Coating of VO$_2$-based thin film has been extensively studied for fabricating energy-saving smart windows. One of the most efficient ways for fabricating high performance films is to create multi-nanolayered structure. However, it has been highly challenging to make such layers in the VO$_2$-based films using conventional methods. In this work, a facile two-step approach is established to fabricate multilayered VO$_2$/TiO$_2$ thin films. We first deposited the amorphous thin films upon sputtering, and then anneal them to transform the amorphous phase into alternating Ti- and V-rich multilayered nanostructure via a spinodal decomposition mechanism. In particular, we take advantage of different sapphire substrate planes (A-plane (11–20), R-plane (1–102), C-plane (0001), and M-plane (10-10)) to achieve different decomposition modes. The new approach has made it possible to tailoring the microstructure of the thin films for optimized performances by controlling the disorder-order transition in terms of both kinetic and thermodynamic aspects. The derived thin films exhibit superior optical modulation upon phase transition, significantly reduced transition temperature and hysteresis loop width, and high degradation resistance, these improvements indicate a high potential to be used for fabricating the next generation of energy saving smart windows.

There has been a long-standing demand for nanoscale phase separation owing to its connection to material functionalities. In recent years, intensive efforts have been devoted to understanding the connection$^{1-4}$, and varied approaches for creating functional thin films have been reported, e.g., DNA-mediated self-assembly$^5$, feedback-driven self-assembly$^6$, and electrochemical techniques$^7$. Conventional methods for fabricating thin films usually involve procedures such as template intermediates and/or post treatments, which make the fabrication process complicated and hence unstable. Self-assembly via spinodal decomposition is a promising solution since spinodal decomposition has proven to be efficient in controlling structural features at nanoscale$^8$–$^{10}$. The spinodal decomposition is a mechanism for the rapid decomposition of one thermodynamically stable mixture of liquids or solids into two coexisting phases$^{11}$. In contrast to a nucleation-growth process that results in a random mixture of the two, spinodal decomposition is characterized by long-range spatial correlation, quasi-periodicity, and self-organization with a nearly sinusoidal composition modulation$^{12}$. The structure with compositional fluctuations formed by spinodal decomposition tend to form at nanometer scale$^{13}$. Thus, spinodal decomposition provides a practical route to produce a finely dispersed microstructure that can significantly enhance the material properties.

Most two-phase spinodal systems are consist of two phases with similar crystal structures and physical properties, e.g., metallic alloys$^{11}$, SnO$_2$-TiO$_2$ system$^{14-16}$, Al$_2$O$_3$-Cr$_2$O$_3$ system$^{17}$ and AlN-SiC system$^{18}$. This similarity
limits the functionality of many decomposed systems. Spinodal decomposition of the TiO$_2$/VO$_2$ (TVO) system, which was discovered by Zama and Ueda in 1998 and recently investigated in bulk materials by Ž. Hiroi et al.\textsuperscript{19,20}, is of great interest because of its unique properties of the two components (TiO$_2$ and VO$_2$). VO$_2$ is a crucial component for achieving multi-functionalities of thin film since reversible first-order semiconductor-metal phase transition is accompanied by a drastic change in the optical, electrical, and magnetic properties between its two phases\textsuperscript{21–24}. TiO$_2$ is a commonly used wide band gap insulator and acts as an antireflection compound for VO$_2$ to increase the transmittance of a thin film in both visible and infrared regions\textsuperscript{25–27}. Therefore, transparent TVO thin films provide an attracting application in smart windows, that is, windows that capable of regulating solar/heat transmission for energy efficiency and comfort\textsuperscript{28}. With the advantages of simple structure, automatic control without the use of switching devices, a new approach to enable large-scale producing TVO smart windows at a lower cost is highly desired.

Our previous work\textsuperscript{29} has shown the feasibility of spinodal decomposition on TVO thin films. However, the mechanism of spinodal decomposition in TVO system has not been fully uncovered, the decomposition-microstructure-property relation has not been explored. In the present work, TVO thin films with spinodal structures by performing room temperature sputtering-annealing are prepared using various sapphire substrates (A-plane, R-plane, C-plane and M-plane). We explore the decomposition-microstructure-property relation, reveal the mechanism of spinodal decomposition in TVO system, and we estimate the practical value of all the spinodal structures in smart window area. Our work provides an accurate self-assembled route to fabricate and control VO$_2$-based multilayered thin films.

Results and Discussion

Samples are abbreviated as A-A, A-R, A-C, A-M for amorphous TVO on A-plane (11–20) sapphire, R-plane (1–102) sapphire, C-plane (0001) sapphire, M-plane (10-10) sapphire substrates respectively. Representative spinodal decomposition samples on different sapphire substrates were abbreviated as SD-A, SD-R, SD-C, SD-M. Single component VO$_2$ thin film samples were abbreviated as V-A, V-R, V-C, V-M and TiO$_2$ thin film samples were T-A, T-R, T-C, T-M.

Spinodal decomposition is illustrated on a phase diagram (Fig. 1). Usually, phase separation occurs whenever a material transforms into the thermodynamically unstable regions. The borderline of the unstable region to the stable region, often called the binodal curve, was first reported in TVO by Zamma and Ueda in 1998\textsuperscript{19} from calculations based on the common tangent construction of the free-energy diagram. Below the bimodal curve, there is a spinodal region, which was re-plotted from the literature data obtain from annealing experiments on the crystalline solid solution TVO on the previously mentioned sapphire substrates were abbreviated as C-A, C-R, C-C, C-M. Single component VO$_2$ thin film samples were abbreviated as V-A, V-R, V-C, V-M and TiO$_2$ thin film samples were T-A, T-R, T-C, T-M.

Figure 1. Phase diagram of the VO$_2$-TiO$_2$ system. Reprinted (adapted) with permission from (Ž. Hiroi, et al. Spinodal Decomposition in the TiO$_2$-VO$_2$ System. Chem. Mater. 25, 2202–2210 (2013). Copyright (2013) American Chemical Society.
Thin film composition was determined by XPS analysis (Fig. S2), the molar ratio of Ti to V is 0.33 for all the samples, and hence the composition can all be written as $T_{0.25}V_{0.75}O_2$. The composition ($T_{0.25}V_{0.75}O_2$) and the annealing temperature (500 °C) of the thin film are illustrated by the vertical and horizontal red dashed lines in Fig. 1, respectively. At the crosspoint, the final decomposed phases should be $T_{0.18}V_{0.82}O_2$ (V-rich) phase and the $T_{0.49}V_{0.51}O_2$ (Ti-rich) phase.

Researches$^{32–34}$ have found that the epitaxial growth of VO$_2$ and TiO$_2$ on sapphire substrates has different out-of-plane orientations in terms of the sapphire type, as follows:

A-sapphire: (101) VO$_2$(R)/(11–20) Al$_2$O$_3$, (101) TiO$_2$(R)/(11–20) Al$_2$O$_3$;
R-sapphire: (101) VO$_2$(R)/(1–102) Al$_2$O$_3$, (101) TiO$_2$(R)/(1–102) Al$_2$O$_3$;
C-sapphire: (100) VO$_2$(R)/(0001) Al$_2$O$_3$, (100) TiO$_2$(R)/(0001) Al$_2$O$_3$;
M-sapphire: (001) VO$_2$(R)/(10–10) Al$_2$O$_3$, (001) TiO$_2$(R)/(10–10) Al$_2$O$_3$;

Confirmed by XRD results (Fig. S3), spinodal decomposition samples share the same orientations with the single component ones, thus we achieve different decomposition modes. Note that both the Ti-rich and V-rich peaks are located between the peak of pure VO$_2$ and that of TiO$_2$, the composition of the separated phases are V-doped TiO$_2$ (Ti-rich phase) and Ti-doped VO$_2$ (V-rich phase), respectively.

Standard lattice parameters of rutile TiO$_2$ are $a = 4.852$, $c = 2.953$ (PDF: 78-1510), and of tetragonal VO$_2$ are $a = 4.554$, $c = 2.8557$ (PDF: 79-1655). The lattice mismatch in TVO system is 0.61% along the $a$ axis and 3.3% along the $c$ axis. In this case, spinodal decomposition modulation in the TVO system should occur along the $c$ axis to minimize the elastic strain energy at the interface. The expected multilayers should be parallel to the (001) plane of TVO. This hypothesis is confirmed in TVO bulk crystals where spinodal decomposition occurs only for $hkl$ reflections with $l = 0$$^{29}$. Similarly, spinodal decomposition occurs only along the $c$ axis, i.e., [001] direction in the TiO$_2$/SnO$_2$ system$^{35,36}$. Combined with the XRD results, we can infer the direction of decomposed multilayers will be slanted with respect to the substrate for SD-A and SD-R, perpendicular to the substrate for SD-C, and parallel to the substrate for SD-M. Schematic diagrams of the microstructure of the spinodally decomposed TVO thin films are shown in Fig. 2. Figure 2 also shows the cross-sectional EDS elemental mapping of Ti and V (originate from the STEM in Fig. S4), in high consistence with the schematic structures. The overall thickness of the TVO film was measured to be about 120 nm (Fig. S5), the thickness of Ti-rich layer is estimated to be ~20 nm (~ thickness of V-rich layer is ~40 nm).

Evolution of the separated phases during spinodal decomposition was monitored on SD-M samples annealed for different annealing time, as shown in Fig. 3. Since there is no thermodynamic barrier to the reaction inside the spinodal region (Fig. 1), spinodal decomposition proceeds solely via diffusion mechanism, and the schematic diagram of the element (Ti or V) content fluctuation evolution is shown in Fig. 3(a). It is a sinusoidal wave curve, the amplitude increases along with annealing time and the amplitude is limited by the composition of original solid solution. The film thickness of amorphous sample (A-M) is about 120 nm, investigated by TEM (Fig. 3(b)) and the film surface is flat. TEM proves that A-M was predominantly amorphous since only few crystalline domains are present. Moreover, in HRTEM of Fig. 3(c), there is a pronounced epitaxial crystalline layer of ~10 nm forms in the interface between the substrate and TVO film. The interplanar crystal spacing is measured to be 2.9 Å, matching well with the 2$d$ value calculated from XRD (002) peaks of sample C-M (44.45°, $d = 1.46$ Å). It is reasonable to state that the sapphire substrate is effective in promoting epitaxial growth and the epitaxial thin layer can act as seeds of the two separated phases in the following annealing process.

EDS elemental mapping, and EDS line scanning are shown in Fig. 3(d),(e) and (f) for annealing times of 1 h, 5 h, 10 h, respectively (originate from the STEM images in Fig. S6). The images of each EDS line scan, which starts from the interface between the substrate and TVO and ends at the surface of TVO film, agree well with the schematic diagrams in Fig. 3(a), supporting the diffusional scenario. At the beginning of annealing (1 h, Fig. 3(d)), the as-grown film is a homogeneous solid solution and only little fluctuation can be observed. With the annealing, fluctuations grow until individual phases can be identified (5 h, Fig. 3(e)), but the phase separation is incomplete and appears to be wavy lamellar structures at this stage. After sufficient annealing (over 10 h, Fig. 3(f)), the final equilibrium of phase separation with relatively sharp interface structure has been established. The final phase is stable with extending the annealing time at the fixed annealing temperature, because compared with the 10 h annealed sample, the longer time annealed (20 h) one displays similar XRD intensity (Fig. S7), similar transmittance spectra (Fig. S8(a and b)), and similar hysteresis loops (Fig. S8(c)).

For application purposes, spinodally decomposed TVO thin films (SD-A, SD-R, SD-C, SD-M) are regarded as VO$_2$ and TiO$_2$ multilayer thin films. Based on the semiconductor-metal transition of VO$_2$, those thin films are expected to be utilized as smart windows$^{36}$. The vis-near-infrared transmittance spectra of the composite films were characterized at 20 °C (before phase transition) and 90 °C (after phase transition) to determine their optical modulation capability, as shown in Fig. 4(a–d). Transmittance spectra of single VO$_2$ samples (V-A, V-R, V-C, V-M) are also shown for comparison. The application of VO$_2$ for smart windows relies on the enhancement in both luminous transmittance ($\Delta T_{\text{Lum}}$) and solar modulating ability ($\Delta T_{\text{sol}}$), which are determined using the following equation$^{36}$:

$$ T_\rho = \int_{\psi} \int_{\lambda} T(\lambda) d\lambda d\psi $$

$$ \Delta T = \Delta T_{\text{sol,20°C}} - \Delta T_{\text{sol,90°C}} $$

(1)

(2)
where $T(\lambda)$ is the transmittance at wavelength $\lambda$, $\rho$ denotes $lum$ or $sol$ for calculations, $\psi_{lum}$ is the standard efficiency function for photopic vision, and $\psi_{sol}$ is the solar irradiance spectrum for an air mass of 1.5 (corresponding to the sun standing 37° above the horizon). The optical features of samples are summarized in Table 1.

In Fig. 4(a–d) and Table 1, each spinodally decomposed TVO film (SD-A, SD-R, SD-C, SD-M) displays thermochromic properties, compare with the optical properties of the recently reported VO$_2$-based thermochromic films prepared by magnetron sputtering (listed in Table S2), one can see that all the film can potentially be applied as smart coating material. However, compared to the single VO$_2$, the relative tendency is not uniform across the four types. Comparing SD-A to V-A, the $T_{lum}$ remains constant, while the $\Delta T_{sol}$ increases significantly from 6.1% for V-A to 9.6% for SD-A. The transmittance difference of typical wavelength of 2000 nm ($\Delta T_{2000\text{nm}}$) is measured as 46.4% for V-A and 51.7% for SD-A. For SD-R relative to V-R, and both $T_{lum}$ and $\Delta T_{sol}$ decrease while $\Delta T_{2000\text{nm}}$ increases. This indicates that the Ti-rich coatings slightly increase the total transmittance, but lead to a red shift of the absorption edge in Fig. 4(b), consistent with the function of TiO$_2$ coatings in VO$_2$ based thin films$^{37}$. SD-C exhibits an increase in $T_{lum}$, but more obvious decrease in $\Delta T_{sol}$ compared to V-C (Fig. 4(c)).

Figure 2. Schematic diagrams of the microstructure of spinodally decomposed TVO for (a) SD-A, (b) SD-R, (c) SD-C and (d) SD-M, and the related EDS elemental mapping (Ti and V) analyses of the selected area in Fig. S4.
is reasonable because the perpendicular orientation of the microscopic structure causes incomplete coverage of the V-rich layers on the substrate thus increases the total transmittance for the higher transparent property of Ti-rich layer\textsuperscript{29}, and lowers the thermochromic functional area. SD-M displays relatively high thermochromic performance with \( T_{\text{Lum}} \) of 32.3% at 20 °C, 35.9% at 90 °C, \( \Delta T_{\text{Sol}} \) of 6.6%, and \( \Delta T_{2000\text{nm}} \) of 51.9%. These data are slightly lower than those of V-M. For the relatively high-level Ti-doping in V-rich layers, the total transmittance improvement and red shift phenomena are similar to SD-R and SD-A. More detailed band gap calculation data are discussed and shown in Fig. S9.

**Figure 3.** (a) Schematic diagram of element (Ti or V) content fluctuation in phase separation evolution progress. (b) TEM image of A-M sample. (c) High resolution TEM image of the select red square area in image (b). (d-f) EDS elemental mapping of the selected area (white square in Fig. S6) and line scanning of selected line (yellow line in Fig. S6) analyses for (e) sample annealing for 1 h, (f) sample annealing for 5 h, (g) sample annealing for 10 h. All the EDS line scanning images begin from the interface between TVO film and substrate and end at the surface of TVO film.

**Figure 4.** (a–d) Vis-near-infrared transmittance spectra at 20 °C and 90 °C of samples (a) V-A, SD-A, (b) V-R, SD-R, (c) V-C, SD-C, (d) V-M, SD-M. (e–h) Temperature-varied transmittance hysteresis loops of samples (e) V-A, SD-A, (f) V-R, SD-R, (g) V-C, SD-C, (h) V-M, SD-M. Insets are the first-order differential curves of transmittance to temperature (dT/dt).
The annealing at 500 °C for 10 h can lead to a complete phase separation via our RTS-A method. All spinodally decomposed TVO thin film bears anisotropic stress, and thus, it is promising to be utilized in optical switch to be applied on smart coatings. The decomposed films on A-, R-, and M-sapphire also show both the reduced transition temperature and the narrowed hysteresis loop of the thermochromic V-rich layer. The spinodally decomposed TVO film has been achieved on different sapphire substrates (A-plane (11–20) sapphire, R-plane (1–102) sapphire, C-plane (0001) sapphire, M-plane (10–10) sapphire substrates). All decomposed films display nano-scaled multilayer structures with well-ordered alternating Ti-rich and V-rich parallel layers, while the multilayered TVO structure and substrate have different orientations. The decomposed films tend to be slanted on the nano-scaled multilayer structures with well-ordered alternating Ti-rich and V-rich parallel layers, while the multilayered TVO structure and substrate have different orientations. The decomposed films tend to be slanted on the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is governed by a diffusional mechanism. The spinodally decomposed layers are perpendicular to the substrate, from Ti-rich also exist. Nevertheless, since the orientation relationship between V-rich layer and the substrate is
d

| Sample | $T_{\text{h}}$ ($\degree$C) | $T_{\text{c}}$ ($\degree$C) | $\Delta T_{\text{h}}$ ($\degree$C) | $\Delta T_{\text{c}}$ ($\degree$C) | $T_{\text{c, heating}}$ ($\degree$C) | $T_{\text{c, cooling}}$ ($\degree$C) | $\Delta T$ ($\degree$C) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| V-A    | 40.7            | 40.0            | 40.5            | 34.4            | 6.1             | 46.4            | 57.6            | 52.8            | 4.8             |
| SD-A   | 42.7            | 39.7            | 45.4            | 35.8            | 9.6             | 51.7            | 50.6            | 47.0            | 3.6             |
| V-R    | 39.8            | 38.7            | 39.6            | 33.0            | 6.6             | 43.7            | 52.7            | 45.3            | 7.4             |
| SD-R   | 22.7            | 29.1            | 38.8            | 34.1            | 4.7             | 50.5            | 51.6            | 47.5            | 4.1             |
| V-C    | 41.1            | 40.7            | 43.3            | 35.8            | 7.5             | 45.0            | 55.8            | 50.7            | 5.1             |
| SD-C   | 41.5            | 42.1            | 48.6            | 45.3            | 3.3             | 17.6            | 67.1            | 61.1            | 6.0             |
| V-M    | 45.0            | 41.8            | 44.5            | 36.5            | 8.0             | 52.5            | 55.6            | 48.8            | 6.8             |
| SD-M   | 32.3            | 35.9            | 44.7            | 38.1            | 6.6             | 51.9            | 50.1            | 46.3            | 3.8             |

Table 1. Optical properties of single VO$_2$ samples and spinodal decomposition samples.
self-assembled multilayer-structures and outstanding regulating optical properties indicate that spinodal decomposition is an ideal approach for fabricating VO₂-based smart windows.

Methods

Amorphous TVO thin films (A-A, A-R, A-C, A-M) were first deposited by magnetron sputtering (ULVAC, ACS-4000-C4) on A-sapphire, R-sapphire, C-sapphire, M-sapphire substrates respectively, and then annealed for spinodal decomposition. The deposition of these amorphous TVO samples was carried out by co-sputtering from a VO₂ ceramic target at 70 W dc power and a TiO₂ ceramic target at 100 W rf power at room temperature with Ar and O₂ flow of 39 and 1 sccm, respectively. Representative spinodal decomposition (SD) samples (SD-A, SD-R, SD-C, SD-M) were then obtained by annealing the amorphous samples at 500 °C for 10 h at 1 mTorr. For comparison, crystalline solid solution TZO (C-A, C-R, C-C, C-M) were prepared under nearly identical conditions as the amorphous samples, except that the substrate temperature was kept at 450 °C while sputtering. Single component VO₂ thin film samples (V-A, V-R, V-C, V-M) and TiO₂ thin film samples (T-A, T-R, T-C, T-M) were prepared at 450 °C by alternatively DC sputtering a VO₂ ceramic target at 70 W and RF sputtering a TiO₂ ceramic target at 100 W. A schematic diagram of the preparation processes can be found in Fig. S1(a).

X-ray photoemission spectroscopy (XPS) analysis was conducted on ThermoFisher ESCA lab250 to detect the elementary composition and content of TVO. Thin film X-ray diffraction (XRD) analysis was carried out on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5418 Å) using the 0–20 scanning model. Transmission electron microscopy (TEM) observations were carried out with the electron microscope (FEI, TECNAI G² F20) equipped with an EDS analyzer (OXFORD, X-Max®). The optical transmittance of the films in the wavelength range from 350 nm to 2600 nm at 20 °C and 90 °C was measured using a UV-Vis spectrophotometer (HITACHI, UV-4100). The temperature was measured precisely with a temperature sensor in contact with the surface of films and controlled by a temperature controlling unit.

In addition, summary of the acronyms in this manuscript has been listed at the last of the supporting information in Table S3.

Data availability statement. All data generated or analysed during this study are included in this published article and its Supplementary Information files.

References

1. MaCmanus-Driscoll, J. L. et al. Strain control and spontaneous phase ordering in vertical nanocomposite heteroepitaxial thin films. Nat. Mater. 7, 314–320 (2008).
2. Tazawa, M., Yoshimura, K., Jin, P. & Xu, G. Design, formation and characterization of a novel multifunctional window with VO₂ and TiO₂ coatings. Appl. Phys. A: Mater. Sci. Process. 77, 455–459 (2003).
3. Zheng, L., Bao, S. & Jin, P. TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film as smart window: Combination of energy-saving, antifogging and self-cleaning functions. Nano Energy 11, 136–145 (2015).
4. Y imnirun, R., Ananta, S. & Cann, D. P. The effects of the spinodal microstructure on the electrical properties of TiO₂–SnO₂ ceramics. J. Solid State Chem. 178, 613–620 (2005).
5. Schultz, A. H. & Stubicak, V. S. Separation of Phases by Spinodal Decomposition in Systems Al₂O₃-Cr₂O₃ and Al₂O₃-Cr₂O₃-Fe₂O₃. J. Am. Ceram. Soc. 75, 809–821 (1992).
6. Eto, Y., Yasuda, T., Muraoka, Y. & Okamoto, Y. Spontaneous Decomposition in the TiO₂–VO₂ System. Chem. Mater. 25, 2202–2212 (2013).
7. Arai, K., Okumura, M., Kikuchi, T. & Misaki, H. Spinodal decomposition of TiO₂–SnO₂ ceramics. J. Solid State Chem. 178, 613–620 (2005).
8. O’Callahan, B. T. et al. Inhomogeneity of the ultrafast insulator-to-metal transition dynamics of VO₂. Nat. Commun. 6, 6849 (2015).
9. Zhang, H. T. et al. Wafer-scale growth of VO₂ thin films using a combinatorial approach. Nat. Commun. 6, 8475 (2015).
10. Chen, Z. et al. Strain control and spontaneous phase ordering in vertical nanocomposite heteroepitaxial thin films. Nano Lett. 13, 1596–601 (2013).
11. Dey, K. K. et al. VO₂ nanorods for efficient performance in thermal fluids and sensors. Nanoscale 7, 6159 (2015).
12. Apfel, K. W. et al. Phase-Separation in the Sic-Aln Pseudobinary System - the Role of Coherency Strain-Energy. J. Am. Ceram. Soc. 75, 809–821 (1992).
13. McGurk, W. J. & Hauke, P. E. Optical negative refraction in bulk metamaterials of nanowires. Science 321, 930–930 (2008).
14. Hitachi, UV-4100. The temperature was measured precisely with a temperature sensor in contact with the surface of films and controlled by a temperature controlling unit.
15. Y imnirun, R., Ananta, S. & Cann, D. P. The effects of the spinodal microstructure on the electrical properties of TiO₂–SnO₂ ceramics. J. Solid State Chem. 178, 613–620 (2005).
16. Eto, Y., Yasuda, T., Muraoka, Y. & Okamoto, Y. Spontaneous Decomposition in the TiO₂–VO₂ System. Chem. Mater. 25, 2202–2212 (2013).
17. Arai, K., Okumura, M., Kikuchi, T. & Misaki, H. Spinodal decomposition of TiO₂–SnO₂ ceramics. J. Solid State Chem. 178, 613–620 (2005).
18. O’Callahan, B. T. et al. Inhomogeneity of the ultrafast insulator-to-metal transition dynamics of VO₂. Nat. Commun. 6, 6849 (2015).
19. Zhang, H. T. et al. Wafer-scale growth of VO₂ thin films using a combinatorial approach. Nat. Commun. 6, 8475 (2015).
20. Sun, G. et al. Low-temperature deposition of VO₂ films with high crystalline degree by embedding multilayered structure. Solar Energy Materials and Solar Cells 161, 70–76 (2017).
21. Tanaka, M., Yoshimura, K., Jin, P. & Xu, G. Design, formation and characterization of a novel multifunctional window with VO₂ and TiO₂ coatings. Appl. Phys. A: Mater. Sci. Process. 77, 455–459 (2003).
22. Zheng, L., Bao, S. & Jin, P. TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film as smart window: Combination of energy-saving, antifogging and self-cleaning functions. Nano Energy 11, 136–145 (2015).
23. O’Callahan, B. T. et al. Inhomogeneity of the ultrafast insulator-to-metal transition dynamics of VO₂. Nat. Commun. 6, 6849 (2015).
24. Zhang, H. T. et al. Wafer-scale growth of VO₂ thin films using a combinatorial approach. Nat. Commun. 6, 8475 (2015).
25. Sun, G. et al. Low-temperature deposition of VO₂ films with high crystalline degree by embedding multilayered structure. Solar Energy Materials and Solar Cells 161, 70–76 (2017).
26. Tanaka, M., Yoshimura, K., Jin, P. & Xu, G. Design, formation and characterization of a novel multifunctional window with VO₂ and TiO₂ coatings. Appl. Phys. A: Mater. Sci. Process. 77, 455–459 (2003).
27. Zheng, L., Bao, S. & Jin, P. TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film as smart window: Combination of energy-saving, antifogging and self-cleaning functions. Nano Energy 11, 136–145 (2015).
28. O’Callahan, B. T. et al. Inhomogeneity of the ultrafast insulator-to-metal transition dynamics of VO₂. Nat. Commun. 6, 6849 (2015).
29. Zhang, H. T. et al. Wafer-scale growth of VO₂ thin films using a combinatorial approach. Nat. Commun. 6, 8475 (2015).
30. Sun, G. et al. Low-temperature deposition of VO₂ films with high crystalline degree by embedding multilayered structure. Solar Energy Materials and Solar Cells 161, 70–76 (2017).
31. Tanaka, M., Yoshimura, K., Jin, P. & Xu, G. Design, formation and characterization of a novel multifunctional window with VO₂ and TiO₂ coatings. Appl. Phys. A: Mater. Sci. Process. 77, 455–459 (2003).
32. Zheng, L., Bao, S. & Jin, P. TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film as smart window: Combination of energy-saving, antifogging and self-cleaning functions. Nano Energy 11, 136–145 (2015).
33. O’Callahan, B. T. et al. Inhomogeneity of the ultrafast insulator-to-metal transition dynamics of VO₂. Nat. Commun. 6, 6849 (2015).
34. Zhang, H. T. et al. Wafer-scale growth of VO₂ thin films using a combinatorial approach. Nat. Commun. 6, 8475 (2015).
35. Sun, G. et al. Low-temperature deposition of VO₂ films with high crystalline degree by embedding multilayered structure. Solar Energy Materials and Solar Cells 161, 70–76 (2017).
36. Tanaka, M., Yoshimura, K., Jin, P. & Xu, G. Design, formation and characterization of a novel multifunctional window with VO₂ and TiO₂ coatings. Appl. Phys. A: Mater. Sci. Process. 77, 455–459 (2003).
37. Zheng, L., Bao, S. & Jin, P. TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film as smart window: Combination of energy-saving, antifogging and self-cleaning functions. Nano Energy 11, 136–145 (2015).
38. Chen, C.

34. Sun, G.

39. Morin, F. J. Oxides Which Show a Metal-to-Insulator Transition at the Neel Temperature.

40. Nishikawa, M., Nakajima, T., Kumagai, T., Okutani, T. & Tsuchiya, T. Ti-Doped VO₂ Films Grown on Glass Substrates by Excimer-Laser-Assisted Metal Organic Deposition Process. Jpn. J. Appl. Phys. 50, 01BE04 (2011).

41. Chen, S., Liu, J., Wang, L., Luo, H. & Gao, Y. Unraveling Mechanism on Reducing Thermal Hysteresis Width of VO₂ by Ti Doping: A Joint Experimental and Theoretical Study. J. Phys. Chem. C 118, 18938–18944 (2014).

42. Ladd, L. A. & Paul, W. Optical and Transport Properties of High Quality Crystals of V₂O₅ near Metallic Transition Temperature. Solid State Commun. 7, 425–428 (1969).

43. Ji, Y. X., Li, S. Y., Niklasson, G. A. & Granqvist, C. G. Durability of thermochromic VO₂ thin films under heating and humidity: Effect of Al oxide top coatings. Thin Solid Films 562, 568–573 (2014).

44. Long, S. et al. Thermochromic multilayer films of WO₃/VO₂/WO₃ sandwich structure with enhanced luminous transmittance and durability. RSC Adv. 6, 106435–106442 (2016).

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (NSFC, 51572284), and the Shanghai Sailing Program (17YF1429800). And the authors are grateful for The Youth Innovation Promotion Association, Chinese Academy of Sciences (No. 2018288).

Author Contributions

G.S. wrote the main manuscript text under guidance of X.C. and P.J. Y.Y. and X.G. contributed to the result discussion. S.L., N.L. and R.L. assisted for sample synthesis and basic characterization. G.S. conceived the experiments under supervision of H.L. and P.J. X.C. and P.J. planned and supervised this study. All authors participated in discussions and manuscript writing.

Additional Information

Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-23412-4.

Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018