0
2# (Fig.1(c))	26.82	0.290	28.2
3# (Fig.1(d))	26.88	0.306	26.7
4# (Fig.1(e))	26.84	0.4	20.4
5# (Fig.1(f))	26.76	>0.4	<20.4

4. Conclusion

Highly oriented VO_2(B) films were grown on ITO glass at 450°C, while highly oriented VO_2(B) + V_6O_{13} films were grown at 480°C by rf magnetron sputtering. Single phase V_6O_{13} films were obtained from VO_2(B) + V_6O_{13} films by annealing at 480°C in vacuum. It is found that the V_6O_{13} crystal size becomes smaller with the increase of annealing time. This result was attributed to oxidation causing the lattice to distort. XPS analysis revealed that, although for all the samples the energy position is found to be almost constant, the broader $V_{2p3/2}$ line of the annealed sample is due to smaller crystal size of V_6O_{13}.

Acknowledgments

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