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# Preparation and phase transition properties of nanostructured zirconium-doped vanadium oxide films by reactive magnetron sputtering

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ABSTRACT

Nanostructured zirconium (Zr)-doped vanadium oxide (VOx) films were prepared at low temperature on glass substrates by reactive direct current magnetron sputtering followed by in-situ annealing process. The effect of Zr content on the chemical composition, structure, morphology and metal–semiconductor transition properties of the deposited films was investigated systematically. It was found that Zr doping significantly reduced the grain size of VOx films due to increased density of nucleation centers, but was found almost not to influence the structure and the +4 valence vanadium concentration. Interestingly, the hysteresis width was hugely modulated from 30.0 to 5.8 °C while the phase transition temperature upon cooling increases from 42.0 to 56.7 °C as the Zr/V atomic ratio in the deposited film increases from 0 to 13.9%. However, the phase transition temperature upon heating initially decreases with Zr/V atomic ratio, attains a minimum of 53.8 °C at a Zr/V atomic ratio of 8.5%, and then increases with increase in Zr/V atomic ratio. The decrease in hysteresis width with the increase in Zr contents can be attributed to the increased density of nucleation defects introduced by Zr doping. This work shows that Zr doping can effectively regulate the morphology and the phase transition characteristics of VOx films.



## 1. Introduction

Vanadium dioxide ($VO_2$) undergoes a first-order metal–semiconductor transition (MST) at a critical temperature (68 °C for pure bulk $VO_2$), associated with the structural change from the low-temperature monoclinic phase to the high-temperature rutile phase. The crystallographic structure transformation results in significant changes in optical and electrical properties as well as terahertz transmission [1–6]. Due to these unique MST properties, $VO_2$ films have been intensively exploited in many potential applications such as switching elements, smart windows, storage devices and terahertz modulators [1–6]. Different practical applications require different MST properties, especially the hysteresis width [7–10]. Storage-type applications need a large hysteresis width (>15 °C) while sensor-type applications require a small hysteresis width [7–10].

In recent years, many techniques including ion implantation [11], laser ablation [12], pulsed laser deposition [13,14], polymer-assisted deposition [9,15], chemical vapor deposition [16], sol–gel method [17] and complex process (multiple-step preparations which include: (i) focused-ion-beam lithography, followed by chemical removal of the exposed areas; (ii) pulsed-laser deposition; (iii) chemical lift-off and (iv) thermal anneal) [2] have been used to regulate the hysteresis width of $VO_2$ films for various practical applications. Unfortunately, in these methods mentioned above, relatively high-cost substrates (silicon [6], fused $SiO_2$ [11] or single-crystal sapphire [18]) and/or high temperature (1000 °C [11], 850 K [18], 505 °C [3]) are required. Although reactive magnetron sputtering has been extensively used to prepare vanadium oxide (VOx) films, there are few reports on the sputtered VOx films with controllable hysteresis width. Importantly, reactive magnetron sputtering can prepare large and uniform films more easily than pulsed laser deposition or laser ablation, and can prepare higher-quality films than polymer-assisted deposition or sol–gel method. Hence, it is necessary to prepare VOx films with tunable hysteresis width by reactive magnetron sputtering.

We have prepared VOx films by reactive direct current (DC) magnetron sputtering and investigated the effect of film thickness on the hysteresis width [4]. Unfortunately, all the deposited VOx films show large hysteresis widths (38.4–32.2 °C). In this experiment, zirconium (Zr) was doped into VOx films in order to more effectively modulate the hysteresis width. Although $VO_2$–$ZrV_2O_7$ composites [19], V–O–Zr [20] and $V_2O_5/ZrO_2/SiO_2$ [21] catalysts have been studied, few works studied VOx films doped with Zr to regulate the MST properties of the

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films. In this work, nanostructured Zr-doped VOx films were prepared at low temperature on glass substrates by reactive DC magnetron sputtering. The structure, morphology and MST properties of the films were analyzed systematically with variation of the Zr content. The experimental results show that both MST properties and morphologies of the deposited films were hugely modulated by simply changing the Zr content. This work may give an added impetus on the applications of this technologically important material.

## 2. Experimental details

Zr-doped VOx films were prepared at low temperature on glass substrates by means of reactive DC magnetron sputtering technique using V:Zr targets [22,23] consisting of V metallic discs (99.9% purity, 80 mm diameter, 4 mm thickness) and Zr metallic chips (99.9% purity, 1 mm thickness). Fig. 1 shows the photograph of the V:Zr target used in the present work. In Fig. 1, the effective sputtering field is the part between the two blue lines, namely the concave space whose center is highlighted by the red circle with a diameter (d) of about 46 mm. The Zr chips numbered 1, 2, 3 and 4 were attached on the effective sputtering field, as shown in Fig. 1. It is well known that the Zr contents of the deposited films will increase with the increase in the effective sputtering area of Zr chips. Thus, we can control the Zr contents by simply changing the effective sputtering area of Zr chips. At the same time, sputtering yields must be taken into account, since various materials show large differences in sputtering yields in general. Fortunately, the sputtering yield of V is on the whole the same as that of Zr. Therefore, the Zr content in the deposited films probably agrees with the value calculated according to the effective sputtering area. This has been verified not only by our experiment but also by the work of Ding et al. [23] and Soltani et al. [24]. In order to improve the uniformity, the substrates were kept rotating at a high speed of about 30 rpm. The effective sputtering area of Zr-chips was varied in the range of 0–12% in order to control the Zr contents in the deposited films. The glass substrates were cleaned ultrasonically followed by drying in a high pressure $N_2$ gas [7]. The base pressure for the system was less than $1 \times 10^{-3}$ Pa. The working gas Ar (99.99% purity) and the reactive gas $O_2$ (99.99% purity) are introduced separately into the chamber by using two mass flow controllers. The target was pre-sputtered in pure Ar for 10 min in order to get rid of any possible contaminations of the target surface. For convenience of discussion, the key preparation parameters and the designations of the corresponding films were listed in Table 1.

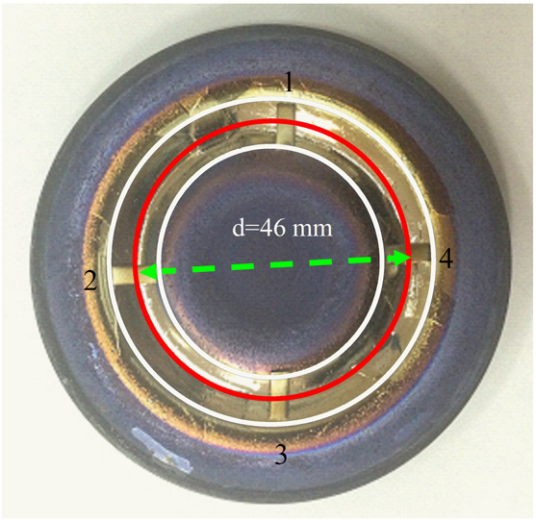


**Fig. 1.** The photograph of the V:Zr target used in the present work. The Zr chips numbered 1, 2, 3 and 4 were attached on the concave space, namely the effective sputtering field.

**Table 1**
The key preparation parameters and the designations of the corresponding films.

| Sample | Reactive oxygen flow rates (SCCM) | Substrate temperature (°C) | Deposition time (min) | Annealing time (min) | Annealing temperature (°C) | Zr-chips area (%) |
|---|---|---|---|---|---|---|
| S1 | 1 | 100 | 30 | 30 | 350 | 0 |
| S2 | 1 | 100 | 30 | 30 | 350 | 2 |
| S3 | 1 | 100 | 30 | 30 | 350 | 8 |
| S4 | 1 | 100 | 30 | 30 | 350 | 12 |

X-ray photoelectron spectroscopy (XPS, XSAM 800) was applied to characterize the chemical compositions of the deposited films. The base pressure of the XPS system was lower than $3 \times 10^{-7}$ Pa. X-ray photoelectron spectra were produced using a nonmonochromatized X-ray source ($h\nu = 51{,}486.6$ eV). Ar ions were used as the sputtering ion beams whose energy and current density were 1500 eV and 1 mA, respectively. The binding energies were determined by using C1s peak at 284.8 eV as a reference. The XPS peak was fitted by using a Shirley function with software XPS peak 4.1. Field emission scanning electron microscope (SEM, Hitachi S4800 with operating voltage of 5 kV) and energy dispersive spectrometer (EDS, Oxford instruments X-Max 51-XMX0019) were applied to characterize the morphologies and the element distribution of the deposited films, respectively. Accelerating voltage of 20 kV and collecting time of 20 s are used for acquiring EDS spectra. Raman spectra were performed using a 532.2 nm laser on a Raman microscope spectrometer (Horibar Corporation, LabRAM HR800). The resolution of the Raman system and the overall uncertainty in the presented spectra are less than $\pm 0.65$ $cm^{-1}$ and $\pm 0.2$ $cm^{-1}$, respectively. Optical transmission was measured by using a Shimadzu Spec-1700 UV–visible spectrophotometer equipped with heating units.

## 3. Results and discussions

### 3.1. XPS analysis

In order to characterize the detailed compositions of the films, XPS measurements were carried out for all the deposited films. Fig. 2 shows the wide range XPS spectra of the deposited films. The O1s and V2p core level spectra as well as the close-ups of the Zr peak near 185 eV are shown in the insets of Fig. 2. In the case of the S2, S3 and S4 films, zirconium element was detected in the XPS spectra, indicating that zirconium was doped into the deposited films. Besides vanadium, oxygen and zirconium, other contamination elements such as silicon and carbon were also detected in the XPS spectra. Here, silicon comes from the glass substrate and carbon arises from the surface contamination. According to the corresponding areas and atomic sensitivity factors [25], the Zr/V atom ratios in S1, S2, S3 and S4 films are calculated as 0, 1.8, 8.5 and 13.9%, respectively.

In order to study the valence state of vanadium in more detail, the high resolution scans of the $V2p_{3/2}$ core levels were fitted by applying a Shirley function with software XPS peak 4.1 and shown in the inset of Fig. 2. It can be seen that all the deposited films show two valence states of vanadium, namely +4 vanadium with a binding energy of 516.03–516.10 eV and +5 vanadium with a binding energy of 517.30–517.44 eV. These binding energies are consistent with the reported values [17,26]. According to the equations described in the previous work [27], the fractional percentages of +4 and +5 valence were calculated as 73.9 and 26.1% for S1, 72.7 and 27.3% for both S2 and S3, and 72.2 and 27.8% for S4, respectively. This indicates that the chemical compositions of the deposited films are not sensitive to the Zr content.

Fig. 3 shows the XPS spectrum of the Zr3d for the film with a Zr/V atom ratio of 13.9%. Two dominant peaks are detected at the binding energy of 181.9 and 184.2 eV, corresponding to the $Zr3d_{5/2}$ and $Zr3d_{3/2}$,