Fabrication of Epitaxial W-doped VO$_2$ Nanostructured Films for Terahertz Modulation Using the Solvothermal Process

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Abstract

We report a feasible and high-throughput method for high-quality W-doped VO$_2$ nanostructured epitaxial films on r-sapphire substrates fabrication. Single-phase, smooth vanadium dioxide thin films with uniform distribution of tungsten (up to 2.3 %) are formed with the solvothermal process from ethylene glycol/water $V^{4+}$ and $W^{6+}$.
solutions. Compositional analysis (XPS and EDX), structural analysis (XRD, Raman spectroscopy, SAED), as well as detailed analysis of the surface morphology and substrate-film interface (SEM, AFM, HRTEM) confirm the formation of nanoscale (50-60 nm) epitaxial W:VO$_2$ (M$_1$) on r-sapphire with epitaxial relationships (100) VO$_2$ $\parallel$ (1012) Al$_2$O$_3$ and [010] VO$_2$ $\parallel$ [0110] Al$_2$O$_3$. The nanostructured films demonstrate excellent terahertz (THz) transmission properties: phase transition temperature of 31 °C, giant THz modulation depth of over 60%, and broad bandwidth ($\geq$ 2 THz) operation. Hence, they can be efficiently used as active material for tunable THz manipulation devices.

**Keywords**

VO$_2$, metal-insulator transition, nanostructured film, W-doping, solvothermal synthesis, THz modulator

**Introduction**

Terahertz (THz) (0.1 – 10 THz) communications and optoelectronics are rapidly growing areas of modern science and technology. Research on this topic began at the end of last century, and presently THz radiation is widely used in security systems, medicine and chemical technology, quality control of building materials and food, and have numerous potential applications.$^{1-4}$ However, current technologies for THz modulation and switching are still underdeveloped compared to those in more developed microwave and optical frequency domains.$^{5}$ A number of promising applications are limited by a quality factor and efficiency of modulators.$^{6}$ This entails the necessity for developing new functional materials with ultrafast changes in optical properties. A special role here belongs to phase change materials, which are widely discussed as key components of THz manipulation devices.$^{7,8}$

Vanadium dioxide (VO$_2$) undergoes a reversible metal-to-insulator phase transition (MIT)
at a critical temperature ($T_{\text{MIT}}$) of 68 °C between insulating monoclinic VO$_2$ (M$_1$) with high THz transparency and metallic rutile VO$_2$ (R) with strong THz absorbance and reflection.$^{9,10}$ This ultrafast ($< 80$ fs)$^{11}$ phase transition also involves sharp changes in electrical resistance and can be triggered by various types of stimuli, including thermal heating, electrical current excitation, light irradiation and mechanical strain. Such unique properties make VO$_2$ films promising candidates for the role of active medium in tunable THz amplitude modulators,$^{12}$ switches,$^{13}$ tunable absorbers,$^{14}$ emitters,$^{15}$ photonic crystals$^{16}$ and metamaterials.$^{17}$

To improve the performance of THz switches and modulators it is necessary to achieve large THz modulation depth (MD), low insertion loss and low MIT temperature, providing a low thermal/optical trigger threshold.

A number of gas-phase deposition methods have been utilized to form VO$_2$ (M$_1$) films including PLD,$^{18,19}$ MOCVD,$^{20,21}$ magnetron sputtering,$^{22,23}$ ALD$^{24,25}$ and MBE.$^{26,27}$ However, most of these techniques require expensive vacuum equipment, unsuitable for large-scale manufacturing of VO$_2$ based devices. Recently, more cost effective, high-yield and flexible solution-based deposition approaches, such as sol-gel,$^{28,29}$ hydro- and solvothermal crystallization,$^{30,31}$ polymer-assisted deposition$^{32,33}$ and inkjet printing technology$^{34,35}$ have been adopted for deposition of thin VO$_2$ films. Among those, solvothermal method provides numerous advantages, such as operational stability, low cost and high crystallinity of the product, which makes it the most attractive for mass production.$^{36}$ However, this method often results in metastable monoclinic polymorph VO$_2$(B),$^{37}$ or oxygen-deficient VO$_2$.$^{38}$ Nevertheless, these VO$_2$ phases can easily be transformed into VO$_2$ (M$_1$) by subsequent thermal treatment. This process also retains the morphology of the as-grown product.$^{39-41}$

A number of strategies was proposed to reduce the VO$_2$ MIT temperature including chemical doping,$^{42}$ stoichiometry engineering,$^{43}$ epitaxial strain,$^{44}$ and hydrogenation.$^{45}$ So far, tungsten (W$^{6+}$) is recognized as the most effective doping element for lowering the $T_c$ by approximately 25-30 °C per at% W.$^{46-48}$ Recently, a number of outstanding results have been achieved in lowering the vanadium dioxide MIT temperature by cationic doping while
maintaining superior THz performance. Émond et al used PLD to prepare W-doped VO₂ films with a critical temperature of 36 °C and THz MD of 54%.⁴⁹ Ji et al⁵⁰ succeeded in obtaining Nb-doped vanadium dioxide films with a critical temperature of 31 °C and THz MD of 63% using a DC reactive magnetron sputtering technique. Similar technology was used by Wu et al to obtain Cu-doped VO₂ films with the THz MD of 40.1% and a critical temperature of 51 °C.⁵¹ These studies also indicated the necessity to obtain high crystal quality of the films, in order to maintain excellent THz transmission. This allows expecting a supremacy of THz transmission for epitaxial films with minimal deformations in the bulk and at the film-substrate interface.

The above suggests the prospects of applying solvothermal process for epitaxial growth of doped VO₂ films for THz applications. Thus, here we propose a low-cost and eco-friendly process for the epitaxial growth of W:VO₂ (M₁) films on r-Al₂O₃ substrate by solvothermal reaction in ethylene glycol/water solvents with subsequent post-annealing. Resulting VO₂ (M₁) films with W-content up to 2.3 at% allow diminishing phase transition temperature down to 31 °C, maintaining THz MD of 60% at 0.3–2.3 THz.

Results and discussion

Film morphology, orientation and composition

The surface morphology of W:VO₂ films on r-Al₂O₃ substrates is represented with uniform isotropic spherical grains having average sizes of 30-60 nm (Fig. 1). Doping VO₂ films with tungsten leads to a significant decrease in the grain size of the film (Table 1). This is a manifestation of the general regularity known for solid solutions formation: an increase in the number of constituents, as well as an increase in the differences in the sizes and electronic structure of their atoms (or ions), always energetically and kinetically complicates the crystallization of the common crystal lattice. The deformation of the bond lengths and coordination spheres of the matrix around the substitutional atoms leads to a decrease in
the coherent scattering regions and the sizes of individual grains of the microstructure. This pattern is better known for metal alloys, although its manifestations can be seen among other inorganic materials, including solid solutions based on vanadium dioxide, for example, W-doped VO$_2$, Nb-doped VO$_2$, Ce-doped VO$_2$.

![Figure 1: SEM images of (a) S1, (b) S2, (c) S3, and (d) S4 films, respectively.](image)

The quantitative description of films surface morphology was performed using atomic force microscopy (Fig. 2). AFM scanning maps exhibit a clear trend of decreasing the grain size and, as a consequence, decreasing the root mean square (RMS) and average roughness ($R_a$) of the films with an increase in the tungsten content, which is consistent with SEM data (Table 1).

Small absolute values of RMS indicate that VO$_2$ thin films are extraordinarily smooth. The results indicate significantly improved quality of the films compared to those reported in the recent papers obtained with traditional gas-phase and solution methods.

According to the TEM studies, the typical thickness of the films is 50 – 60 nm (Fig. SI3). All the films form continuous surface coating, with no well-defined grain boundaries, suggesting Stranski-Krastanov mechanism of film growth. General tendency of slightly decreasing film thickness with increasing W content can be traced. We suspect the defects introduced by the deposited tungsten atoms both create new crystallization clusters and
Figure 2: AFM scans of (a) S1, (b) S2, (c) S3, and (d) S4 films, respectively.

Negatively affect the kinetics of homogeneous crystallization. Increasing tungsten content, thus, leads to both decreasing film growth rate and film flattening. It coincides well with Stransky-Krastanov mechanism of film growth and the decreasing grain size with W content, as well traced by SEM and AFM. No significant difference in the internal film structure was detected by TEM with W content variation. EDX analysis of the films reveals less tungsten content within the film’s volume compared to that, expected from the solution composition. Moreover the profile analysis indicates the signs of surface tungsten enrichment (Fig. SI2), which can be ascribed to surface segregation during annealing. Selected area elec-

Table 1: $R_a$, RMS and grain size values for S1-S4 films

<table>
<thead>
<tr>
<th>Sample</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS, nm</td>
<td>6.5</td>
<td>5.9</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>$R_a$, nm</td>
<td>5.2</td>
<td>4.7</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Grain size, nm</td>
<td>56±4</td>
<td>47±3</td>
<td>41±1</td>
<td>37±1</td>
</tr>
</tbody>
</table>
Figure 3: The HRTEM image of cross-sectioned W-doped VO$_2$ (S3) film on r-Al$_2$O$_3$ with ED.

Figure 4: $\phi$-scanning analysis results for (a) S1, (b) S2, (c) S3, and (d) S4 films, respectively.
tron diffraction patterns reveal well-defined crystallinity of the films with exactly the same small area ED pattern observed all along the specimen (Fig. 3). ED patterns of films and substrate allow for deduction of the epitaxial relation to be (100) VO$_2$ || (10\overline{1}2) Al$_2$O$_3$ and [010] VO$_2$ || [01\overline{1}0] Al$_2$O$_3$, showing agreement with previous report.\textsuperscript{54}

X-ray diffraction $\theta - 2\theta$ profiles of the undoped and W-doped VO$_2$/r-Al$_2$O$_3$ samples (Fig. SI1 in the Supporting Information) indicate the only detectable reflection of the deposited films at $2\theta = 37^\circ$, along with those of pure sapphire substrate. The reflection intensity weakens with W content, due to hampered crystallization upon the introduction of tungsten atoms. The reflection also shifts to lower angles as the W content increases (see inset of Fig. SI1). Obviously, tungsten dopant induces an expansion of the VO$_2$ unit cell due to the substitution of V$^{4+}$ by the larger W$^{6+}$ ions. Angular position of the reflection corresponds to (200) VO$_2$ (M$_1$). Indeed, $\phi$-scans confirm the biaxial texture of the obtained films (Fig. 4). No any other reflections are found neither in $\theta - 2\theta$ nor in $\phi$-scans, indicating high purity and epitaxial nature of the obtained VO$_2$ films.

Elemental surface composition of the S1–S4 films was analyzed by the XPS method. Deconvolution analysis for V2p$_{3/2}$ and V2p$_{1/2}$ regions reveals two vanadium components present in the samples, corresponding to V$^{4+}$ and V$^{5+}$ valence states (Fig. 5 (a,c,e,g)).\textsuperscript{55} The calculated atomic concentrations of the components is listed in Supplementary Table S1. The presence of V$^{5+}$ can be explained by the surface oxidation with the supposed formation of the equilibrium V$_6$O$_{13}$ phase in the upper atomic layers of the films.\textsuperscript{54}

V$^{4+}$:V$^{5+}$ ratio in the films is influenced by two factors: the surface roughness (in this case, a lower surface roughness, corresponding to a smaller grain size, and hence a larger surface area, indicates an increased content of V$^{5+}$) and the amount of doped tungsten. The first tendency manifests itself in growing V$^{5+}$ concentration while switching from S1 to S2. With the further increase in the W$^{6+}$ content, replacing V$^{4+}$ in the lattice, the surface area changes insignificantly, but vanadium is reduced from V$^{5+}$ to V$^{4+}$, which is necessary to compensate for the charge. As expected, the V$^{5+}$ content in this case decreases from sample
S2 to sample S4.

In Fig. 5 (b,d,f,h), the two peaks at 35.2 eV and 37.3 eV are consistent with the 4f_{7/2} and 4f_{5/2} peaks of W^{6+}, which confirms that tungsten exists as W^{6+}. Atomic concentrations of W calculated from the XPS spectra of V3p and W4f are 0%, 0.5%, 1.4% and 2.3% for S1, S2, S3 and S4, respectively. These contents are higher than expected nominal values for S3 and S4 samples. This occurs probably due to surface segregation of tungsten atoms, which agrees well EDX scan results.

Phase composition of the S1–S4 films was studied by Raman spectroscopy. As shown

Figure 5: XPS analysis of undoped and W-doped VO₂(M₁) films. (a,b)–S1, (c,d)–S2, (e,f)–S3, and (g,h)–S4, respectively.
in Fig. 6, all Raman spectra of crystalline undoped and W-doped VO$_2$ films exhibit similar spectral profiles. Undoped VO$_2$ film shows the typical peaks at 143($A_g$), 195($A_g$), 224($A_g$), 261($B_g$), 309($A_g$), 338($A_g$), 391($A_g$), 441($B_g$), 500($A_g$) and 616($A_g$) cm$^{-1}$, corresponding to the monoclinic VO$_2$ ($M_1$) phase.$^{56}$ For W-doped VO$_2$ films, Raman peaks of the monoclinic VO$_2$ phase samples shift to the lower wavenumbers, get broader and weaker compared with those of the undoped film. No miscellaneous peaks are found, besides those belonging to the sapphire substrate, indicating successful forming of V$_{1-x}$W$_x$O$_2$ solid solutions. The fact of the shifting and broadening of the Raman lines can be explained by an increase in the defects concentration caused by the dopant ions in the lattice and a partial transition from VO$_2$ ($M_1$) to VO$_2$ (R) under Raman laser irradiation. Similar effect was previously reported by Manning et al for W-doped VO$_2$ films$^{57}$ and Ji et al for Nb-doped VO$_2$ films.$^{50}$

**Electrical properties and THz transmission**

Fig. 7 (a) shows electrical resistivity curves as functions of temperature for undoped and doped VO$_2$ thin film samples S1–S4 during the heating/cooling cycle. All dependences demonstrate identical trend corresponding to the common behaviour of the VO$_2$ ($M_1$) crystal:
Figure 7: (a) Normalized resistivity $R(T)/R_{S1}(25\, ^\circ C)$ trends, (b) derivatives of $\log(R(T))$ as a function of temperature during the cooling (dash) and heating (solid) cycles for S1–S4 films, and (c) dependence of $T_{heat}$ and $T_{cool}$ on the W-doping.

A slow decrease in the resistivity of the insulating phase below transition temperature, and an abrupt decrease at metal-insulator transition.\textsuperscript{58} To describe the change of the MIT transition temperature ($T_{MIT}$) and the sharpness of resistivity change, $T_{heat}$ and $T_{cool}$ are defined as the corresponding peak positions of the derivative curves $d(log(R))/dT$, during heating and cooling, respectively. $T_{MIT}$ was defined as $T_{MIT} = (T_{heat} + T_{cool})/2$.

Another important parameter, the width of the temperature hysteresis $\Delta H$ was defined as the difference between $T_{heat}$ and $T_{cool}$. The magnitude of the electrical transition was calculated as $\rho_{MIT}/\rho_{R}$ ($\rho_{R}$ being the resistivity in the conducting phase). All hysteresis characteristics of the MIT for S1–S4 films are given in Table SI1. For pure VO$_2$ thin film, the magnitude of the hysteresis loop is about 3.5 orders at the MIT temperature of 63 °C that is slightly lower in comparison with $T_{MIT}$ of the bulk material (68 °C). This fact is primarily
explained by the contribution of the strain at the film-substrate interface. The degradation of MIT performance for W-doped VO$_2$ can mainly be attributed to an increase of carriers concentration and defectiveness of the the W-rich layers. Nevertheless, even for S4 sample, which exhibits a MIT at the temperature of 31.3 °C, the magnitude of the electrical hysteresis exceeds $10^2$. This is significantly higher than the data usually reported in the literature for heavily doped VO$_2$ films, which once again emphasizes the high crystalline perfection of thin films (Supplementary Table S2).

Fig. 7 (c) shows the dependence of the temperatures on the amount of doped tungsten. The difference between $T_{\text{heat}}$ and $T_{\text{cool}}$ barely changes between the samples, and amounts to 5.5-6 °C. On the other hand, steepness drop of the electrical hysteresis loops upon doping with W is primarily associated with a decrease in the grain size and, as a consequence, an increase in the number of grains forming the film. Each grain has an individual amount of alloying tungsten, which is minimally different from the average. This amount of tungsten determines the individual MIT temperature for each grain, so a film with a large number of grains has a wide range of MIT temperatures, which increases the transition temperature range. In addition, our observation of segregation of tungsten at grain boundaries indicates the inhomogeneity of these boundaries and different concentrations of surface defects on them. These factors can also further increase the temperature spread relative to the average value and the temperature hysteresis of MIT upon doping with W. The result obtained is nevertheless inspiring, as a narrow width of hysteresis loops is required to create high-performance devices with fast response.

Hysteresis loops for the temperature-dependent average THz transmission in the 0.3–2.3 THz range of the undoped and W-doped VO$_2$ samples are shown in Fig. 8.

Transmittance of the VO$_2$ film is defined as the difference between the maximum and minimum lock-in voltage in the THz pulse transmitted through the VO$_2$/r-sapphire sample normalised to the same magnitude of the pulse transmitted through a bare r-sapphire substrate. MD is defined as $\text{MD} = (T_{\text{cold}} - T_{\text{hot}})/T_{\text{cold}}$. Specifically, the transmissions of
samples S1, S2, S3, S4 are 90%, 88%, 83% and 78%, respectively, at room temperature $T_{\text{cold}}$, and 11%, 16%, 21% and 31% at the temperature $T_{\text{hot}}$ (above $T_{\text{MIT}}$). Corresponding MDs are 87.9%, 82.1%, 74.2%, and 60.5%, respectively. Corresponding THz transmission spectra and time-domain lock-in signals are shown in Supplementary Fig. S4. Supplementary Table S3 compares electrical and THz properties for different reported film types, and the main characteristics, $T_{\text{MIT}}$ and MD from the outlined papers are plotted in Fig. 9.

Several techniques have previously been used to tune the $T_{\text{MIT}}$ while maintaining a large MD. Record results have been achieved so far for niobium-doped vanadium dioxide on silicon. Interestingly, the efforts to prepare a vanadium dioxide film with solution assistance have not previously been shown the distinguished combination of extremely low $T_{\text{MIT}}$ and high MD. In contrast to earlier findings, Supplementary Table S3 illustrates that the current S4 film has both MD and $T_{\text{MIT}}$ values comparable to the record Nb-doped VO$_2$/Si, and was obtained by the solvothermal method.
Conclusions

In summary, the uniform epitaxial ultra-smooth VO₂ (M₁) and W-doped VO₂ (M₁) nanoscale films were successfully grown on r-Al₂O₃ substrates using a simple solvothermal process with subsequent post-annealing. Epitaxial relations (100) VO₂ || (1012) Al₂O₃ and [010] VO₂ || [0110] Al₂O₃ are established for the films independent on W content. Results of XPS, Raman spectroscopy, SAED and EDX suggest incorporation of up to 2.3 at% W into the lattice of VO₂ (M₁), forming a substitutional solid solution. Expectedly, tungsten doping leads to a sharp decrease in the VO₂ MIT temperature down to 31 °C at W-doping level of 2.3%. High-quality W:VO₂ (M₁) nanostructured films exhibit an extremely large THz field modulation depth, reasonably decreasing from 87.9% for pure VO₂ (M₁) film to 60.5% for highly-doped V₀.977W₀.023O₂, while retaining narrow hysteresis width of 5.5-6.0 °C. High THz transmittance of the insulating state, superior modulation depth, combined with low VO₂ MIT temperature meets the requirements of THz manipulation devices.
Materials and methods

Materials

All chemical compounds used in the synthesis were purchased from Sigma-Aldrich. Single crystal r-cut sapphire (r-Al$_2$O$_3$) substrates were provided by Monocrystal Co., Ltd. Vanadium pentoxide (V$_2$O$_5$) and oxalic acid (H$_2$C$_2$O$_4$ · 2H$_2$O) were used as starting materials to prepare the vanadium precursor. A mixture of deionized (DI) water and ethylene glycol (EG) was used as a solvent. Ammonium paratungstate ((NH$_4$)$_{10}$W$_{12}$O$_{41}$) was chosen as doping agent. All of these reagents were used without further purification.

Preparation of precursor solution

The fabrication strategy for VO$_2$ and V$_{1-x}$W$_x$O$_2$ films is shown in the Supplementary Fig. S3. V$_2$O$_5$ and H$_2$C$_2$O$_4$ · 2H$_2$O were mixed at a mole ratio of 1:3 in DI water with continuous magnetic stirring for 6h at 80 °C for preparing aqueous V$^{4+}$-containing solution. Then, required amount of EG (DI water : EG = 1 : 1 V/V), was added under their stirring wherein the color of the solution changed from transparent blue to transparent green. The calculated amount of (NH$_4$)$_{10}$W$_{12}$O$_{41}$ was dissolved in DI-EG solvent to obtain W$^{6+}$-containing solution. Finally, V$^{4+}$ and W$^{6+}$ resultants with specific molar ratios were diluted with the same solvent to obtain precursor solution of the required concentration. As a result, the concentration of V$^{4+}$ cations was 3.125 mmol/l. Based on the concentration of W$^{6+}$ cations, the samples were denoted as S1 (0 mmol/l), S2 (1.56 × 10$^{-2}$ mmol/l), S3 (3.13 × 10$^{-2}$ mmol/l) and S4 (4.69 × 10$^{-2}$ mmol/l).

Preparation of VO$_2$ and V$_{1-x}$W$_x$O$_2$ films

Thin W:VO$_2$ (M$_1$) films on r-Al$_2$O$_3$ substrates were fabricated with solvothermal deposition with subsequent annealing. One side polished r-Al$_2$O$_3$ crystals (0.7 × 1.7cm$^2$) were cleaned with nitric acid, DI water and acetone and placed into the high-density 25 ml PPL lined
autoclave in strictly vertical position using Teflon holder. Then, the precursor solution was slowly transferred into the PPL cup with a filling ratio of 0.60 and sealed into a stainless autoclave. The autoclave was kept at 180 °C for 20 h, and then cooled down naturally. The films deposited on the substrates were washed with DI water and acetone several times and dried 30 min at room temperature. Post-annealing was carried out in an inert atmosphere (3 mbar, Ar flow (3.5 l/h)) in two steps. The first annealing step at 400 °C for 30 min was involved to remove any EG residues, and then, the annealing temperature was increased to 600 °C for 1h. The samples were cooled down with furnace. All the samples without special notification are heat-treated. The value of x in V_{1-x}W_xO_2 denotes the W atomic percentage in the feed.

**Film characterisation**

Quantitative compositional studies was carried out using X-ray photoelectron spectroscopy (XPS) at SPECS (Germany) instrument with Mg K – α excitation (E_{ex} =1254 eV). The spectra were acquired in V2p, V3p and W4f regions and treated with CasaXPS software package for component analysis and deconvolution of spectra using Shirley type background and pseudo-Voigt peak functions under fixed FWHM for spectral components of same element.

Film phase purity and crystallinity were investigated by X-ray diffraction (XRD) on a Rigaku SmartLab in the primary beam (λ = 1.54046Å). The diffraction in 2θ- and φ-scanning modes were performed with 0.02 ° steps at a speed of 5 °/min. Raman spectra were recorded using a Renishaw InVia spectrometer under 514 nm 20 mW defocused laser irradiation (∼ 20 μm spot) at room temperature.

Film surface morphology was examined by scanning electron microscopy (SEM) using a Carl Zeiss NVision 40 electron microscope. Surface morphology also was assessed from atomic force microscope topographic images, 2 μm × 2 μm in size using a NTEGRA Aura (NT-MDT). The AFM instrument was operated in tapping mode using silicon probes Micro-
Elucidation of film thickness, microstructure, epitaxial relations and local atomic composition was performed using Libra 200 (Carl Zeiss, Germany) electron microscope with chromatic aberration correction, equipped with Ω-filter and EDX X-Max 80T detector. A common procedure of FIB sample preparation using FEI Quanta 200 3D dual beam instrument was used for cutting-out of cross-sectional specimen.

**Electrical and THz optical characterizations**

Film resistance was measured with a standard four probe method in the temperature range of 25–90 °C (heating and cooling rate 1 °C · min⁻¹) using the Keithley 2700 multimeter. THz characterization was performed using the setup, reported in ref., beam spot on the sample was approximately 1.5 mm, and resistance was controlled on-the-fly by the Ohm-meter, for consistency in thermal measurement.

**Associated content**

**Supporting Information Available**

The Supporting Information contains additional XPS data for samples; Comparison of MIT behavior of undoped and W-doped VO2 films grown on r-Al2O3 substrates; Extended physical-chemical analysis of the thin films (including XRD patterns, EDS profile and TEM images); Schematic representation of the synthesis; Detailed THz transmission spectra for all samples; Comparison of electrical and THz properties of VO2 films

**Notes**

The authors declare no competing financial interest.
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