Crystallization and inter-diffusional behaviors in the formation of VO₂(B) thin film with layered W-doping

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Abstract: To achieve a better material for uncooled infrared (IR) detector, polycrystalline VO₂(B) thin films with layered W-doping were fabricated on Si substrates by magnetron sputtering, and the best temperature coefficient of resistance (TCR) value reached −4.1%/K. The film synthesis was in a two-step route, first deposition at room temperature and then post-deposition annealing at 450 °C, to better control the crystallization behavior. Various transmission electron microscopy (TEM) methods were employed to investigate three sets of multi-layered films with different deposition time, 10, 20, and 30 min, with especial emphasis on the effect of layered W-doping scheme on the formation of multiple VO₂(B) layers. Spatial-resolved energy dispersive X-ray spectroscopy (EDS) revealed the alternative patterns of W-rich layers and W-poor layers, while the thinner films exhibited better crystallinity and texturing. By comparison with an as-deposited film, it was found that the inter-diffusion between the two types of layers was completed in the deposition step while both remained in amorphous structure. A stable W solution of about 8 cat% in VO₂(B) layers measured from all these films indicated that the layered doping can tailor the multi-layered microstructure to optimize the performance of VO₂(B) films.

Keywords: VO₂(B) thin film; layered W-doping; crystallization; transmission electron microscopy (TEM); solid-solution

1 Introduction

Uncooled infrared (IR) detectors utilize thermistor materials to register the resistance change due to IR radiation. This effect is commonly measured by the temperature coefficient of resistance (TCR) [1,2]. A large TCR value could allow the detection of small temperature change induced by incident IR radiation. At

the same time, the resistance of the thermistor material should be low enough due to the small driving voltage for the current read-out circuitry, as well as for the consideration of noise reduction [1,3]. In recent years, VO₂ thin films are preferably used in uncooled IR detector, since they exhibit relatively large TCR value and suitable resistance at room temperature [4]. VO₂ structures could be in three polymorphic allotropic phases: *M*-phase (monoclinic), *R*-phase (rutile), and *B*-phase (monoclinic). The low-temperature semiconductor *M*-phase undergoes a phase transition to high-temperature metallic *R*-phase at about 68 °C [5],

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which brings dramatic changes in electrical and optical characteristics, and hence higher TCR values [6–8]. However, the narrow transition range and high $1/f$ noise make it inconvenient in practical use [8,9]. This leaves the metastable B -phase as a better candidate for the uncooled IR detector material with no phase transition and thermal hysteresis in working temperatures below 100 °C [10–14].

The metastable $\text{VO}_2(B)$ thin films can be prepared by popular film deposition techniques, including pulsed laser deposition [1,14–17], metal-organic chemical vapor deposition [13,18], ion beam sputtering [3], and magnetron sputtering [9,19–22]. In general, all these deposition processes could be summarized into two routes: the one-step route by direct deposition at high temperature, and the two-step route by deposition first at low temperature and a follow-up heat treatment at high temperature. In the two-step route, the as-deposited thin films are always found to be amorphous [13,14,23], and this allows well controls of the crystallization process of $\text{VO}_2(B)$ phase, hence to reach optimized properties.

In most applications, the performance of $\text{VO}_2(B)$ thin films could be further improved by high-valence doping. It has been shown that doping W^{6+} ions increases the number of 3d state electrons and thus decreases the thermal activation energy, hence to enhance TCR value and reduce resistivity concurrently [9,21,24]. Doping has also an effect on $\text{VO}_2(B)$ crystallization behavior [1,9,14,21]. W-doping into $\text{VO}_2(B)$ thin film could be realized in two modes: the *in-situ* mode via co-deposition [9], and the diffusional mode via layered doping which could be in either sandwich [21] or multi-layered form [23]. The layered doping is indirect process, which depends on the inter-diffusion between the as-deposited VO_x and W layers during deposition or crystallization process; hence the effect of layered doping could be controlled by either altering number of W layers or changing the W layer thickness. Indeed, for the fast deposition technique such as the magnetron sputtering, this inter-diffusional behavior should play a key role for dopant in the deposition and crystallization processes.

In this work we take a comprehensive transmission electron microscopy (TEM) study for $\text{VO}_2(B)$ thin films with layered W-doping in various forms, prepared by reactive magnetron sputtering in the two-step route. Their best TCR value reaches $-4.1\%/K$. The analysis of

crystallization and inter-diffusional behaviors may provide us further information to understand and control the performance of $\text{VO}_2(B)$ -based uncooled IR detector.

2 Experimental

The VO_x with layered W-doping were deposited on Si substrate with thick SiO_2 layer (about 300 nm) by MSP3200B magnetron sputtering system (Beijing Chuangshi Werner Technology Co. Ltd., Beijing, China) at room temperature. The system was equipped with magnetron guns (USA GUN) each having a diameter of 3 inches. An un-throttled base pressure of 5×10^{-4} Pa was achieved using a combined vacuum system of mechanical and turbo molecular pumps. A flow of high-purity Ar gas (99.99%) of 30 sccm was injected into growth chamber, keeping the working pressure at 0.7 Pa. The distance between the target and the substrate was 6.7 cm. VO_x layers were radio frequency sputtered from V metal target (99.9%) in O_2 (99.9%, 2.5% content of total gas flow) and Ar (99.99%) mixture atmosphere, and W-doping layers were direct current sputtered from W metal target (99.9%) in Ar atmosphere. The thickness of each layer was controlled by modulating the sputtering time of W and V targets. Finally, all the as-deposited thin films were annealed at 450 °C for 2 h in Ar atmosphere [23].

Based on different schemes for the multi-layered doping, four thin films were deposited: two with uniform thickness of W-doping layers are VW10-I and VW30-I, under total sputtering time of 10 and 30 min, respectively; the other two films with graded thickness of W layers are VW10-II and VW30-II. Three undoped films V10, V20, and V30, as well as doped films VW20-I and VW20-II were also fabricated for comparison. The detail deposition schemes are shown in Table 1. The square resistances of the thin film were measured using a four-point probe system (280SI) with a controllable heating system. The TCR value was calculated via $\text{TCR} = d \ln(R_0)/dT$, where T is 28 °C and R_0 is the corresponding square resistance. Figure 1 shows the temperature dependent resistivity curves for the thin films, and the cooling curves coincide well with the heating curves, indicating no semiconductor-to-metal transition effect and thermal hysteresis. The related TCR and R_0 values are listed in Table 2. Since

Fig. 1 Temperature dependence of square resistance curves for the thin films.

Table 1 Deposition schemes of the samples

Sample	Parameter	VO _x layer	W layer
V10	Power (W)	200	—
	Time (s)	600	—
VW10-I	Power (W)	200	40
	Time (s)	150	5
	Number of layers	4	3
VW10-II	Power (W)	200	40
	Time (s)	150	4/5/6
	Number of layers	4	3
V30	Power (W)	200	—
	Time (s)	1800	—
VW30-I	Power (W)	200	40
	Time (s)	250	5
	Number of layers	7	6
VW30-II	Power (W)	200	40
	Time (s)	250	3/4/5/6/7/8
	Number of layers	7	6

Table 2 R_0 and TCR values of the thin films, and total thickness measured by TEM

Sample	R_0 (kΩ)	TCR (K ⁻¹)	Thickness (nm)
V10	99.3	-1.9%	25
VW10-I	51.5	-3.0%	30
VW10-II	33.3	-4.1%	20
V30	200.0	-1.2%	86
VW30-I	31.6	-2.66%	90
VW30-II	24.1	-2.83%	90

the thickness of each layer was resulted from manual control of sputtering time, the actual thickness of the films was measured from TEM.

X-ray diffraction (XRD) data were collected using an X-ray diffractometer (D/MAX 2200PC, Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5409 \text{ \AA}$) in the range $10^\circ \leq 2\theta \leq 60^\circ$. Morphology of natural surface was analyzed by a scanning electron microscope (SEM, Supra55, Carl Zeiss, Germany). The cross-section TEM samples were prepared by first gluing the thin films face-to-face, then followed by the standard process including mechanical cutting, polishing, and ion milling. Microstructures and

composition analysis were characterized by a field-emission electron microscope operated at 200 kV (Tecnai-F20, FEI, USA) which was equipped with an energy dispersive spectrometer (EDS, EDAS Instrument, USA).

3 Results

3.1 Phase and microstructure

The XRD patterns of multi-layered thin films (Fig. 2)

Fig. 2 XRD patterns of V10, VW10-I, VW10-II, and V30 showing VO₂(B) phase only, while extra VO₂(M) phase is detected in VW30-I and VW30-II; reflections of Si are from the substrate.

show three main peaks corresponding to (001), (002), and (003) reflections of $\text{VO}_2(B)$ phase (JCPDS Card No. 81-2392). The results also indicate that these $\text{VO}_2(B)$ thin films exhibit a preferred or texturing orientation along the [001] direction [9,14,15]. The sharp reflection at 33.03° belongs to Si substrate. Besides, no peak is found corresponding to either W or WO_3 phase. These indicate that the metastable $\text{VO}_2(B)$ is formed after annealing at high temperature in noble gas atmosphere, although the (011) reflections for $\text{VO}_2(M)$ (JCPDS Card No. 43-1051) could still be seen in VW30-I and VW30-II.

TEM observations for the thinner and thicker series of $\text{VO}_2(B)$ films are given in Figs. 3 and 4, respectively. All the d values of interplanar distances in the

high-resolution TEM (HRTEM) images are attributed to $\text{VO}_2(B)$. Since the ionic W^{6+} incorporates into $\text{VO}_2(B)$ lattice and results in the expansion of cell volume in the W-doped thin films, the d values for the W-doped $\text{VO}_2(B)$ phase are a little higher than that of the undoped one. The undoped V10 film exhibits a typical polycrystalline microstructure, while the doped VW10 films show multi-layered structures, in which the light contrasts represent $\text{VO}_2(B)$ layers and the dark contrasts should correspond to W-doping layers. However, the original scheme of multi-layers has turned into a two-layer film for VW10-II, which corresponds also to the highest TCR, while the multi-layered structures are retained in other doped films. HRTEM and selected area electron diffraction (SAED) reveal good crystallinity

Fig. 3 Each row presents the low-magnification TEM image, along with the HRTEM and SAED of V10, VW10-I (row 2), and VW10-II (row 3). (c) FFT of rectangular inset in (b). (i) SAED pattern reveals texturing for reflections from (001) planes.

Fig. 4 Each row presents the low-magnification TEM image, along with the HRTEM and SAED pattern of V30, VW30-I (row 2), and VW30-II (row 3). (f, i) SAED patterns show similar texturing in VW30-I and VW30-II.

for both $\text{VO}_2(B)$ and W-doping layers in VW10, as shown in Fig. 3. In VW30, in contrast, only $\text{VO}_2(B)$ layers exhibit good crystallinity while the W-doping layers remain as amorphous structure as shown in Fig. 4.

All the $\text{VO}_2(B)$ layers in these films are polycrystalline with finite grain sizes. In VW10 and VW30 films and along the normal direction, there is only one grain in each $\text{VO}_2(B)$ layer as revealed by HRTEM. The grain sizes in film planes are all much larger than each layer thickness. As shown in Fig. 5, SEM image from VW20-II further reveals that the grain sizes are larger than layer thicknesses by one order of magnitude. Moreover, W-doping makes the VO_2 grains much larger than the undoped film, while the surfaces of

doped films are visibly flat and compact.

The polycrystalline films also exhibit textured microstructures, and the SAED patterns often exhibit texturing for reflections from (001) planes, as revealed in Figs. 3 and 4. It is found that the degree of texture increases from V30, VW30-I to VW30-II films, i.e., from no texture to $\alpha = 43^\circ$ and $\alpha = 35^\circ$, respectively, where α measures the angle of aggregated (001) spots that is inversely proportional to the degree of texture. The highest texturing or the smallest α (11°) comes from the VW10-II film, which has the best TCR and widest $\text{VO}_2(B)$ layer among our samples.

According to the degree of texture, there is certain misorientation among (001) plane. W-rich layers, as the dopant and barrier layers, restrict the thickness of the

Fig. 5 SEM images of the natural surface from (a) V2O, (b) VW20-I, and (c) VW20-II.

VO₂ layers, which further reduce the misorientation of adjacent grains in some probability. It is convincing to assume that smaller misorientation between adjacent grains could enable the increasing opportunity for such grains to grow together into a larger one. Moreover, although there is no more outer W-rich layer to restrict the outmost VO₂ layer, it still has larger grains which are proved by the SEM image. The possible reason is that either the W-rich layer itself or the diffusion behavior between two layers could affect the nucleation and growth behavior of VO₂ layer.

3.2 Distribution of W dopants

W-doping in layered form affects not only the phase or microstructure formation, but the dopants may not be

distributed as uniform as in co-deposition, which is commonly employed. However, VO₂ films are usually quite sensitive to electron beam irradiation, which makes the films quickly damaged by the EDS point analysis for local W concentration; one such case is demonstrated by HRTEM (Fig. 3(e)). To minimize this effect, we use exclusively the line-scan mode to measure W concentration across these films, which allows us to extract point spectra from corresponding locations and to superimpose them if needed. One such case is demonstrated in Fig. 6: an EDS line-scan is performed for the VW10-II film, which confirms, together with its high angle annular dark-field (HAADF) image, the two-layer configuration of this 20 nm-thick film formed by 12/8 nm-thick W-poor and W-rich

Fig. 6 (a) EDS line-profiling and contrast from red dotted line in HAADF image of VW10-II. (b) EDS point spectra of W-poor and W-rich layers, which are consisted of W, V, and O with different V/W ratio.

layers respectively. We take twelve spectra in each layer and sum them up as given in Fig. 6(b), hence to reduce the spectral noises for better quantification of W concentration. This gives the W solution level in $\text{VO}_2(B)$ phase as 8.0 and 56.3 cat% in the W-poor and W-rich layers, respectively.

Similar EDS line-scans are also carried out for VW30-I and VW30-II films, as given in Figs. 7(a) and 7(b) respectively, together with corresponding HAADF images. Indeed the amorphous W-rich layers exhibit much brighter contrast as compared to the $\text{VO}_2(B)$ layers in both HAADF and W profiling. Here each maximum or minimum in both W concentration profiles corresponds to the center position of an amorphous layer or $\text{VO}_2(B)$ layer, respectively. These maxima and minima should measure directly W solution levels in corresponding layers, in the assumption that the layer width is wider than the effective EDS probe during the experiment. These values are all listed in Tables 3 and 4.

Although the layer thicknesses should be uniform or

uniformly increased according to the multi-layer schemes, the actual thicknesses are found rather different from the expected trends. The measurements of layer thickness are performed in two ways, one directly from TEM images and another from HAADF profiling. In the latter, we define layer-boundaries from the steepest positions of these HAADF profiles, taken as maxima and minima in their derivative forms. Both sets of thicknesses are given in Tables 3 and 4; their differences are minimal, indicating both measurements are reliable. The W-rich layers in VW30-I have thicknesses all around 5 nm except one exceeding 7 nm, while those in VW30-II range of 3.5 and 7 nm; the $\text{VO}_2(B)$ layers should all in the same thickness in both films, and in fact, it measures in 7.5–8.8 nm and 7.8–9.6 nm respectively, except a much wider layer of 19.5 nm in VW30-II. The last case results most probably from missing one W-doping layer between the first and the second (3.5 and 5.0 nm thick) during the deposition process.

Fig. 7 EDS line-profiling and contrast from red dotted line in HAADF images of (a) VW30-I and (b) VW30-II.

Table 3 W solution levels of corresponding layers in VW30-I

	W-rich layer						W-poor layer						
Thickness from TEM (nm)	4.9	5.3	5.3	5.3	7.1	5.2	7.6	8.1	8.8	8.3	7.5	7.8	9.4
Thickness from HAADF (nm)	4.8	5.4	5.4	5.4	7.5	5.4	7.5	7.5	8.8	8.1	7.5	8.1	8.8
W solution level (at%)	31	31	31.1	30.3	38.3	32.2	1.2	11.4	15.4	14.9	16.4	19	11.8

Table 4 W solution levels of corresponding layers in VW30-II

	W-rich layer					W-poor layer							
Thickness from TEM (nm)	3.6	5.2	6.2	6.2	6.7	8.2	20.1*	8	9.7	8.3	8.1	8.1	8.1
Thickness from HAADF (nm)	3.5	5.0	5.6	5.8	7.0	8.4	19.5*	8.9	9.6	8.9	8.9	7.8	7.8
W solution level (at%)	10.2	37.7	56.8	59.4	72.1	1.6	7.9	13.9	9.4	11.3	5.9	5.9	5.9

* The total thickness of two neighboring W-poor layers which were attributed to one missed W-doping layer.

In this study the utilized electron probe has a size of about 2 nm, which could expand to effective size of 3–5 nm in these EDS profiling. The slope between the two layers in the profile for VW10-II exceeds 5 nm slightly (see Fig. 6(a)), which may have included further effects from tilting or roughness of the layer-boundaries. Most layer thickness in VW30-I is just slightly wider than 5 nm, and the differences between the maxima and minima are significantly smaller than VW30-II; hence the former film may have suffered from the tilting effect of the film plane from the edge-on condition during TEM experiment. Indeed, the contrasts between the W-rich and W-poor layers as well as the sharpness of their interfaces in HAADF image for VW30-I are visibly lower than for VW30-II (Fig. 7). Therefore, only the maxima and minima in VW30-II could represent the true W solution levels in corresponding layers, except for the first 3.5 nm thick W-rich layer (10.2 cat%) which is much lower than the successive 5.0 nm layer (37.7 cat%). Such a low value reveals clearly the effect of a wider probe; hence the effective probe size is closer to 5 nm than 3 nm. It is worth noting that the W solution in the first and last $\text{VO}_2(B)$ layers is lower than those in between, which is due to the fact that it is neighbored by only one W-doping layer.

4 Discussion

The resultant microstructure, crystallinity, layer thickness, and W solution could all contribute to the performance of $\text{VO}_2(B)$ thin films. These features also interact with each other during the deposition and

annealing process. W-rich layers remain amorphous in VW30 films but not in VW10, indicating that the crystallization and dopant diffusion should affect each other strongly. To better understand the inter-diffusional behavior between W-rich and $\text{VO}_2(B)$ layers, an as-deposited thin film, a-VW20-II that had not been annealed, was also analyzed here for comparison. As shown in Fig. 8, HRTEM image and SAED pattern indicate that both the alternating W-poor and W-rich layers are formed in amorphous structure. EDS line-profiling for a-VW20-II together with HAADF image reveal quite similar W distribution as for VW30 films (Figs. 8(d) and 8(e)). Moreover, their W solution levels are quite close to the annealed films: W-poor and W-rich layers measure average values of 7.8 and 61 cat%, respectively (see Table 5). This similarity indicates that both VW30 and VW10 films are also fully amorphous right after deposition, and the crystallization of W-poor layers into $\text{VO}_2(B)$ structure starts in the annealing process.

Similar W distribution patterns between as-deposited and annealed films reveal that the inter-diffusion between VO_x and W layers occurs at room temperature during deposition. To compare the diffusional behaviors between the deposition and annealing stages, we plot in Fig. 9 all the reliable data of W solution against their

Table 5 W solution levels of corresponding layers in a-VW20-II

	W-rich layer			W-poor layer	
Thickness from TEM (nm)	4.6	5.4	7.2	5.9	9.1
Thickness from HAADF (nm)	4.6	5.4	7.2	5.9	9.1
W solution level (at%)	55.9	63.2	63.8	8.6	7.0

Fig. 8 (a) Low-magnification TEM image, (b) HRTEM image, and (c) SAED pattern of a-VW20-II. (d) EDS line-profiling and (e) contrast from red dotted line in HAADF image.

thickness collected from W-rich (triangle symbols) and W-poor layers (round and square symbols) in VW30-II, VW10-II, and a-VW20-II. For either W-rich or W-poor layers, W levels in the as-deposited and annealed films are nearly the same, indicating such inter-diffusion between layers has almost completed at room temperature, since it is much easier for V/W atom entering the amorphous layer. In another word, the inter-diffusion and crystallization processes are separately proceeded in the deposition and annealing stages. This completed inter-diffusion indicates that the solution limit for W in the W-poor crystalline $\text{VO}_2(B)$ layers is already reached in their amorphous precursor states, and hence their distribution is almost horizontal and independent to layer thickness (see Fig. 9). Since inter-diffusion completes between two types of amorphous layers, it could be concluded that two stable amorphous structures co-exist in the as-deposited films, one in V(W)O_x composition with less than 10 cat% of dopant and another in VWO_x composition with 50 cat% or more of W dopant.

Although the crystallinity is relatively low, it is interesting to notice that the W-rich layers crystallize into the same $\text{VO}_2(B)$ phase in VW10 films by annealing, while those in VW30 are not. Since the W levels in those different W-rich layers are quite similar, we may conclude that thinner film thickness, or shorter deposition time, makes it easier for the W-rich layers to crystallize by post-deposition annealing. The inhibition of, or imperfect, crystallization in W-rich layers should be due to the suppression of nucleation with high concentration of solutes, according to the thermodynamic picture [25]. Furthermore, as reported by Chen *et al.* [14] and Émond *et al.* [1], a small amount

of M -phase can co-grow in the B -phase when thin films grow thicker, which is indeed the case in our thicker VW30 films. The increasing degree of texture from thicker to thinner films might be due to the fact that there are more nucleation centers in thicker layers, hence diminishing this interfacial effect.

As shown in Table 2, not only the doped films always give better performance than those without doping, but the thinner VW10 films register also higher TCR than VW30, especially for VW10-II to reach 4.1%/K (in absolute value). The latter film has the highest texture, best crystallinity, and a single wide layer (~12 nm), which is the closest to reach single-crystal. Previous calculation has proved that the single-crystalline VO_2 structure could give TCR as high as 6.7%/K [26–28], due to larger grains with less grain-boundaries to generate lower site density of defects in the bandgap [1,29]. Besides, 8 cat% W in $\text{VO}_2(B)$ strikes a good balance between sufficient number of 3d electrons and negative effect in crystallinity by W substitution. Whether this thick $\text{VO}_2(B)$ layer in VW10-II film is created by a collective, more dynamic inter-diffusional process to merge all the W-rich layers into a single layer, or which is due to a certain unknown process, is beyond the scope of this study. Nonetheless, designing W-doping scheme and layer thickness in the two-step route is demonstrated to benefit the tailoring of film chemistry and microstructure in a more controllable way. Therefore, their correlated behaviors could create synergetic effect to optimize the performance of $\text{VO}_2(B)$ film in the uncooled IR detector.

5 Conclusions

With multi-layered W-doping and fabricated by magnetron sputtering, $\text{VO}_2(B)$ thin films has achieved a TCR of $-4.1\%/K$. TEM observation found that the multi-layered films were consisted of $\text{VO}_2(B)$ layers with W solution of about 8 cat% and W-rich VWO_x layers, which were crystalline or amorphous when the films were thin or thick, respectively. It is revealed that the inter-diffusion between the original W-doping and VO_x layers has been completed in the deposition process at room temperature, while the crystallization process started in the following annealing process at 450 °C. The layered doping scheme could not only affect the crystallinity of $\text{VO}_2(B)$ phase and its degree of texture, but also provide a balance between doping and the microstructure that can be designed to optimize the

Fig. 9 W solution against their thickness collected from W-rich and W-poor layers in VW30-II, VW10-II, and a-VW20-II.

performance of VO₂(B) films in the uncooled IR detector.

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