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Synthesis and properties of Mo and W ions co-doped porous nano-structured VO$_2$ films by sol–gel process

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Abstract Porous nano-structured vanadium dioxide (VO$_2$) films doped with Mo and W ions had been synthesized by sol gel process by employing a sol containing ammonium molybdate and ammonium tungstate with the addition of cetyltrimethyl ammonium bromide (CTAB). The effects of molybdenum and tungsten co-doping and CTAB addition on the structure, morphologies, crystalline and optical properties of VO$_2$ films were investigated systematically in this study. The composition and microstructure were detected by X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy. The Mo and W ions co-doped porous nano-structured VO$_2$ films showed excellent infrared transmittance (nearly 70 %), large transmittance difference (55 %) before and after the phase transition, low transition temperature (35 °C), wide hysteresis width (22 °C) and fast phase transition. The results suggest that such Mo and W ions co-doped porous nano-structured VO$_2$ film is an ideal fundamental material for optical data storage.

Keywords Mo and W ions co-doped ·
Vanadium dioxide · Sol–gel process · Porous film ·
Optical properties

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1 Introduction

In this era of data explosion, the continuously increasing amount of data has generated the need for high speed computers and large storage capacities. One of the most important challenges is the development of materials and techniques to extend the data storage capacities [1]. Optical recoding has many advantages over other storage techniques [1, 2]. Consequently, the demand for truly rewritable optical recording media is in uninterrupted growth in recent years. For materials used in rewritable optical data storage, apart from economical, environmental and technical restrictions, the most important requirements for the application of optical data storage materials are: (1) a reversible and bistable transformation, (2) the materials should be fatigue resistant, (3) fast response speed, leading to fast switching cycles, (4) allowing storage of data almost infinitely [1, 3].

Vanadium dioxide (VO$_2$) film is an excellent supporting material for the practical use of data storage due to its phase transition properties [4]. The first-order metal-to-semiconductor transition (MST) of VO$_2$ can be triggered thermally or optically with a ultra fast phase transition (within 500 fs) [5, 6]. Besides, VO$_2$ films can survive stress change above 10^8 cycles [7]. All these properties are suitable for applications in optical data storage.

There are, however, several restrictions which have to be considered upon using VO$_2$ films for data storage application. For example, the phase-transition temperature (T_t) of the VO$_2$ film is about 68 °C, which is too high on conventional storage applications. Besides, the hysteresis widths (ΔT) of VO$_2$ films are too narrow (1–4 °C), which is not suitable for large storage capacities. Porous nano-structure has proved to be useful in T_t reduction and ΔT broadening [8]. And the T_t of VO$_2$ film can be further

reduced by doping with metals such as tungsten and niobium, but doping with metals results in the optical phase-transition properties weakening of the VO_2 film, which is unfavorable for application [9]. Mo and W ions co-doping is reported useful in lowing T_t and keep the optical properties [10]. So imagine if we fabricated porous nano-structured films with Mo and W ions co-doped, the application shortcomings of VO_2 films may be made up.

In our former experiments, undoped porous nano-structured VO_2 films are fabricated by sol–gel process with the addition of surfactant Cetyltrimethyl Ammonium Bromide (CTAB). The T_t and ΔT of the film are 56 and 34 °C, and both can be controlled by the CTAB concentration. In the present work, Mo and W ions co-doped porous thin films are synthesized from a Mo and W ions co-doped sol with the addition of block copolymer CTAB successfully. The films show excellent optical properties, low phase transition temperature (35 °C), wide hysteresis width (22 °C) and fast phase transition. VO_2 films possess these properties meet the requirements of optical data storage and are of great importance in practical application.

2 Experimental

2.1 Preparation of precursor solution

In a typical synthesis procedure, 10 g vanadium pentoxide (V_2O_5, 99.9 % pure) powder was heated to 880 °C in a crucible until molten, and then poured it into 400 mL deionized water at room temperature. After vigorous stirring for 2 h, a brownish sol was formed. The Mo and W ions co-doped precursor was first mixed ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot4H_2O$, >99.0 % pure) and ammonium tungstate ($(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$, >99.0 % pure) with vanadium pentoxide powder as additives to introduce doping ions, and then followed the same way as described above to form a Mo and W ions co-doped precursor. The sol was aged for 2 days, then 0.7 g cetyltrimethyl ammonium bromide (CTAB, average molecular weight: 364.5) powder was homogeneously mixed with V_2O_5 sol (20 mL) or Mo and W ions co-doped V_2O_5 sol (20 mL) as porous structure directing agent. The CTAB sphere colloid could be anchored to the surface of the V_2O_5 colloid by the combined electrostatic force and hydrogen bonding in the solution. A sticky solution was formed, 10 mL ethanol was then added into dilute it and the blended sol was stirring for 24 h to get brick-red sol. The samples with different synthesis conditions were defined as V1 (pure VO_2 film), V2 (pure VO_2 film with CTAB), V3 (Mo and W ions co-doped VO_2 film), V4 (Mo and W ions co-doped VO_2 film with CTAB).

2.2 Preparation of VO_2 film

The mica substrates were pre-treated in ethanol, hydrochloric acid and aqueous ammonia to remove some organic contaminations on the surface of the natural substrate. The deposition was carried out by spin coating method, precursor films were formed on the treated mica substrates with a spin speed of 1,400 r/min. Then, the films were dried at 90 °C for 20 min. This process was repeated thrice to increase the film thickness. Then the V_2O_5 films were reduced to VO_2 films by annealing them at 505 °C in a static nitrogen atmosphere for 1 h in a furnace, with a heating rate of 8 °C/min. The obtained precursor gel films were reduced into thermochromic VO_2.

2.3 Characterizations

The morphologies of the films were studied by S-4800 scanning electron microscopy (SEM). The crystalline structure of the films was determined by X-ray diffraction (XRD) using X'Pert diffractometer with Cu Kα ($\lambda = 0.15406$ nm) radiation source at an X-ray grazing angle of 1.5°. The optical properties of the films were investigated by Tensor27 (Bruker, Germany) spectrophotometer to analyze the transmittance of the films in the infrared range below and above the phase transition temperature. The temperatures were measured with an appended temperature sensor in contact with the films and it was controlled via a temperature controlling unit. Hysteresis loops were measured by collecting the transmittance of films at a fixed wavelength (4 μm) at approximately 2 °C intervals.

3 Results and discussion

3.1 XPS

Typical surface XPS spectrum of the undoped, and Mo and W ions co-doped samples recorded at room temperature are presented in Fig. 1. All the XPS spectrum clearly show the intense peaks of V and O, the spectrum of Mo and W ions co-doped film in Fig. 1 exhibits weak peaks of Mo and W, which indicates the incorporation of Mo and W atoms in the VO_2 films [10]. Usually, the phase of vanadium oxides can be determined by the characteristic V $2p_{3/2}$ peak position because it is the most sensitive to phase change [11]. The V $2p_{3/2}$ binding energy of the presented samples in Fig. 1 are respectively 516.8 eV (undoped) and 516.2 eV (Mo and W ions co-doped), in the range of V^{4+} $2p_{3/2}$, suggesting the valence of the vanadium is +4 for the two samples. The peaks correspond to C 1 s and N 1 s attributing to the contaminations on the films surface [12].
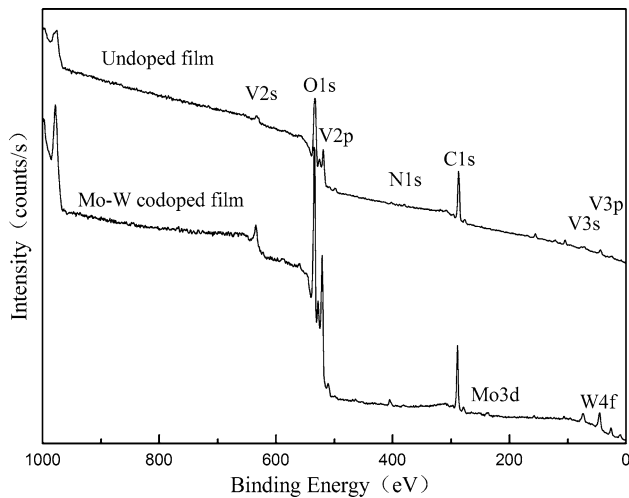
Fig. 1 XPS spectrum of undoped and Mo and W ions co-doped VO$_2$ films

Figure 2 shows the XPS spectrum of high resolution scans of the Mo 3d, W 4f core levels of the Mo and W ions co-doped sample. According to the conclusion of Fig. 2 and the standard binding energy of MoO$_3$ and WO$_3$, the doping ions exist in the films in the form of Mo^{6+} and W^{6+}. The concentrations of the Mo and W ions in the VO$_2$ films are determined by the deconvolution of Mo and W range spectra, and measuring the areas for the peaks of Mo 3d, W 4f$_{7/2}$ and V 2p, taking account of the atomic sensitive factors (ASF) of molybdenum, tungsten and vanadium [10]. The Mo concentrations are estimated by comparing the product of the area at the Mo 3d peaks multiplied by the molybdenum ASF to that of the area at the V 2p peak multiplied by the vanadium ASF. Tungsten concentration is estimated by comparing the product of the area at the W 4f peaks multiplied by the tungsten ASF to that of the area at the V 2p peak multiplied by the vanadium ASF [10, 13]. For the Mo and W ions co-doped VO$_2$ film, the concentrations of Mo and W dopants are 1.02 and 0.36 at.%, respectively. The measured doping ions concentrations are somewhat lower than the initial molar atomic ratio of Mo/V and W/V calculated by the quality of additives and V$_2$O$_5$, the difference should be caused by the redistribution of doping ions during deposition process [10].

3.2 SEM

Scanning electron microscopy (SEM) photos for coating VO$_2$ films of different synthesis conditions are presented in Fig. 3a–d. Figure 3a shows the SEM photograph for the pure VO$_2$ film. The film is uniform and compact with large
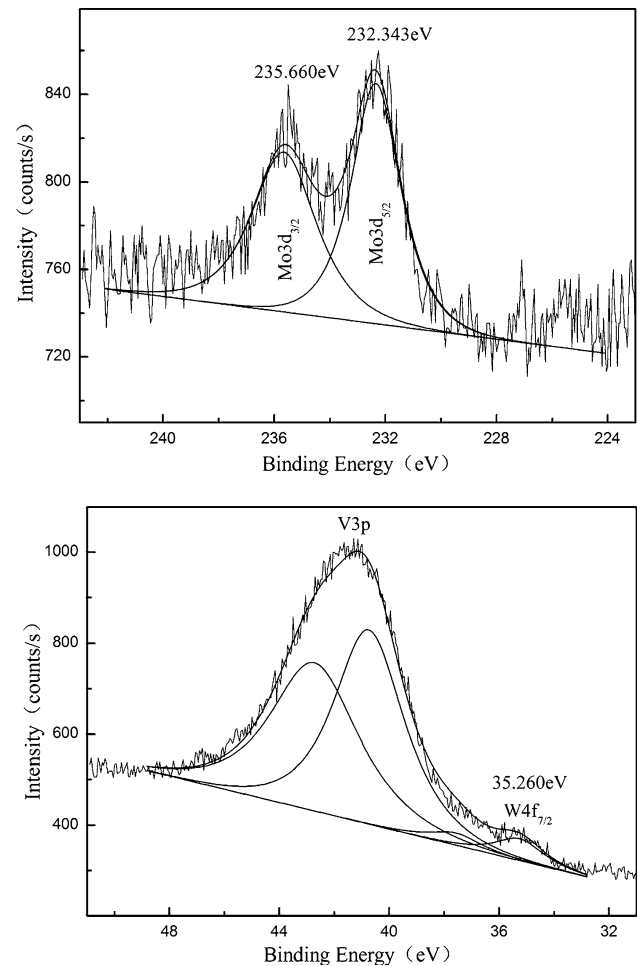

Fig. 2 XPS spectrum of high resolution scans of the Mo 3d, W 4f core levels of the Mo and W ions co-doped VO$_2$ film

grains, and fuzzy boundaries can be seen from the figure. The grain size is reduced obviously in Fig. 3b, the nanostructure feature is observable for the entire film, indicating CTAB has a strong effect on the morphology of the film. The reduced grain size could be ascribed to the presence of CTAB impeded the crystal growth during film deposition and annealing [14]. The pores and loose grain boundaries in sample (b) are attributed to the degradation of CTAB and the shrinkage of the gel film during annealing [15]. The morphology of the Mo and W ions co-doping film is shown in Fig. 3c, the film is compact, and the grain sizes are reduced slightly compared to sample V1, just as reported by Yan [10]. Figure 3d reveals a morphology similar to V2, porous nano-structure is obtained and grain size is reduced apparently compared with sample V1, indicating that the effect of CTAB on impeding the crystal growth still exists in Mo and W ions co-doped VO$_2$ films. However, Mo and W ions co-doped porous film gets larger grain size and smoother surface, the
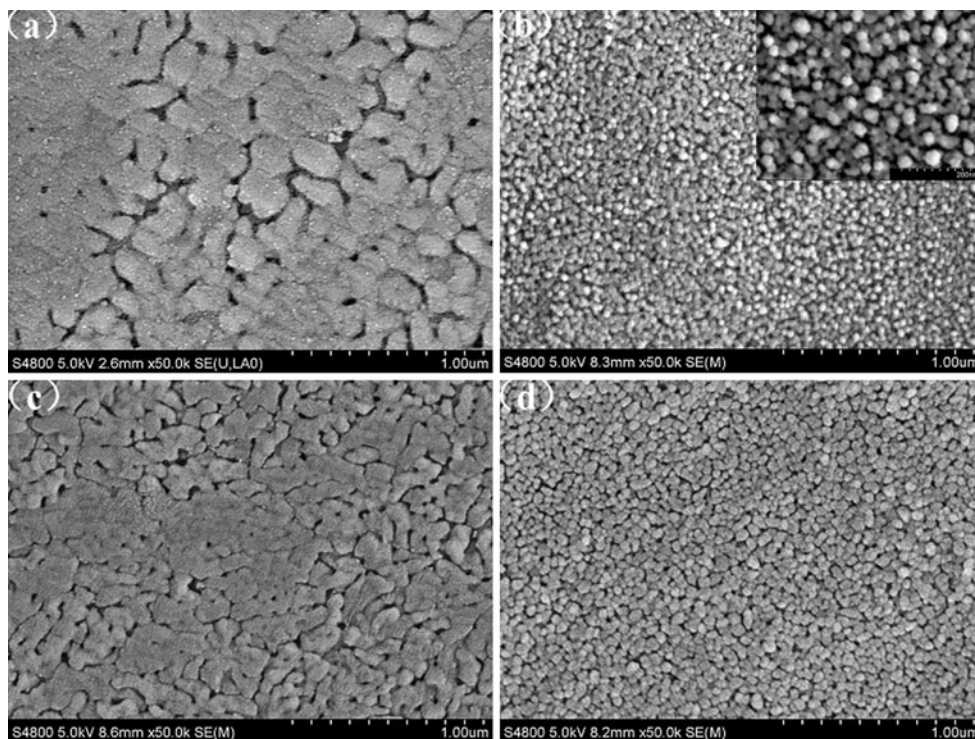
Fig. 3 SEM photos of V1 (**a**), V2 (**b**), V3 (**c**) and V4 (**d**). Samples were obtained by different synthesis conditions, V1: Pure VO_2 film, V2: VO_2 film with CTAB, V3: Mo and W ions co-doped VO_2 film and V4: Mo and W ions co-doped VO_2 film with CTAB

difference should be caused by the reduction of interfacial energy on film and substrate [16].

3.3 XRD

Figure 4 recorded XRD patterns of samples V1-4, all the samples exhibit one sharp diffraction peak at about $2\theta = 27.7°$, which corresponds to the (011) plane of monoclinic VO_2. The covered films are so thin that the diffraction peaks of the mica substrate appear. The peaks of the spectrums at $2\theta = 17.76°, 26.47°, 35.91°, 45.33°$ correspond to different diffraction peaks of muscovite. The peak at $2\theta = 17.76°$ disappears and the peak at $2\theta = 26.47°$ are weakened in the spectrum of V3, due to the thickness of the thin film. No other vanadium oxides (such as V_2O_5 and V_2O_3) are detected. In addition, peaks of MO_3 and WO_3 are not observed in the XRD patterns, ascribing to MO_3 and WO_3 doping into films as the solute donor and forming solid solutions with VO_2. The X-ray patterns for all the samples reveal that the vanadium dioxide crystal grows on the mica substrate with preferred orientated (011) plane, which is the most stable low-index face with the lowest energy of the monoclinic phase [10]. Nevertheless, the (011) diffraction peak of VO_2 films are broadened with CTAB addition (V2 and V4), which is largely due to grain refinement [17].
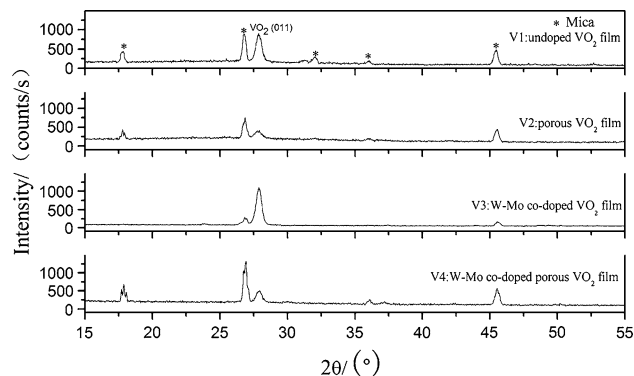

Fig. 4 XRD patterns of V1, V2, V3 and V4 with a grazing angle of 1.5°

3.4 FTIR in VO_2 films

Figure 5 shows the thermal hysteresis loops of the optical transmittance at a fixed wavelength of 4 μm for VO_2 thin films synthesized at different conditions. The figures clearly illustrate the influence of Mo and W ions co-doping and porous nano-structure on phase transition of VO_2 films. The temperature corresponding to the maximum of each $dT_r/dT-T$ curve is defined as the phase transition temperature of each branch; T_1 and T_2 equal to the T_t of heating and cooling branches, respectively. The MST temperature of the film is defined as $T_t = (T_1 + T_2)/2$, and the hysteresis width (ΔT)
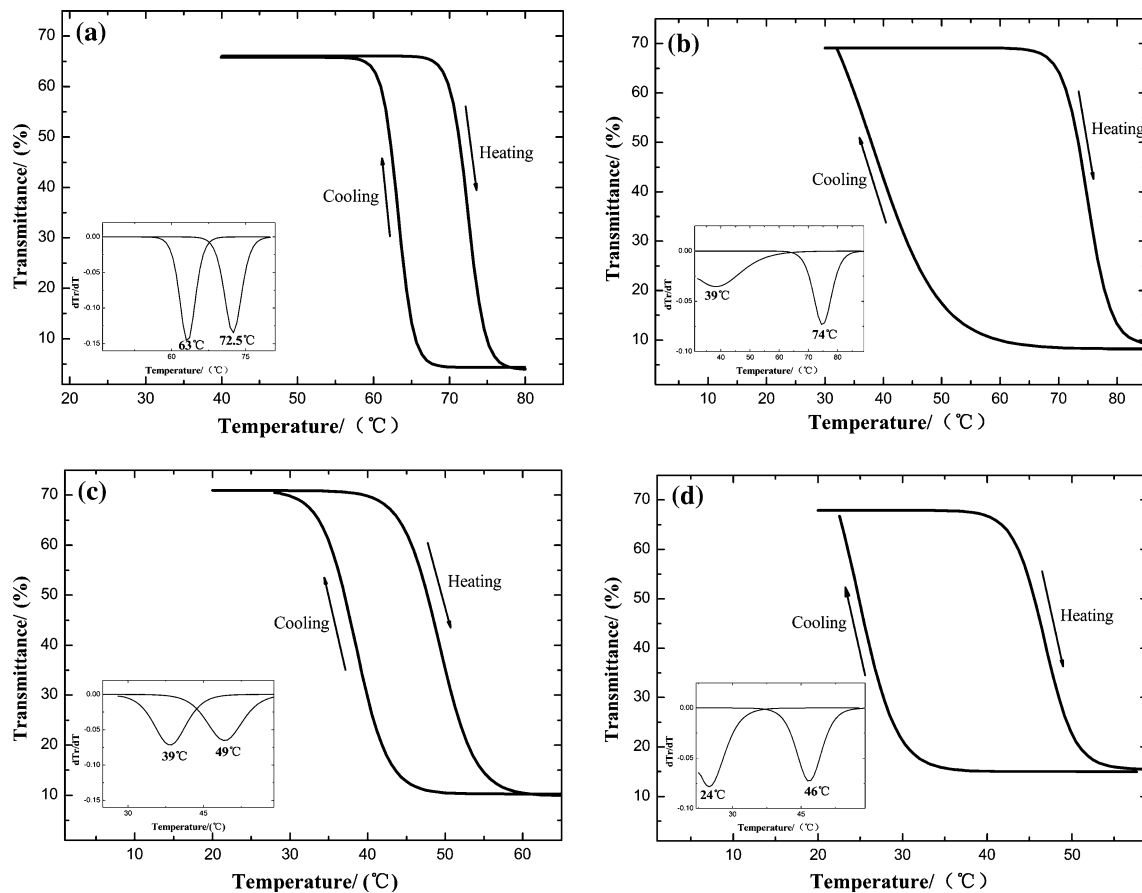
Fig. 5 Transmittance hysteresis curves at wavelength of 4 μm and corresponding first order derivative curves for VO₂ films with different synthesis conditions. **a** Pure VO₂ film; **b** VO₂ film with CTAB; **c** Mo and W ions co-doped VO₂ film; **d** Mo and W ions co-doped VO₂ film with CTAB

is defined as the difference between the T_1 and T_2. The sharpness of the MST for heating or cooling run is characterized by the full width at half maximum of the $dT_r/dT{-}T$ curve (dT_r/dT represents the derivative of the temperature (T) dependence transmittance (T_r)) [6].

The transition temperatures are 68, 56.5, 44 and 35 °C and hysteresis widths are 8, 35, 10 and 22 °C for four samples, respectively. The T_t and ΔT for pure VO2 film (Fig. 5a) is in accord with generally reported (68, 1–8 °C) [10]. The largest ΔT of 35 °C is obtained from an undoped porous nano-structured VO₂ film (Fig. 5b). Several characters can be concluded. First, compared with the pure VO₂ film, ΔT is broadened obviously for size reduction and porous nano-structure. In addition, T_1 is quite close, whereas T_2 is much lower than pure VO₂ film, implying the MST in cooling stage of phase transition cycle undergoes an obvious lagging, which probably due to the existence of a large active energy [18]. And consequently, T_t of V2 is reduced from 68 to 56 °C. Besides, the sharpness of MST for V2 is reduced, which is due to the relatively broad size distribution and grain correlation [19].

The T_t of the Mo and W ions co-doped film (V3) is reduced to 44 °C as reported [10], and ΔT is approximate to pure VO₂ film. The main goal of this work is to lower the T_t and broaden ΔT, which has been all successfully achieved, the sample V4 shows excellent infrared transmittance (nearly 70 %), large transmittance difference (55 %) before and after the phase transition, low transition temperature (35 °C) and wide hysteresis width (22 °C). The curve of V4 has basically several apparent features of the following respects. The T_t is the lowest in four samples for the co-effect of Mo and W ions co-doping and grain size reduction. A large ΔT is also obtained for V4. The hysteresis loop of VO₂ film synthesized in this way not only reveals the effect of Mo and W ions co-doping in lowing the T_t, but also signifies the broadening of ΔT and reduction of T_t in porous nano-structured films. Besides, the sharpness contrast is significantly improved compared with V2, revealing the good switching properties from low temperature monoclinic structure to a tetragonal rutile-type structure at high temperature [20].
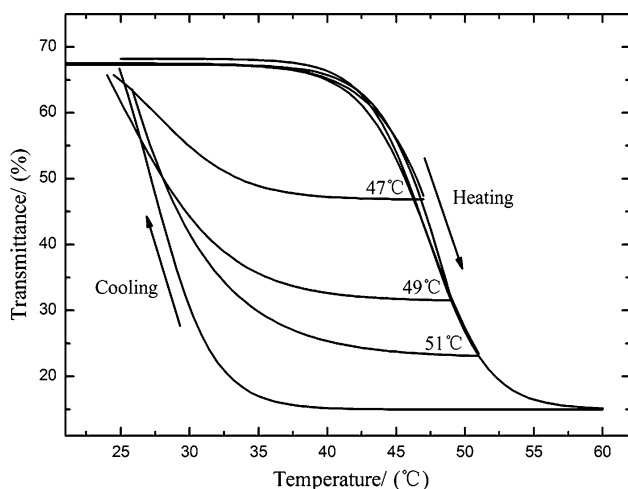
Fig. 6 The first-order reversal curve of the Mo and W ions co-doped VO$_2$ film

Figure 6 is the first-order reversal curve (FORC) of the Mo and W ions co-doped VO$_2$ film, which shows the hysteresis plots of optical transmittance against temperature acquired with the same heating rate. The curve is obtained as follows: starting at a temperature of 25 °C (fully semiconductor state), then heating up to various reversal temperatures, and finally coming back to the semiconductor state, obtaining a FORC for each reversal temperature [21]. Three reversal temperatures (47, 49, 51 °C) across the transition are chosen to analysis the hysteresis phenomenon. From the diagrams, tunability of the optical transmittance is achieved by collecting the optical transmittance data of three temperatures, and a slightly decreased slope of the corresponding cooling curve with temperature is observed. Different temperatures correspond various optical transmittance changes, implies a control of the data storage capacities across the transition [21].

4 Conclusions

Mo and W ions co-doped porous nano-structured VO$_2$ films had been prepared on mica substrates via sol–gel and spin-coating methods using CTAB as porous structure directing agent. The film showed low transition temperature (35 °C), wide hysteresis width (22 °C), fast phase transition and excellent abilities in the regulation of infrared light transmittance (MST related transmittance difference: near 55 % at 4 μm). Low transition temperature implies low excitation energy, wide hysteresis width increases storage capacity and improved phase transition can provide fast data transfer rate. The mainly shortcomings of VO$_2$ applied in optical data storage are overcome.

The results suggest that such Mo and W ions co-doped porous nano-structured VO$_2$ film is an ideal fundamental material for optical data storage.

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