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# Influence of low Bi contents on phase transformation properties of VO<sub>2</sub> studied in a VO<sub>2</sub>:Bi thin film library†

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A thin-film materials library in the system V–Bi–O was fabricated by reactive co-sputtering. The composition of Bi relative to V was determined by Rutherford backscattering spectroscopy, ranging from 0.06 to 0.84 at% along the library. The VO<sub>2</sub> phase M1 was detected by X-ray diffraction over the whole library, however a second phase was observed in the microstructure of films with Bi contents > 0.29 at%. The second phase was determined by electron diffraction to be BiVO<sub>4</sub>, which suggests that the solubility limit of Bi in VO<sub>2</sub> is only ~0.29 at%. For Bi contents from 0.08 to 0.29 at%, the phase transformation temperatures of VO<sub>2</sub>:Bi increase from 74.7 to 76.4 °C by 8 K per at% Bi. With X-ray photoemission spectroscopy, the oxidation state of Bi was determined to be 3+. The V<sup>5+</sup>/V<sup>4+</sup> ratio increases with increasing Bi content from 0.10 to 0.84 at%. The similarly increasing tendency of the V<sup>5+</sup>/V<sup>4+</sup> ratio and *T<sub>c</sub>* with Bi content suggests that although the ionic radius of Bi<sup>3+</sup> is much larger than that of V<sup>4+</sup>, the charge doping effect and the resulting V<sup>5+</sup> are more prominent in regulating the phase transformation behavior of Bi-doped VO<sub>2</sub>.

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## 1. Introduction

The correlated electron material VO<sub>2</sub> has been widely researched due to its metal to insulator transition (MIT), which takes place at a critical temperature (*T<sub>c</sub>*) of ~68 °C.<sup>1–3</sup> The MIT of VO<sub>2</sub> is accompanied by a structural phase transformation from the monoclinic structure at *T* < *T<sub>c</sub>* to the tetragonal structure at *T* > *T<sub>c</sub>*. Across the MIT, the electrical resistivity of VO<sub>2</sub> changes up to 5 orders of magnitude and the optical transmittance in the infrared spectral region changes from highly transparent to reflective. These properties make it promising for applications such as smart windows,<sup>4,5</sup> Mott-transition FET<sup>6</sup> and nano-actuators.<sup>7,8</sup>

For practical use, the *T<sub>c</sub>* of VO<sub>2</sub> needs to be tailorable to fulfill the different demands of applications. Among the approaches of tuning *T<sub>c</sub>*, an addition of a third element (frequently called elemental doping) has been widely studied. Furthermore, by investigating the influence of additional elements on the MIT properties of VO<sub>2</sub>, more insights into the mechanism of the MIT can be gained.<sup>9–11</sup> The debate over the MIT mechanism has lasted for decades, with two perspectives, either attributing the MIT to electron correlation (Mott-transition) or lattice structure change (Peierls-transition).<sup>12–15</sup>

Most dopants can be categorized into two groups: (I) includes those with higher ionic radii and valence compared to V<sup>4+</sup>, *e.g.*, W<sup>6+</sup>, Mo<sup>6+</sup>, Nb<sup>5+</sup>,<sup>16–18</sup> (II) includes those with smaller ionic radii and lower valence, *e.g.*, Cr<sup>3+</sup>, Al<sup>3+</sup>.<sup>19,20</sup> Addition of group I elements to VO<sub>2</sub> reduces *T<sub>c</sub>* values, which is sometimes ascribed to the lattice distortion induced by the dopant, while others attribute the reduced *T<sub>c</sub>* to the charge doping and increased carrier density stemming from the dopants.<sup>10,21,22</sup> Concerning group II, additional phases of VO<sub>2</sub> can form as a result of doping, *e.g.*, M2 and T phase, making these systems more complex. In summary, it is still not well determined whether the change of *T<sub>c</sub>* is due to a structural change or a charge effect. Recently, research on rare-earth doped VO<sub>2</sub> provides more insights, as those elements have higher ionic radii but lower valence than V<sup>4+</sup>.<sup>23</sup> *E.g.*, Eu<sup>3+</sup> was reported to decrease *T<sub>c</sub>* by 6.5 K per at%; Tb<sup>3+</sup> leads to a reduction of *T<sub>c</sub>* at lower level of element content (<5 at%) and an increment at higher levels.<sup>23,24</sup>

In this work, Bi is chosen as dopant, because Bi<sup>3+</sup> has a 78% higher ionic radius (0.103 nm) but lower valence compared to V<sup>4+</sup>. The crystalline structure, composition, microstructure and phase transformation properties of Bi-doped VO<sub>2</sub> in form of a thin film composition spread are studied to get more insights into the effect of this dopant on the MIT of VO<sub>2</sub>.

## 2. Experimental

The thin film samples were fabricated by reactive co-sputtering on a 100 mm long, 5 mm wide Si (100) strip from a V target

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(99.95% purity, 100 mm diameter, Nova Fabrica) and a  $\text{Bi}_2\text{O}_3$  target (99.9% purity, 100 mm diameter, Evochem) using a magnetron sputter system (AJA International, USA). Fig. 1 shows the geometric layout of the two targets and the substrate. V and  $\text{Bi}_2\text{O}_3$  targets are positioned opposite to each other, and the Si strip is positioned along the V– $\text{Bi}_2\text{O}_3$  target direction. During the deposition, the substrate was static. As a result, the amount of sputtered material on the substrate strip varies at different positions with regard to the relative distance between the target and substrate. Empirically, the spatial profile of thickness in the used setup follows roughly a linear decrease along the library (from substrate positions closer to the source to positions further apart from the source), which is illustrated by the wedge shape of the thickness distribution of deposited material for each source in Fig. 1. Due to the spatial profile of the sputtered V and Bi atoms, a continuous Bi gradient forms along the strip, which is hereinafter referred to as  $\text{VO}_2\text{:Bi}$  library. Pulsed DC power of 300 W (pulsing frequency of 10 kHz, reverse time of 5  $\mu\text{s}$ ) was applied to the V target and rf power of 10 W was applied to  $\text{Bi}_2\text{O}_3$ . For sputtering, 80 sccm of Ar was introduced into the chamber and the process pressure was set to 0.4 Pa. A plasma emission monitor (PEM) system (Flotron, Nova Fabrica, Lithuania) was used to dynamically control the oxygen flow rate, in order to obtain single phase  $\text{VO}_2$ . Details about the control mechanism can be found elsewhere.<sup>25</sup> The oxygen flow was about 6.4 sccm. The deposition temperature was 520 °C.

For the characterizations, measurement areas (MAs) were defined every 9 mm along the strip (Fig. 1). The crystalline structure of the library was determined by X-ray diffractometry (XRD, Bruker D8 Discover). The composition spread of the library was studied using Rutherford backscattering spectrometry (RBS) at the 4 MV accelerator facility of RUBION/Ruhr University Bochum, with a measurement spot size of 1 mm. Oxidation states of V and Bi were investigated by X-ray photoelectron spectroscopy (XPS, Kratos Axis Nova) using Al  $K\alpha$  as exciting source. Microstructure and morphology of the library was studied by scanning electron microscope (SEM, Jeol JSM-7200F). Transmission electron microscopy (TEM, Jeol JEM-

2100Plus) was performed on selected areas using cross-sectional samples. The phase transformation properties of the library were studied by temperature-dependent resistivity  $\rho(T)$  measurements using four-probe method. A four-point probe head with 20 pins ( $5 \times 4$  groups) was used, which can measure five MAs simultaneously to achieve high throughput. The distance between the pins is 0.5 mm and the distance between each group of pins is 4.5 mm. During the measurement, the library is fixed on a temperature-controlled stage, with temperature cycling from 20 °C to 100 °C and temperature stability of  $\pm 0.05$  °C.

## 3. Results and discussion

### 3.1 Composition spread and crystalline structure

Fig. 2a shows RBS spectra of the  $\text{VO}_2\text{:Bi}$  library with well-separated and background-free bands for V and Bi. All spectra are well simulated with SIMNRA software and areal densities for V and Bi were determined, from which the relative Bi content was calculated as shown in Fig. 2b.<sup>26</sup> The Bi content increases from about 0.06 at% at the V-rich side to 0.84 at% at the Bi-rich side of the library. It is noteworthy that the Bi content here is the ratio  $\text{Bi}/(\text{V} + \text{Bi})$ , not the Bi proportion of the whole thin film composition. The absolute values of the areal densities for Bi and V determined by RBS have experimental errors of about 8% due to a systematic uncertainty in the normalization of the detection setup. The  $\text{Bi}/(\text{Bi} + \text{V})$  ratio, however, is independent from the normalization, because it is cancelled out. The residual uncertainty is given by the statistical

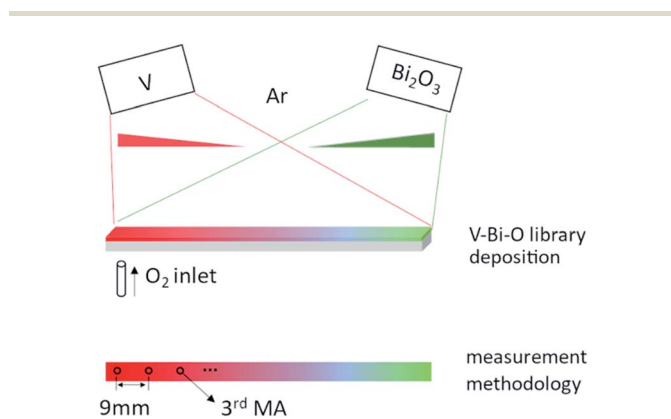


Fig. 1 Schematic (not to scale) of the co-sputter deposition of the  $\text{VO}_2\text{:Bi}$  library and its measurement areas (MAs) for characterizations (top view), the wedge shapes in the schematic denote the thickness gradients of sputtered material from each target in the library.

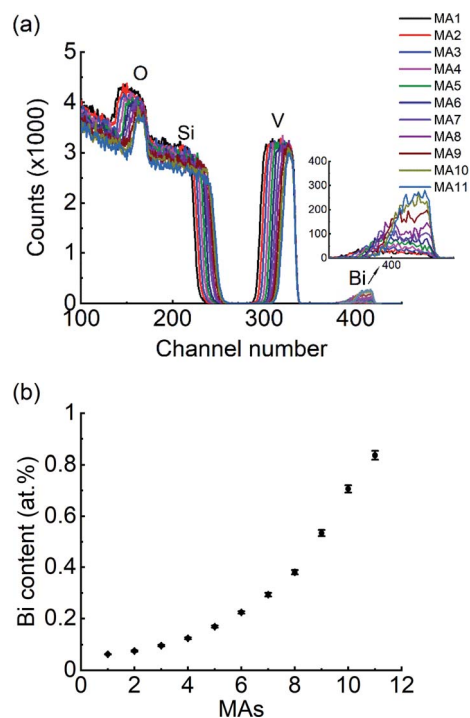


Fig. 2 (a) RBS spectra acquired from all MAs of the V–Bi–O library. The inset is an enlarged Bi channel. (b) Bi content ( $\text{Bi}/(\text{Bi} + \text{V})$  ratio) along the library with error marked, which is within 4% (relative error).



errors of the element signals. Even though there is only a very little amount of Bi, the RBS signal can be well analyzed and has a statistical error of 3% (about 1% for the V signal). The resulting relative error of the ratio is almost 4%, *e.g.*,  $0.84 \pm 0.03$  at% for MA11.

The RBS spectra also give information about the thickness variation along the library. Film thicknesses could be determined non-destructively by a calculation based on measured areal density and density of  $\text{VO}_2$ . Since there is no referable density data of  $\text{V}_{1-x}\text{Bi}_x\text{O}_2$  films, the density of  $\text{VO}_2$  ( $4.67 \text{ g cm}^{-3}$ ) was used. This estimate is acceptable due to the low Bi content in the library. Based on the calculation, the thickness of film ranges from 206 nm at the V-rich end (1<sup>st</sup> MA) to 77 nm at the Bi-rich end (11<sup>th</sup> MA), which also shows a tendency of linear decrease as presented in the ESI (Fig. S1).†

Fig. 3 shows the XRD patterns from V-rich to Bi-rich sides of the  $\text{VO}_2$ :Bi library. All films show almost identical diffractions patterns. The diffraction peaks appear at  $2\theta = \sim 27.9^\circ$ ,  $37.1^\circ$ ,  $39.8^\circ$ ,  $55.6^\circ$ ,  $57.8^\circ$ , which can be indexed as (011), (21-1), (002), (220), (022) of  $\text{VO}_2$  M1 respectively. Unlike Cr- and Al-doped  $\text{VO}_2$ , no M2 or T phases were observed in  $\text{VO}_2$ :Bi library, probably due to the low amount of Bi. Similarly, no bismuth oxides were detected by XRD neither. A detailed analysis on the (011) peaks are presented in the ESI (Fig. S2).† The main (011) peaks in all XRD patterns in Fig. 3 did not show obvious position shift with increase of Bi, and the overall (011) peak position of the  $\text{VO}_2$ :Bi thin film is about  $27.98^\circ \pm 0.02^\circ$ . Only a decrease in the peak intensity was observed, which might be attributed to decreased film thicknesses in the library.

### 3.2 Analysis of the oxidation states by XPS spectroscopy

Fig. 4a shows the  $\text{V}2\text{p}-\text{O}1\text{s}$  XPS spectrum of a 0.17 at% Bi- $\text{VO}_2$  sample with peak fitting illustrated. Spectra from other MAs are similar with respect to peak position and peak shape (Fig. 4c). Details about peak fitting can be found elsewhere.<sup>27</sup> The  $\text{V}2\text{p}_{3/2}$  peak in Fig. 4a is asymmetric with a shoulder towards the higher binding energy, which indicates the existence of  $\text{V}^{5+}$  component in the spectrum, although no other  $\text{V}_2\text{O}_{2n+1}$  phase was observed in the XRD patterns. In deconvolution of  $\text{V}2\text{p}_{3/2}$  peak, two components appear at 516.1 and 517.3 eV, corresponding to  $\text{V}^{4+}$  and  $\text{V}^{5+}$  respectively. Given that the detection depth of XPS is generally well below 10 nm, the  $\text{V}^{5+}$  signal might be partly ascribed to surface oxidation of  $\text{VO}_2$ . By using the same

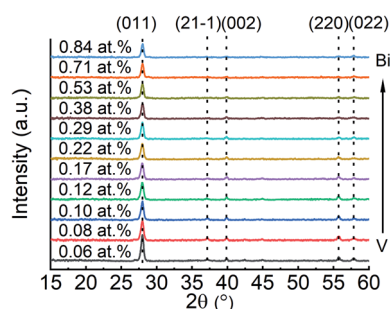


Fig. 3 Stacked XRD patterns of the  $\text{VO}_2$ :Bi library at different MAs.

fitting parameters, deconvolution was performed on all spectra of the library using the software ESCAPE (Kratos) and the  $\text{V}^{5+}/\text{V}^{4+}$  ratio was plotted against the Bi content in Fig. 4b with quantification error indicated. At the V-rich side of the library (MA1, MA2), the amount of  $\text{V}^{5+}$  is higher and drops. From 3<sup>rd</sup> MA on, the  $\text{V}^{5+}/\text{V}^{4+}$  ratio increases with Bi content along the library. Fig. 4a inset shows the Bi 4f spectrum from the 0.17 at% Bi- $\text{VO}_2$  sample. The Bi 4f<sub>7/2</sub> appears at  $\sim 159.4$  eV, indicating a valence of +3. XPS spectra of Bi from different MAs are also quite similar with respect to the peak position and shape, but with different peak intensity due to different Bi contents.

### 3.3 Analysis of microstructure by electron microscopy

The microstructures of the films in the  $\text{VO}_2$ :Bi library are displayed in Fig. 5. The films of Bi ranging from 0.06 to 0.17 at% exhibit similar dense morphology with grain size in the range of  $\sim 100$ – $200$  nm, and the grains show sharp facets. For the Bi of 0.22 and 0.29 at%, the grains' facets tend to be blunt, and some grains grow up to size of  $\sim 270$  nm. From Bi content of 0.38 at%, there is another feature appearing on the surface with bright contrast, as shown in Fig. 5. It seems to emerge at the grain boundary area of  $\text{VO}_2$ . With increasing Bi content to 0.84 at%, the appearance of the feature does not change significantly, instead its surface coverage largely increases.

A TEM cross-sectional sample with the feature included was prepared using focused ion beam (FIB) to further study this area. Fig. 6b shows the cross-sectional HAADF image of the 0.38 at% Bi- $\text{VO}_2$  film. As the contrast of the image is associated with the atomic number Z, the brighter structures visible at the bottom and the top of the film indicate the presence of a second phase consisting of heavier elements compared to  $\text{VO}_2$ . A corresponding EDX map shown in Fig. 6c reveals that the second phase contains Bi. Fig. 6d show a bright field image where the Bi-rich grains are in the Bragg contrast. An acquired selected area diffraction (SAD) pattern from this region (Fig. 6e) allows to identify the diffraction spot belonging to the Bi-rich phase, marked as DF. The measured interplanar distance of 0.314 nm corresponds to the (112) plane of the  $\text{BiVO}_4$  phase – well visible in the dark-field image in Fig. 6f. Fig. 6g and h show the  $\text{VO}_2$  phase in the Bragg contrast and its indexed SAD pattern.

Although no  $\text{BiVO}_4$  was detected by XRD in the library, the detailed microstructure study reveals that the solubility limit of Bi into  $\text{VO}_2$  is about  $\sim 0.29$  at%. Compared to the reported content of other dopants, *e.g.*, 2.5 at% of W, the solubility of Bi into  $\text{VO}_2$  is much lower, which might be attributed to the large difference in the ionic radius (0.103 nm for  $\text{Bi}^{3+}$  versus 0.058 nm for  $\text{V}^{4+}$ ). In addition, it is interesting to observe in the TEM image that the  $\text{BiVO}_4$  does not form a columnar structure as  $\text{VO}_2$  does. Instead, the phase is discontinuously formed at the grain boundary of  $\text{VO}_2$  on the top of the surface and at the  $\text{VO}_2$  film-substrate interface.

### 3.4 Analysis of phase transformation properties by temperature-dependent resistivity measurements

The phase transformation properties of the library were studied by temperature-dependent resistance measurements ( $R(T)$ ). The



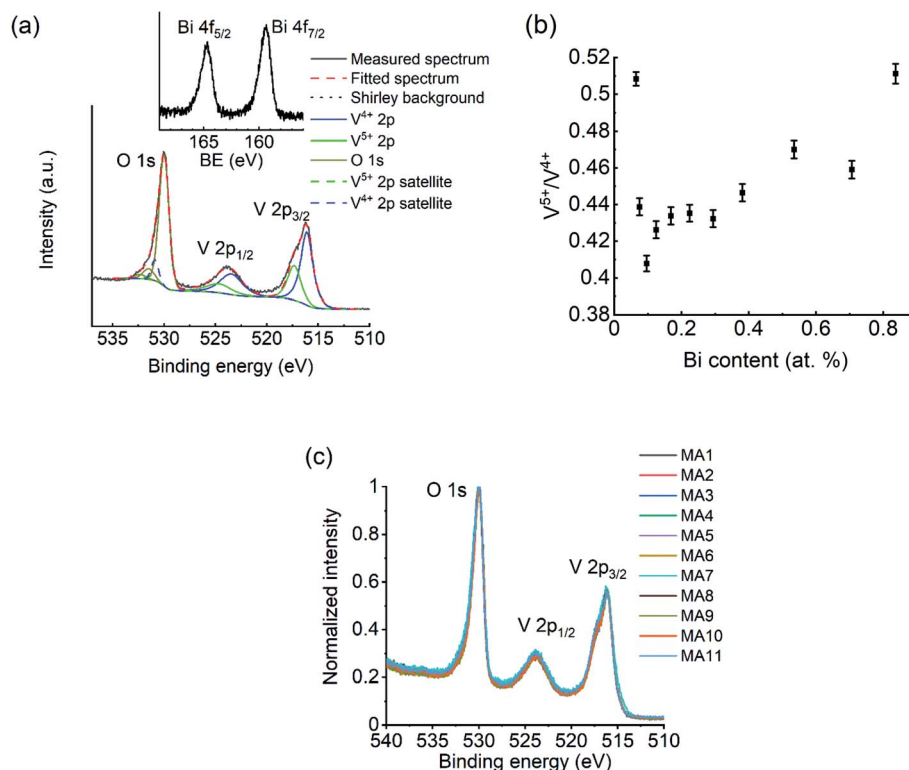


Fig. 4 (a) XPS spectrum of a  $\text{VO}_2\text{:Bi}$  sample with 0.17 at% Bi content. The  $\text{V}2\text{p}-\text{O}1\text{s}$  region is shown and deconvoluted to its components. The inset shows the spectrum of  $\text{Bi} 4\text{f}$ . (b) The  $\text{V}^{5+}/\text{V}^{4+}$  ratio from the deconvolution is shown in dependence of Bi content, with quantification error indicated. (c)  $\text{V}2\text{p}-\text{O}1\text{s}$  spectra from different MAs.

temperature-dependent resistivity  $\rho(T)$  of the thin film was calculated using film thickness  $t$ :  $\rho = 4.532 \times t \times R$ . Fig. 7a shows  $\rho(T)$  curves of the library: the films show resistivity drops of about 3 orders of magnitude across the MIT. With increasing Bi content, the resistivity drop decreases to above 2 orders of magnitude as the resistance of the metallic state increases. Meanwhile, the hysteresis loops of  $\rho(T)$  curves become slightly wider.  $T_c$  were determined by the first derivative of the heating  $\rho(T)$  curve,  $d \log \rho/dT$ , which was plotted as a function of Bi

content in Fig. 7b. The  $T_c$  at the V-rich side is  $75.2^\circ\text{C}$  and decreases to  $74.7^\circ\text{C}$  for the 0.08 at%  $\text{Bi}-\text{VO}_2$  film. Within the Bi content range from 0.08 to 0.29 at%,  $T_c$  increases by  $\sim 2$  K from  $74.7$  to  $76.4^\circ\text{C}$ . For higher Bi contents of 0.38–0.84 at%, there is only a slight change of  $\sim 0.4$  K. A partial linear fit was performed in the  $T_c$ -increasing section (0.08–0.29 at%) and it was determined that the  $T_c$  increases by 8 K per at% Bi. The slight change in  $T_c$  for  $\text{Bi} > 0.29$  at% is in good agreement with the discovery in microstructure observation, *i.e.*, the second phase  $\text{BiVO}_4$  is

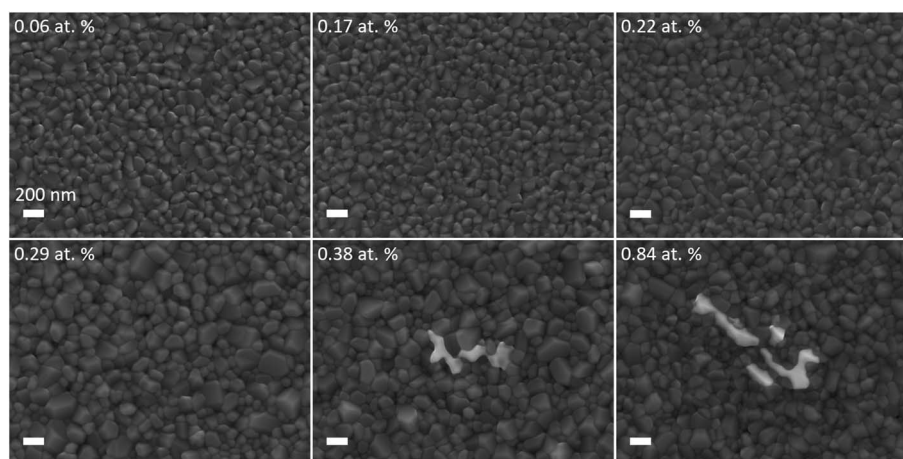


Fig. 5 SEM surface images of films from the  $\text{VO}_2\text{:Bi}$  library with different Bi contents.



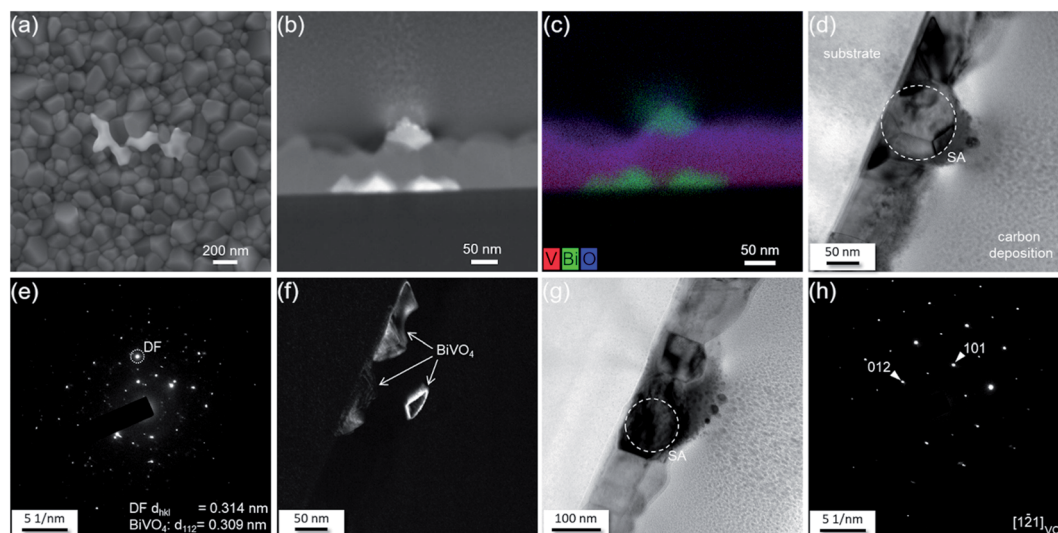


Fig. 6 Results of electron microscopy characterizations. (a) SEM image showing a second phase on the surface of the 0.38 at% Bi-VO<sub>2</sub> film. (b) HAADF image of the film with (c) corresponding EDX map. (d) Bright-field TEM image of the film with highlighted selected diffraction area (SA). (e) SAD with highlighted plane corresponding to the BiVO<sub>4</sub> phase shown in dark field TEM image (f). (g) Bright-field TEM image of the VO<sub>2</sub>-phase in Bragg contrast and corresponding SAD (h).

present in the VO<sub>2</sub>:Bi library as Bi > 0.29 at%. As shown in Fig. S3,<sup>†</sup> the resistivity of the VO<sub>2</sub>:Bi library at lower temperatures, *e.g.*, 40 °C, didn't change too much. In comparison, at higher temperatures, *e.g.*, 100 °C, it increases more obviously. Although the second phase BiVO<sub>4</sub> has much higher resistivity (~10<sup>8</sup> Ω cm), its presence didn't elevate the overall resistivity of the VO<sub>2</sub>:Bi library, probably due to its low amount. Interestingly, the tendency of resistivity change of metallic VO<sub>2</sub>:Bi thin film (at 100 °C) along the increasing Bi content is coincident with the change of  $T_c$ : after a slight decrease at 0.08 at%, it increases within the Bi content of 0.08–0.29 at%, until Bi > 0.29 at%, where only a slight change is observed.

In the thin film library, the Bi content is not the only parameter which could affect  $T_c$ . There might be also a variation in oxygen-to-vanadium ratio along the library, inherently stemming from the sputter geometry, *i.e.*, the V atomic wedge and a possible O-gradient, as the O<sub>2</sub> inlet is close to the V-rich side of the library (shown in Fig. 1). The resulting variation in stoichiometry of VO<sub>2</sub> can also influence  $T_c$ . For example,  $T_c$  tends to decrease with O-deficiency and increase in over-stoichiometric VO<sub>2</sub>. Another parameter is film thickness, which affects the grain size growth and thus  $T_c$ . It has been reported that smaller grain size can lead to decreased  $T_c$ , because a higher density of grain boundaries results in more defects promoting the phase nucleation.<sup>28</sup>

To rule out the possibility that the increase of  $T_c$  originates from the fabrication method, a V–O reference library was fabricated under the same deposition condition as that of VO<sub>2</sub>:Bi library without sputtering the Bi<sub>2</sub>O<sub>3</sub> target. It is reasonable to assume that the thickness and oxygen variation originated from the deposition layout should be comparable for both libraries. The V–O library studied here was confirmed to be single VO<sub>2</sub> phase at all MAs by XRD measurements (not shown). The  $R(T)$  curves of the V–O reference library were studied and  $T_c$

of the thin films along the V–O library was plotted in Fig. 8 in comparison with that of VO<sub>2</sub>:Bi library.

It turns out that  $T_c$  of the V–O library decreases along the direction from V-rich side to Bi-rich side, contrary to the increasing tendency in the VO<sub>2</sub>:Bi library, which confirms the role of Bi in increasing the  $T_c$  of VO<sub>2</sub>. Moreover, a detailed XPS surface characterization (not shown) on the V–O library also indicated a higher V<sup>5+</sup>/V<sup>4+</sup> and slight decrease of V<sup>5+</sup>/V<sup>4+</sup> at the V-rich side, similar to what was observed in the VO<sub>2</sub>:Bi library. It suggests that O-rich VO<sub>2</sub> forms at the V-rich side due to the sputter layout, which might account for the higher V<sup>5+</sup>/V<sup>4+</sup> ratio and slight decrease of  $T_c$  in the VO<sub>2</sub>:Bi library at first two MAs. For the MAs with higher Bi until 0.29 at%, the influence of Bi doping becomes more profound, which leads to the increase of V<sup>5+</sup>/V<sup>4+</sup> and  $T_c$ . It is noteworthy that  $T_c$  of V-rich VO<sub>2</sub>:Bi thin film is higher than reported value of ~68 °C for VO<sub>2</sub>, which might be partly attributed to the stress of the film, as tensile stress could increase  $T_c$ .<sup>29</sup>

The dopant-induced influence of lattice distortion and charge doping on the phase transformation in doped VO<sub>2</sub> systems is still under debate. For instance, the role of lattice distortion is emphasized in some studies on V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub>.<sup>10,30</sup> They found that the lattice distortion around W atoms promotes the formation of rutile-like VO<sub>2</sub> nuclei in monoclinic lattice, which propagates through the VO<sub>2</sub> M1 matrix and lower the thermal energy barrier for the phase transformation. In contrast, some<sup>21,22</sup> claim that the electron doping enhances the charge carriers in V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub>, due to the extra two electrons from W-doping, which affects the band structure and facilitate the transformation to the metallic phase. Another study<sup>11</sup> suggests that both electronic distribution and local structure perturbation are responsible for the reduction of  $T_c$  in V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub>. A comparative study<sup>31</sup> on W- and Ti-doped VO<sub>2</sub> concludes that the role of charge doping is more prominent in regulating  $T_c$ ,



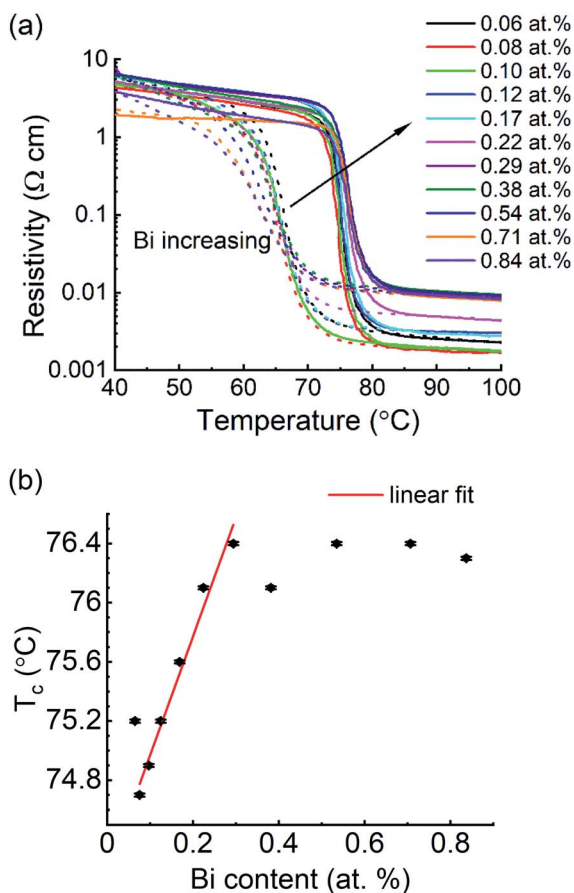


Fig. 7 Phase transformation properties of  $\text{VO}_2\text{:Bi}$  thin films in dependence of Bi content from 0.06 to 0.84 at.%. (a)  $\rho(T)$  curves, solid lines denote heating cycles and dotted lines cooling cycles, (b)  $T_c$  in dependence of Bi content, with a linear fit (red line) in the Bi range from 0.08 to 0.29 at.%. The error of  $T_c$  is from the Gaussian fitting of the first derivative of  $\rho(T)$ ,  $d \log \rho/dT$ .

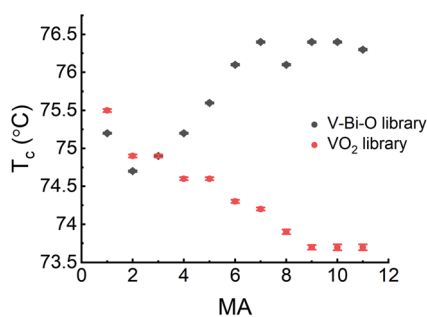


Fig. 8  $T_c$  of V–O reference library and  $\text{VO}_2\text{:Bi}$  library at different MAs. The error of  $T_c$  is from the Gaussian fitting of the first derivative of  $\rho(T)$ ,  $d \log \rho/dT$ .

although the local structure perturbation induced by dopants is also present. In the current study, the large ionic size of  $\text{Bi}^{3+}$  seems not to give rise to significant structure distortion in  $\text{VO}_2$  (M1) to reduce the  $T_c$  values. Instead, the large difference of ionic size between  $\text{Bi}^{3+}$  and  $\text{V}^{4+}$  limits the solubility of  $\text{Bi}^{3+}$  in  $\text{VO}_2$  to  $\sim 0.29$  at.%. In the composition range of the  $\text{VO}_2\text{:Bi}$

library with soluble  $\text{Bi}^{3+}$ , the variations of  $\text{V}^{5+}/\text{V}^{4+}$  ratio and  $T_c$  show an almost similar trend with increasing Bi content, which suggests that the effect of charge doping on the phase transformation behavior is more prominent. When doping with  $\text{Bi}^{3+}$  holes are introduced into the  $\text{VO}_2\text{:Bi}$  system due to the charge compensation and are trapped as discrete  $\text{V}^{5+}$  ions at cation sites neighboring to the  $\text{Bi}^{3+}$ , which is in accordance with the increase of  $\text{V}^{5+}/\text{V}^{4+}$  ratio. The effect of elemental doping with higher or lower valence than  $\text{V}^{4+}$  on tuning the transition temperature is comparable with the non-stoichiometry of  $\text{VO}_2$ .<sup>32,33</sup> Here the  $\text{Bi}^{3+}$ -doped  $\text{VO}_2$  behaves like over-stoichiometric  $\text{VO}_2$  with excess O. As reported,<sup>34</sup> excess O gives rise to more  $\text{V}^{5+}$ , higher  $T_c$  and increasing metallic resistivity, which have all been observed in the current study. In addition, compared to  $\text{V}^{4+}$ ,  $\text{V}^{5+}$  ions tend to stabilize the low-temperature structure, because the  $\text{V}^{5+}$  ion, with small size and empty d orbitals, is in favor of lower anion coordination and not stable in an oxygen octahedron of the high temperature structure.<sup>35</sup> As a result, the  $T_c$  values are increased with Bi doping. Similar correlations have been reported in previous studies on  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ - and most recently Ge-doped  $\text{VO}_2$  systems.<sup>35,36</sup> By using  $\text{Bi}^{3+}$  as dopant, both the size and charge effects of the dopant on the MIT of  $\text{VO}_2$  are evaluated. The higher ion size of  $\text{Bi}^{3+}$  does not cause obvious lattice distortions to reduce the  $T_c$ , which could otherwise support the mechanism of Peierls-transition in  $\text{VO}_2$ . In contrast, the charge doping plays a more prominent role in increasing  $T_c$ , which suggests that the Mott-transition is probably the main cause of the  $\text{VO}_2$  MIT.

## 4. Conclusions

A  $\text{VO}_2\text{:Bi}$  library was fabricated by reactive co-sputtering, with Bi content ranging from 0.06 to 0.84 at.%. Although only  $\text{VO}_2$  M1 phase was detected by XRD, a detailed microstructure study revealed the presence of a second phase  $\text{BiVO}_4$  for  $\text{Bi} > 0.29$  at.%, which suggests that the solubility of  $\text{Bi}^{3+}$  in  $\text{VO}_2$  is limited to  $\sim 0.29$  at.%. The large ionic size of  $\text{Bi}^{3+}$  limits its solubility in  $\text{VO}_2$ , and no obvious lattice distortion was indicated in the X-ray diffraction patterns. Studies on the oxidation state of V by XPS indicates that adding  $\text{Bi}^{3+}$  into  $\text{VO}_2$  generates more  $\text{V}^{5+}$ , meanwhile transformation properties studied by  $\rho(T)$  curves of the  $\text{VO}_2\text{:Bi}$  library shows that  $T_c$  of  $\text{VO}_2\text{:Bi}$  increases from 74.7 to 76.4 °C by 8 K per at% Bi at Bi content range of 0.08–0.29 at.%. The good agreement between increasing  $\text{V}^{5+}/\text{V}^{4+}$  and  $T_c$  suggests that in the  $\text{VO}_2\text{:Bi}$  library the effect of charge doping from  $\text{Bi}^{3+}$  on the phase transformation of  $\text{VO}_2$  is more profound than the lattice distortion.

## Conflicts of interest

There are no conflicts to declare.

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