Enhanced metal-insulator transition in freestanding VO$_2$
down to 5 nm thickness

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ABSTRACT

Ultrathin freestanding membranes with a pronounced metal-insulator transition (MIT) provides huge potential in future flexible electronic applications as well as a unique aspect of the study of lattice-electron interplay. However, the reduction of the thickness to an ultrathin region (a few nm) is typically detrimental to the MIT in epitaxial films, and even catastrophic for their freestanding form. Here, we report an enhanced MIT in VO2-based freestanding membranes, with a lateral size up to millimetres and VO2 thickness down to 5 nm. The VO2-membranes were detached by dissolving a Sr3Al2O6 sacrificial layer between the VO2 thin film and c-Al2O3(0001) substrate, allowing a transfer onto arbitrary surfaces. Furthermore, the MIT in the VO2-membrane was greatly enhanced by inserting an intermediate Al2O3 buffer layer. In comparison to the best available ultrathin VO2-membranes, the enhancement of MIT is over 400% at 5 nm VO2 thickness and more than one order of magnitude for VO2 above 10 nm. Our study widens the spectrum of functionality in ultrathin and large-scale membranes, and enables the potential integration of MIT into flexible electronics and photonics.

INTRODUCTION

Metal-insulator transition (MIT), an appealing strongly correlated electronic phenomenon, offers switchable electronics states, which are ideal for future electronic and photonic applications1. VO2 is considered as one of the most attractive MIT materials, owing to its near room transition temperature (~341 K), where electrical conductivity can change up to six orders of magnitude2-3. Most recently, spurred by the technological interest for flexible electronics, such as flexible artificial neuron4-5 and low-power transistor6. It is of great demand to transform the MIT in VO2 from a conventional epitaxial rigid form to a freestanding flexible one. Meaningful endeavours have achieved the VO2-membranes (typically above 25 nm) using a number of techniques, including ion milling7, wet-etching based method8-10, or mechanical exfoliation from mica substrate11. Furthermore, thanks to the continuous advancement of fabrication techniques, reducing the dimensions while retaining high-quality MIT in a flexible form can potentially lead to new insights into the interplays of lattice and electronic correlation12 and utilization of flexible form of MIT in low-power flexible electronics. Hence, it is highly desirable to adopt a facile and gentle approach to preserve the MIT in freestanding large-scale VO2 down to an
ultrathin region, \textit{i.e.} below 10 nm\textsuperscript{7, 13}.

However, it is extremely challenging to obtain a freestanding ultrathin VO\textsubscript{2} membrane (< 10 nm) with high-quality MIT. This is due to a combination of several fundamental and technical issues, including the fundamental limit of critical thickness\textsuperscript{14}, crystalline defects created during the fabrication\textsuperscript{13}, and unwanted surface states introduced during the sample processing\textsuperscript{8-10}. To date, only the complicated technique of ion milling\textsuperscript{7} managed to achieve a sub-20 nm VO\textsubscript{2}-membranes by compromising the lateral size to tens of micrometres (limited by the growth approach) and a degraded MIT (due to ion-induced structural damages).

In this study, we demonstrate a facile fabrication to retain enhanced MIT in ultrathin and large-scale VO\textsubscript{2}-membranes by utilizing an Al\textsubscript{2}O\textsubscript{3} buffer layer and a water-soluble sacrificial Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6} (SAO) layer\textsuperscript{12, 15-17}, albeit the underneath cubic SAO experiences a non-epitaxial growth on hexagonal c-Al\textsubscript{2}O\textsubscript{3}(0001) substrate. More importantly, by inserting an intermediate Al\textsubscript{2}O\textsubscript{3} buffer layer between the SAO and VO\textsubscript{2} films, the millimetre-scale VO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}-membranes exhibit an enhanced MIT with the VO\textsubscript{2} thickness down to 5 nm. Quantitatively, this enhanced MIT is over 400\% at 5 nm VO\textsubscript{2} thickness and more than one order of magnitude for VO\textsubscript{2} above 10 nm in comparison to the existing ultrathin VO\textsubscript{2}-membranes\textsuperscript{7}.

**Experimental section**

**Sample fabrication**

Single monoclinic (\textit{M})-phase VO\textsubscript{2} films with thickness from 4 to 120 nm were grown by pulsed laser deposition (PLD) on c-Al\textsubscript{2}O\textsubscript{3} substrates with/without an SAO sacrificial layer and/or an Al\textsubscript{2}O\textsubscript{3} buffer layer between them. During the deposition, the laser fluence was fixed at \(\sim 2\) J/cm\textsuperscript{2} with a repetition rate of 5 Hz. The growth temperature and oxygen partial pressure (\(P_{O2}\)) for SAO and Al\textsubscript{2}O\textsubscript{3} were 700 °C and 1 \(\times\) 10\textsuperscript{-5} Torr, respectively. Then the temperature was decreased to 500 °C under the same \(P_{O2}\). VO\textsubscript{2} thin film was deposited at 500 °C with a \(P_{O2}\) of 2 \(\times\) 10\textsuperscript{-4} Torr. After deposition, the sample was \textit{in situ} annealed at 500 °C with a \(P_{O2}\) of 5 \(\times\) 10\textsuperscript{-3} Torr for 1 h. Sequentially, the sample was cooled down to room temperature under the same \(P_{O2}\). Sintered polycrystalline SAO, Al\textsubscript{2}O\textsubscript{3} ceramic pellets and a commercial vanadium single crystal were used as targets. The thickness was controlled by the number of the laser pulse, and
further calibrated by both stylus profilometer and X-ray reflectivity (see Figure S1 in supporting information) Two types of heterostructure are fabricated, namely VO2/SAO/c-Al2O3 and VO2/Al2O3/SAO/c-Al2O3 heterostructures. As the SAO layer is dissolvable in deionized (DI) water15, 18, immersing the heterostructures can detach the VO2- or VO2/Al2O3-membranes from the c-Al2O3 substrates, and get suspended in the DI water, which are ready to be transferred onto any arbitrary substrates. At last, in order to ensure a firm adhesion of the membranes onto the new surface of substrates, e.g. glass, the transferred membranes with the new substrates were annealed in a vacuum (<10^-6 Torr) at 120 °C for 1 h to remove the bubbles and residual water.

Characterization methods

The electrical transport properties were measured with a Quantum Design physical property measurement system (PPMS) in the temperature range from 300 to 400 K. X-ray diffraction (XRD) was performed on a Bruker D8 diffractometer equipped with a Cu Kα1 source at a wavelength of 1.5406 Å operated at 40 keV and 40 mA in grazing incidence (GI) geometry. Raman spectra were performed in backscattering configuration and recorded at 532 nm laser excitation. The resolution for this configuration is 0.5 cm^-1.

RESULTS AND DISCUSSION

Figure 1 shows the deposition, detachment and transfer processes to achieve the VO2 and VO2/Al2O3 membranes. The MIT in VO2 is accompanied by a structural phase transition from a low-temperature M-phase to a high-temperature rutile (R)-phase. Figure 1 also shows optical images of the VO2- and VO2/Al2O3-membranes on glass substrates with a scale up to several millimetres.
Figure 1. Schematics of the process to obtain ultrathin and large-scale VO₂ and VO₂/Al₂O₃ membranes. The as-grown samples, namely VO₂/SAO/c-Al₂O₃ and VO₂/Al₂O₃/SAO/c-Al₂O₃ heterostructures, are dipped in DI water to remove the SAO sacrificial layer. Consequently, ultrathin VO₂- and VO₂/Al₂O₃-membranes are achieved and can be transferred onto any substrates. In the schematics, glass substrates were used as a representative substrate. Eventually, optical images of the ultrathin and large-scale VO₂- and VO₂/Al₂O₃-membranes with a thickness down to 5 nm and a feature-length of mm are captured. The difference between these two types of membranes is the insertion of a buffer layer of Al₂O₃ during the growth.

It is worth mentioning that the efficiency of dissolving the SAO sacrificial layer is dramatically increased after inserting the Al₂O₃ buffer layer. The durations required for dissolving of the SAO layers in the 5 mm × 5 mm of VO₂/SAO/c-Al₂O₃ and VO₂/Al₂O₃/SAO/c-Al₂O₃ heterostructures are 1440 and 10 min, respectively. Moreover, the VO₂/Al₂O₃ membrane can be rolled into microtube during the dissolution of the SAO sacrificial layer in DI water without breaking, suggesting that the VO₂-membrane is highly flexible to bear a large degree of deformation. Specifically, the VO₂/Al₂O₃-membrane remains flat when the thickness of Al₂O₃ is below 10 nm and rolls up into a microtube for thicker Al₂O₃. The self-bending is ascribed to the low bending stiffness of the bilayer membrane system and unreleased strain between the Al₂O₃ and VO₂ layer.
Figure 2. Structural characterisation of VO₂-based heterostructures and membranes. (a) Room temperature Raman scattering curves for the 80 nm VO₂/c-Al₂O₃ heterostructure (abbreviated as 80VO₂/c-Al₂O₃, same notion will be used thereafter), 80VO₂/25SAO/c-Al₂O₃, 80VO₂/30Al₂O₃/25SAO/c-Al₂O₃, 80VO₂-membrane, 80VO₂/30Al₂O₃-membrane. (b) Temperature-dependent HRXRD 2θ-ω scans of VO₂ (011) peak of the 80VO₂/30Al₂O₃/25SAO/c-Al₂O₃ at temperatures ranging from 300 to 370 K. The black arrow lines denote the peak shift across the MIT.

The structural phase of all the epitaxial films and membranes were firstly characterized by Raman spectroscopy with a 532 nm excitation laser source and temperature-dependent high-resolution X-ray diffraction (HRXRD). Figure 2a shows the room temperature Raman scattering curves for the 80 nm VO₂/c-Al₂O₃ heterostructure (abbreviated as 80VO₂/c-Al₂O₃, same notion will be used thereafter), 80VO₂/25SAO/c-Al₂O₃, 80VO₂-membrane, 80VO₂/30Al₂O₃/25SAO/c-Al₂O₃, and 80VO₂/30Al₂O₃-membrane. All the peaks at 194, 223, 264, 308, 340, 387, 440, 499, and 613 cm⁻¹ correspond to the pure M-phase VO₂ in both heterostructure and membrane forms at room temperature. Moreover, the HRXRD measurement was conducted on VO₂/Al₂O₃/SAO/c-Al₂O₃ to confirm the thermal driven first-order SPT. Figure 2b shows that the VO₂(M) (011) peaks at 27.72° in the low-temperature region, i.e. from 300 to 340 K, shifts to rutile VO₂(R) (110) peaks at 27.58° in the high-
temperature region, \textit{i.e.} from 345 to 370 K. When subsequently cooling the samples, the VO$_2$(R) (110) peaks recover to the initial VO$_2$(M) (011) peaks position$^{20-21}$. Therefore, both Raman and HRXRD results demonstrated that the crystallinity of the VO$_2$(M) are well-retained when grown on SAO, and which is barely affected by the transfer process.

The electrical properties of the VO$_2$ heterostructures and membranes were characterized by the temperature-dependent resistivity and corresponding derivative curves, $d(\log\rho)/dT$. Figure 3 shows that the MIT behaviour was preserved in all VO$_2$/SAO/c-Al$_2$O$_3$ samples, though the steepness of resistivity change is compromised and the magnitude of the resistivity change is suppressed in contrast to the epitaxial VO$_2$/c-Al$_2$O$_3$. The degraded MIT behaviour of VO$_2$/SAO/c-Al$_2$O$_3$ can be mainly attributed to the defects in VO$_2$ thin film induced by the SAO sacrificial layer. To overcome this, an Al$_2$O$_3$ buffer layer was inserted between VO$_2$ thin film and SAO sacrificial layer. Figure 3a shows that the resistivity change of VO$_2$/Al$_2$O$_3$/SAO/c-Al$_2$O$_3$ increases by around one order of magnitude and the MIT becomes much steeper. Figure 3b shows the normalized resistivity change, \textit{i.e.} $\rho(T)/\rho(300\text{ K})$, as a function of temperature. Notably, the magnitude of the resistivity changes for VO$_2$/SAO/c-Al$_2$O$_3$ and VO$_2$-membrane are comparable, as well as for VO$_2$/Al$_2$O$_3$/SAO/c-Al$_2$O$_3$ and VO$_2$/Al$_2$O$_3$-membrane. The detailed comparison of MIT of different VO$_2$ can be found in Table S1 in supporting information. The electrical transport measurements suggest that the influence of transferring procedure on its electrical transport properties is negligible.

To further characterize the change of MIT transition temperature ($T_{MIT}$) and the sharpness of resistivity change, several parameters are defined and plotted in Figure 3c. $T_{Heat}$ and $T_{Cool}$ are the specific transition temperature defined as the corresponding peak position of the derivative curves, $d(\log\rho)/dT$, during heating and cooling, respectively. Hence, $T_{MIT}$ can be defined as $T_{MIT} = (T_{Heat} + T_{Cool})/2$. The hysteresis width ($\Delta H$) is defined as the difference between $T_{Heat}$ and $T_{Cool}$. The sharpness of the transition is defined as the full width at half maximum (FWHM) of the derivative curves during heating and cooling, which is derived by Gaussian fitting. Figure 3c shows that both $T_{Heat}$ and $T_{Cool}$ are slightly shifted towards room temperature for VO$_2$/SAO/c-Al$_2$O$_3$ and VO$_2$/Al$_2$O$_3$/SAO/c-Al$_2$O$_3$ and their corresponding membranes by comparing with that of VO$_2$/c-Al$_2$O$_3$. The decrease of $T_{MIT}$ indicates VO$_2$ is compressively strained in both heterostructure and membranes forms by inserting the SAO sacrificial layer and
Al₂O₃ buffer layer⁹,²². The FWHM becomes much broader for VO₂/SAO/c-Al₂O₃ and VO₂/SAO-membrane, suggesting the degraded quality of VO₂¹⁰. After inserting an Al₂O₃ buffer layer between VO₂ and SAO, the resistivity change becomes sharper²³, which again proves the beneficial effect of buffer Al₂O₃.

Figure 3. Effect of Al₂O₃ buffer layer. (a) Resistivity, (b) normalized resistivity changes, i.e. $\rho(T)/\rho(300 \text{ K})$, and (c) derivatives of $\log_{10}(\rho(T))$ as a function of temperature during the cooling (hollow circle) and heating (solid circle) cycles of the various VO₂-based heterostructures and membranes. The symbols and lines represent data points and Gaussian fitting curves, respectively.

The MIT properties of VO₂ are dramatically affected by thickness as well⁷,²⁴. A minimum thickness is needed for the full development of the electronic MIT, such as the study of quantum confinement effects⁷. Therefore, an ultrathin VO₂ membrane is a prerequisite to have a deeper examination of the intrinsic MIT properties and quantum size effects. Figure 4a-e shows temperature-dependent resistivity of VO₂/c-Al₂O₃, VO₂/SAO/c-Al₂O₃, VO₂-membrane, VO₂/Al₂O₃/SAO/c-Al₂O₃, and VO₂/Al₂O₃-membrane with different VO₂ thicknesses. For all VO₂ films with thickness above 20 nm, the MIT properties are retained. It is worth noting that the critical thickness for MIT in VO₂ film increases from 4 nm for VO₂/c-Al₂O₃ to 15 nm for VO₂/SAO/c-Al₂O₃ and 20 nm
for VO₂-membrane, indicating that the VO₂ deteriorates when grown on SAO. Remarkably, the critical thickness recovers to 5 nm for VO₂/Al₂O₃/SAO/c-Al₂O₃ and corresponding VO₂/Al₂O₃-membrane, demonstrating that the quality of the VO₂ is comparable with that of VO₂ directly grown on c-Al₂O₃ substrate²⁵.

Figure 4. Thickness dependent metal-insulator transition of VO₂-based heterostructures and VO₂-membranes. Normalized resistivity change, i.e. $\rho(T)/\rho(300 \text{ K})$, of (a) VO₂/c-Al₂O₃, (b) VO₂/SAO/c-Al₂O₃, (c) VO₂-membrane, (d) VO₂/Al₂O₃/SAO/c-Al₂O₃, and (e) VO₂/Al₂O₃-membrane. The labels of the thickness in all figures correspond to the VO₂ thicknesses in the respective samples.

Figure 5 compares the thickness dependence of the resistivity change across the MIT, $\rho(300 \text{ K})/\rho(370 \text{ K})$ of different ultrathin VO₂-membranes prepared in this work and the pioneer work in ref [7]. One can clearly see the magnitude of the resistivity change during the MIT in this study is over one order of magnitude better than the previous study for VO₂ above 10 nm, which can still be maintained to 400% when the thickness of VO₂ is reduced to 5 nm. In addition to the exceptional MIT, the water-soluable sacrificial SAO layer approach shows celebrated advantages in obtaining both large-scale, high-quality VO₂ membranes with an easy-handling process.
Figure 5. Comparison of the MIT in ultrathin VO$_2$-membranes (less than 25 nm) fabricated by different methods. The thickness dependence of the resistivity change, $\rho(300 \text{ K})/\rho(370 \text{ K})$, across the MIT of VO$_2$-membranes by different fabrication methods.

Conclusion

In summary, we have demonstrated a facile synthesis method to fabricate freestanding large-scale VO$_2$ ultrathin membranes by inserting SAO as a sacrificial layer and Al$_2$O$_3$ as a buffer layer between the VO$_2$ film and c-Al$_2$O$_3$ substrate. Both the $M$-phase crystal structure and the corresponding MIT behaviour are preserved in the VO$_2$- and VO$_2$/Al$_2$O$_3$-membranes form, albeit the SAO cannot be epitaxially grown on c-Al$_2$O$_3$ substrate. Furthermore, the MIT quality of the VO$_2$ membranes is notably improved by employing an Al$_2$O$_3$ buffer layer even for VO$_2$ down to 5 nm, which shows great advantages as compared with the previous studies and guarantees the excellent flexibility for future low-power flexible electronics. Our VO$_2$/Al$_2$O$_3$-membranes demonstrated advantages of the higher magnitude of the MIT resistivity change in a larger area and thinner VO$_2$-membranes than the VO$_2$-membranes prepared by other techniques. Our results could pave the way for practically and versatility integrating high-quality MIT in future flexible electronics and photonics.
Supporting Information

Detailed comparison of MIT of different VO$_2$ films (Table S1); Atomic force microscopy and X-ray reflectivity calibration of film thickness (Figure S1)

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Supporting Information

Enhanced metal-insulator transition in freestanding VO₂ down to 5 nm thickness

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### Table S1

To quantitatively evaluate the quality of our VO$_2$ films and membranes, several key parameters are defined and listed in Table S1.

| Sample                  | $\Delta$A | $T_{\text{heat}}$ (K) | $T_{\text{cool}}$ (K) | $T_{\text{MTT}}$ (K) | $\Delta H$ (K) | $\Delta T$ (K) |
|-------------------------|------------|------------------------|------------------------|----------------------|----------------|---------------|
| VO$_2$/c-Al$_2$O$_3$     | 6223       | 352.3                  | 337.2                  | 344.8                | 15.1           | 4.9           |
| VO$_2$/SAO/c-Al$_2$O$_3$ | 138        | 345.9                  | 333.2                  | 339.6                | 12.7           | 7.4           |
| VO$_2$/membrane          | 83         | 349.2                  | 332.2                  | 340.7                | 17             | 7.2           |
| VO$_2$/Al$_2$O$_3$/SAO/c-Al$_2$O$_3$ | 1238   | 345.8                  | 332.5                  | 339.2                | 13.3           | 5.2           |
| VO$_2$/Al$_2$O$_3$ - membrane | 409     | 347                    | 331                    | 339                  | 16             | 5.4           |

$\Delta$A: $(R(300K)/R(370K))$;

$T_{\text{MTT}} = (T_{\text{heat}} + T_{\text{cool}})/2$;

$T_{\text{heat}}$ and $T_{\text{cool}}$: the transition temperatures defined as the peak position of the derivative curves ($d(\log \rho)/dT$) during heating and cooling.

$\Delta H$: The hysteresis width is defined $\Delta H = T_{\text{heat}} - T_{\text{cool}}$.

$\Delta T$: The sharpness of the transition, which is defined as the FWHM of the derivative curve during heating.
Figure S1

The thickness of VO$_2$ films is calibrated by results of profilometry (Figure S1a,b) and X-ray reflectivity (Figure S1c). Both results are consistent, which provides the thickness controlling by counting the number of the laser pulse. For VO$_2$, 1 nm corresponds to 500 pulses; For Al$_2$O$_3$, 1 nm corresponds to 20 pulses.

Supplementary Figure S1. Thickness calibration of different VO$_2$. The thicknesses of (a) 40000 pulses VO$_2$-membrane and (b) 40000 pulses VO$_2$/600 pulses Al$_2$O$_3$ were measured by Bruker profilometer. (c) The X-ray reflectivity (XRR) of 30000 pulses VO$_2$/c-Al$_2$O$_3$ heterostructure. The thickness of the VO$_2$ film obtained by fitting is 58.8 nm. The thicknesses measured by both methods are consistent. All the thicknesses used in this study are calibrated by the laser pulses.