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Rapid communication

Transversal grain size effect on the phase-transition hysteresis width of vanadium dioxide films comprising spheroidal nanoparticles

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ABSTRACT

Grain size of vanadium dioxide (VO_2) films or isolated particles is known to play an important role in the modulation of temperature dependence of the hysteresis width in semiconductor to metal transition. In order to investigate the effect of grain size on the hysteresis width, we prepare a range of VO_2 films consisting of spheroidal nanoparticles whose mean size was hugely modulated from 49.4 to 77 nm by an annealing time increasing from 15 to 90 min. However, regardless of the annealing time, the films show similar crystal structure and morphology. More interestingly, experimental results show that the hysteresis width is inversely proportional to the average transversal grain size of VO_2 films. We offer quantitative explanations for the observed grain size dependence of the hysteresis width. This work will provide a more precise picture of the role of the grain size on the hysteresis width of VO_2 films.

Vanadium dioxide (VO_2), a metal-transition compound, exhibits a reversible semiconductor to metal transition (SMT) at a critical temperature of ~68 °C [1]. The unique SMT properties accompanying by strong changes in optical and electrical properties [2–5] as well as terahertz transmission [6–8] made VO_2 an attractive candidate for a wide variety of applications such as switching devices [9,10], smart windows [11,12], storage devices [13–15] and terahertz modulators [7,16]. Due to the fact that different practical applications require different SMT properties [5,17,18], it is essential to understand the physical relations between film or nanoparticle microstructures and the SMT properties, particularly the hysteresis width. Recently, the grain size effect of VO_2 thin films or isolated nanoparticles on the hysteresis width has been extensively investigated [18–24].

However, in previous studies mentioned above, a direct and clear-cut correlation between grain size and the hysteresis width is far from being established because the grain shapes, surface morphologies, the degree of film compactness, and/or preferred crystallographic orientation change significantly with the variation of grain size [18–24]. In the present work, with the variation of annealing time, the grain size changes significantly while the grain shape, surface morphology as well as preferred orientation of the deposited VO_2 films does not change. This enables us to effectively investigate the grain size dependence of the hysteresis and thereby develop a deeper understanding of the materials physics associated with the phase transition.

The VO_2 films were prepared on K9 glass substrates at low temperature by means of direct current reactive magnetron sputtering followed by in-situ annealing process. The annealing time is varied from 15 to 90 min in order to obtain VO_2 films with different grain sizes. The experimental details have been described elsewhere [5]. Field-emission scanning electron microscopy (FE-SEM, Hitachi S4800) and the X-ray diffraction (XRD, X′ Pert, Philips) were used to characterize the surface morphology and the crystal structure of the deposited film, respectively. The temperature dependence of transmittance at a fixed wavelength of 1100 nm was measured by UV–visible spectrophotometer (Pharma Spec-1700, Shimadzu Corporation).

Fig. 1 exhibits the effect of annealing times on the surface morphologies of VO_2 thin films. It is obvious that all the films have a similar surface morphology and consist of compact spheroidal nanoparticles regardless of annealing time. The pores in film surface decrease with increase in annealing time up to 45 min, after which the pores increase with annealing time. This suggests that proper annealing time can improve the surface morphology of VO_2 films. To further analyze the characteristics of VO_2 particles, the statistical

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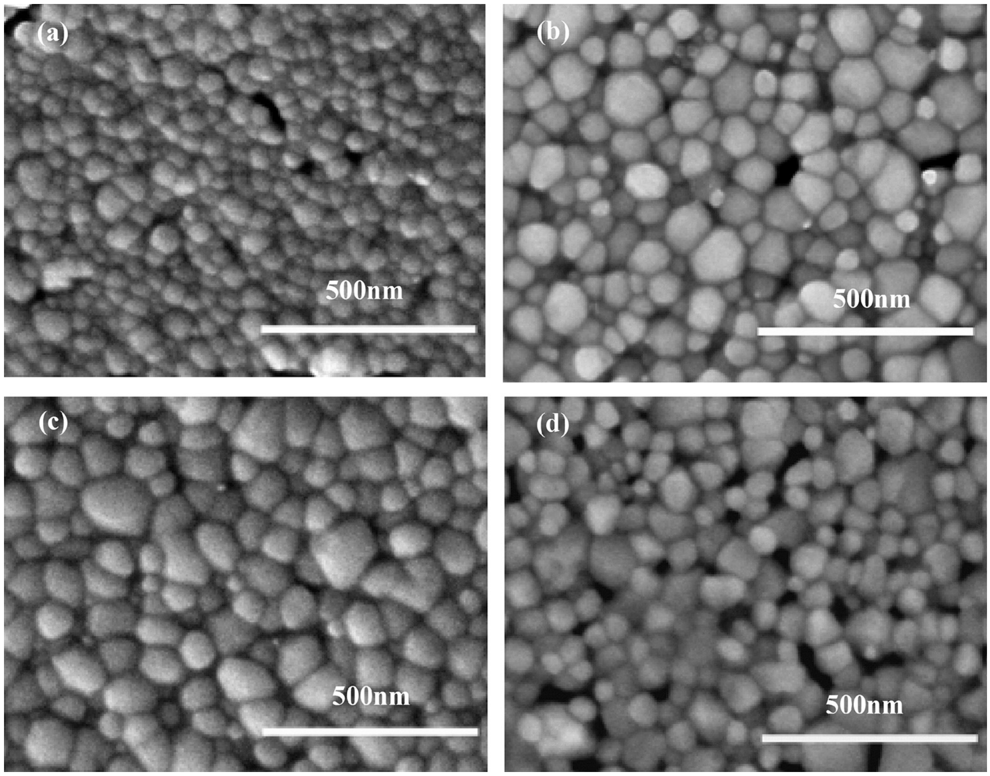

Fig. 1. SEM images of VO_2 films formed at different annealing times: (a) 15 min, (b) 30 min, (c) 45 min and (d) 90 min.

distribution of the grain sizes was measured using the diameter of spheroidal particles. Fig. 2 shows the corresponding size distribution scatter graph, which was plotted by randomly measuring the diameters of 150 grains in a given SEM image. The average transversal grain size of VO_2 films measured from SEM images was listed in Table 1. We can see from Figs. 1 and 2 and Table 1 that the transversal grain size increases significantly with increase in annealing time. We can see from Figs. 1 and 2 and Table 1 that the transversal grain size increases with increase in annealing time up to 45 min, after which the transversal grain size decreases with annealing time. Similar phenomena have also been observed in VO_2 films prepared on the fused silica substrates in aqueous solution [18], VO_2 nanocrystals prepared on high-purity fused silica substrates by ion implantation [20] and β-$FeSi_2$ thin films prepared on silicon (100) substrate by pulsed laser deposition [25].

Fig. 3 shows the XRD patterns of VO_2 films processed at various selected annealing times. It is found that the films are randomly oriented on glass substrates and all the diffraction peaks agree well with the JCPDS file card no. 43-1051 for the monoclinic VO_2. No extra peaks due to any other vanadium oxide phases are detected in the XRD spectra, indicating the formation of single-phase VO_2 films [24,26]. All the films exhibit a strong peak at $2\theta \approx 27.80°$, which is ascribed to the reflection of VO_2 (011) plane. The peaks at $2\theta \approx 39.71$ and 57.44° correspond to (020) and (022) planes of VO_2 phases, respectively. It is obvious that the (011) peak is much stronger than the others, indicating that all the deposited films are polycrystalline and have a (011) preferred orientation. The full-width-at-half maximum of the (011) peaks of the VO_2 film is found to decrease as the annealing time increases. The average crystallite size estimated by the Scherrer's formula increases from ~30 to ~37 nm as the annealing time increases from 15 to 45 min.

Fig. 4(a) shows the optical transmittance at a fixed wavelength of 1100 nm as a function of temperature for VO_2 films. We can see

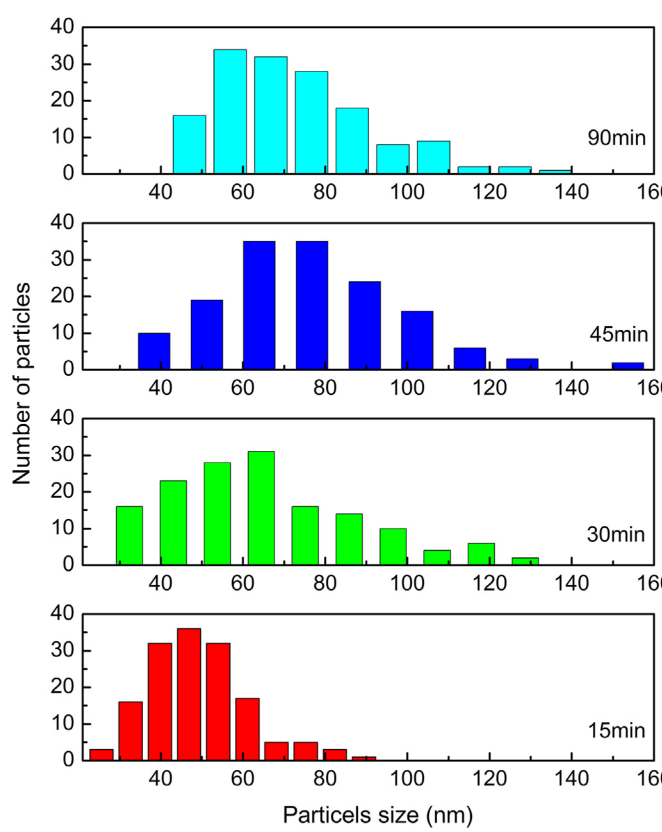

Fig. 2. Scatter graphs of grain size distribution for VO_2 films.