Heterogeneous integration of single-crystalline rutile nanomembranes with steep phase transition on silicon substrates

Dong Kyu Lee, Yunkyu Park, Hyeji Sim, Jinheon Park, Younghak Kim, Gi-Yeop Kim, Chang-Beom Eom, Si-Young Choi & Junwoo Son

Unrestricted integration of single-crystal oxide films on arbitrary substrates has been of great interest to exploit emerging phenomena from transition metal oxides for practical applications. Here, we demonstrate the release and transfer of a freestanding single-crystalline rutile oxide nanomembranes to serve as an epitaxial template for heterogeneous integration of correlated oxides on dissimilar substrates. By selective oxidation and dissolution of sacrificial VO₂ buffer layers from TiO₂/VO₂/TiO₂ by H₂O₂, millimeter-size TiO₂ single-crystalline layers are integrated on silicon without any deterioration. After subsequent VO₂ epitaxial growth on the transferred TiO₂ nanomembranes, we create artificial single-crystalline oxide/Si heterostructures with excellent sharpness of metal-insulator transition ($\Delta\rho/\rho > 10^3$) even in ultrathin (<10 nm) VO₂ films that are not achievable via direct growth on Si. This discovery offers a synthetic strategy to release the new single-crystalline oxide nanomembranes and an integration scheme to exploit emergent functionality from epitaxial oxide heterostructures in mature silicon devices.
Heteroepitaxial growth has been widely used to obtain single-crystal films for developing modern solid-state electronic and photonic devices. In particular, epitaxial oxide heterostructures provide promise for emerging electronics and photonics due to the intriguing phenomena (e.g., metal-insulator transition (MIT), high-electron mobility, ferroelectricity) exhibited by these ionic crystals. Therefore, the stacking of single-crystalline oxide films on dissimilar substrates (e.g., silicon (Si)) will offer ways to integrate the emergent phenomena of oxides with mature electronic and photonic devices.

However, the heteroepitaxial growth of oxide films drastically limits the possible material combinations due to the requirement of lattice matching between the epilayer and substrate. For instance, direct oxide growth on dissimilar materials typically forms defective or polycrystalline layers near the interface between films and substrates, preventing unrestricted integration of single-crystal oxide films onto any desired substrates, especially on mainstream Si substrates.

Release and transfer of freestanding single-crystal sheets with a nanoscale thickness (i.e., epitaxially grown, nanomembranes (NM)) gives the freedom to transfer the released epilayer onto highly mismatched or amorphous substrates, and even allows reusable substrates. While crystalline materials that are intrinsically layered (e.g., two-dimensional (2D) materials) are exfoliated spontaneously due to weak van der Waals bonding, the stacking of single-crystalline oxide films on dissimilar substrates strictly requires the preformation of bond breaking from the substrate.

Many techniques have been employed to form freestanding NMs with a mechanically cleavable plane. For example, physical release methods (e.g., laser lift-off) were originally developed to release epitaxial GaN semiconductor films to break strong bonding. However, these methods are only applicable to the formation of thick semiconductor membranes due to the inevitable structural damage. Moreover, a few monolayers of graphene could be inserted to release single-crystalline oxide membranes from substrates (i.e., “remote” epitaxy). Despite the versatility of this technique, the coalescence of localized nuclei in oxide layers on the graphene, along with the restriction of oxygen environment during growth, prevents the layer-by-layer growth of ultrathin oxide NM with atomic precision and high quality.

By contrast, the freestanding NM was chemically released from the substrate by selective etching of sacrificial layers; these chemical lift-off methods are less destructive than physical methods. However, the harsh wet condition with a strong acid or base etchant typically leaves roughening and residue on the host substrates or released membrane after the chemical etch. Recently, atomically thin perovskite oxide NM was gently released by dissolving water-soluble Sr$_3$Al$_2$O$_6$ sacrificial layers, but the moisture-sensitive nature of these layers prevents long-time exposure of the sacrificial layers, which restricts practical application for heterogeneous integration of oxide NM. Moreover, the development of oxide NM has been limited for perovskite structure among chemical lift-off methods so far.

Here, we demonstrate that single-crystalline rutile oxide NM with the sharpened MIT can be integrated on the technologically influential, but more challenging, Si substrates by new epitaxial lift-off combination (see Fig. 1 for the process schematic). After the synthesis of an epitaxial TiO$_2$/VO$_2$ heterostructure on TiO$_2$ host substrate, the VO$_2$ sacrificial layer is selectively dissolved in dilute H$_2$O$_2$ to release the top TiO$_2$ film with the mechanical supporting layers (Fig. 1b). Contrary to the previous chemical lift-off using extreme pH solution, dilute aqueous H$_2$O$_2$ with mild pH leads to selective etching of epitaxially grown VO$_2$ sacrificial films by phase transformation to two-dimensional layered structure with weak bonding; this selective dissolution of VO$_2$ layer releases millimeter-scale freestanding TiO$_2$ NM from the TiO$_2$/VO$_2$/TiO$_2$ heterostructures at room temperature. Then, the single-crystalline TiO$_2$ NM is transferred onto the Si substrates without any deterioration of crystal quality (Fig. 1c, d).

Interestingly, transferred TiO$_2$ single-crystal NM serves as a template for the heterogeneous integration of single-crystal VO$_2$ films on Si substrate (Fig. 1e). As a result of the VO$_2$ film epitaxially grown on TiO$_2$ NM template, more than three orders of magnitude MIT can be integrated on the technologically influential, but more challenging, Si substrates by new epitaxial lift-off combination (see Fig. 1 for the process schematic). After the synthesis of an epitaxial TiO$_2$/VO$_2$ heterostructure on TiO$_2$ host substrate, the VO$_2$ sacrificial layer is selectively dissolved in dilute H$_2$O$_2$ to release the top TiO$_2$ film with the mechanical supporting layer. The freestanding NM from a host substrate essentially requires the preferential creation of bond breaking from the substrate.

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mapping around (112) reflecting as-grown TiO2 epitaxial films and TiO2 single-crystal NM released on supporting layer and transferred on Si substrates.

The high-resolution X-ray diffraction measurements show single-crystallinity with uniform out-of-plane orientation and no in-plane rotation in released and transferred TiO2 NM. EBSD maps of the as-grown TiO2 epitaxial films on VO2/TiO2 substrates (top) and transferred TiO2 NM on Si substrates (bottom), confirming the single-crystalline out-of-plane orientation. Photograph of 40-nm-thick TiO2 single-crystal NM released on mechanical support with the identical lateral dimension with TiO2 host substrates. OM image of transferred TiO2 NM on carbon TEM grid. AFM image of as-grown TiO2 films and transferred TiO2 NM, which confirms a uniform and flat surface without surface cracks or residues.

**Results**

**Synthesis of freestanding single-crystalline TiO2 nanomembranes.** Prior to release and transfer of TiO2 NM, TiO2 (10–70 nm)/VO2 (~17 nm) heterostructures were epitaxially grown on (001)-oriented TiO2 substrates by pulsed laser deposition (PLD) (Fig. 1a). Symmetrical 2θ–ω scan using synchrotron x-ray scattering on TiO2/VO2/TiO2 detected two (002) Bragg reflections, one from the rutile TiO2 (2θ = 49.54°) film and substrate, and one from VO2 film (2θ = 51.75°) (black line in Fig. 2a)27. Due to the close resemblance in crystal structure and small in-plane lattice mismatch of (001)R-VO2 and (001)-TiO2 (fα ≈ 0.86% along a- and b-axis), TiO2 films are fully strained by biaxial tensile strain; all heterostructures maintain identical in-plane lattice constant (left figure of Fig. 2b). Thus, the thickness of VO2 (~17 nm) was determined to create unstrained and defect-free TiO2 epitaxial films regardless of film thickness27,28.

Then, rigid support layer (e.g., PDMS) was coated on the heterostructure before release to mechanically stabilize the TiO2 NM and to facilitate the subsequent transfer of the released NM10–12,25. By simply immersing these TiO2/VO2/TiO2 heterostructures into the dilute (10%) hydrogen peroxide (H2O2) solution at room temperature (Fig. 1b), a few millimeter-scale TiO2 films were successfully released from their substrates by fully dissolving VO2 sacrificial layers (i.e., denoted as released TiO2 NM), allowing the growth substrate to be removed. The released single-crystal NM was transferred on any arbitrary substrate (i.e., denoted as transferred TiO2 NM), including on SiO2-coated (~80 nm) Si (100) substrates (Fig. 1c). The transferred NM was then heated at 60 °C to form stronger adhesion with substrates and the support layer was slowly detached (Fig. 1d).

Interestingly, the VO2 sacrificial layer was dissolved selectively and rapidly in the dilute H2O2 solution with mild pH (~5.3) (Fig. 1b). The combination of the VO2 sacrificial layer and H2O2 etchant for single-crystal rutile oxide NM in terms of release rate is as effective as that of a Sr3Al2O6 sacrificial layer and H2O for a single-crystal perovskite oxide NM11. The high etching capability of H2O2 on VO2 was confirmed by direct comparison with that of an HNO3 solution with the same concentration as a well-established VO2 etchant with a strong acid (pH ~2)24 (Supplementary Fig. 1): While the residue of VO2 films remained even after 64 s after VO2 films were immersed into strong acid HNO3 solution, the H2O2 solution completely removed VO2 films that were free of any residue on the surface of the TiO2 substrate within 4 s. Furthermore, repeating H2O2 etching preserves the atomically flat surface topography, implying substrate reusability for the production of TiO2 NM (Supplementary Fig. 2). VO2 films...
could be spontaneously oxidized by \( \text{H}_2\text{O}_2 \) and transformed to \( \text{V}_2\text{O}_5 \) and/or water-soluble \( \text{V}_2\text{O}_3 \cdot n\text{H}_2\text{O}(s) \) gels with a layered van der Waals (vdW) structure along the \( c \)-axis; these layered crystals with weak bonding are exfoliated and dispersed in the solution (Supplementary Fig. 3a, b). Since unreacted TiO\(_2\) epitaxial layers cover whole surfaces of VO\(_2\) sacrificial layers during the release process, the release of epitaxial TiO\(_2\) NM by oxidation and dissolution of VO\(_2\) sacrificial layers begins from the edge of the substrate (i.e., side etching); the dissolution (or release) time increases with the lateral size of the TiO\(_2\) substrate (Supplementary Fig. 4). As a result of effective dissolution of the VO\(_2\) sacrificial layer by \( \text{H}_2\text{O}_2 \), the quality and alignment of epitaxial TiO\(_2\) layers are intact during the release and transfer process as observed in symmetric 20-\( \omega \) scans using synchrotron X-ray scattering (Fig. 2a). While the (002)\(_R\) peak from the VO\(_2\) sacrificial layer (\( 2\theta = 51.75^\circ \)) was clearly removed after the selective etching process (red line in Fig. 2a), the (002)\(_R\) peak from \( \sim 40\)-nm-thick (001) TiO\(_2\) single-crystal films with thickness oscillations was observed consistently at \( 2\theta = 49.54^\circ \) in released (red line in Fig. 2a) and transferred TiO\(_2\) NM on the Si substrate (blue line in Fig. 2a) and Supplementary Fig. 5 with Cu K\(_{\alpha}\) X-ray radiation). Moreover, the (002)\(_R\) peak from TiO\(_2\) NM simultaneously appeared with a (400) peak from the Si substrate (\( 2\theta = 54.32^\circ \)) in the transferred TiO\(_2\) NM (blue line in Fig. 2a), which represents that the \( c \)-axis of single-crystal TiO\(_2\) NM was aligned with the out-of-plane orientation of the Si substrate. Azimuthal X-ray diffraction (XRD) \( \phi \) scanning of (112)\(_R\) crystallographic plane showed identical fourfold symmetry of released and transferred TiO\(_2\) NMs with those of the single-crystal (001) TiO\(_2\) host substrate (Supplementary Fig. 6); this result showed in-plane single-crystallinity of NMs without any rotated domains. Additionally, an electron backscatter diffraction (EBSD) map confirmed (001) orientation of rutile crystals over a large area in both as-grown and transferred TiO\(_2\) layers (Fig. 2c).

To obtain more detailed information on the crystal structures of TiO\(_2\) NMs during the release and transfer process, both in-plane and out-of-plane lattice parameters were monitored using reciprocal space mapping (RSM) around the (112) reflection of as-grown, released, and transferred 70-nm-thick TiO\(_2\) layers (Fig. 2b). The RSM data clearly show sharp and intense (112) Bragg reflections and Kiessig fringes from the TiO\(_2\) layer and substrates, and from the VO\(_2\) sacrificial layers in as-grown heterostructures. Since 17-nm-thick VO\(_2\) sacrificial layers are coherently grown on the TiO\(_2\) substrates with identical \( H \) (i.e., in-plane reciprocal space unit), strain-free epitaxial TiO\(_2\) layers with various thickness (10–70 nm) are coherently grown on VO\(_2\)/TiO\(_2\) substrates (Fig. 2b and Supplementary Fig. 7b, c). After selective etching of the VO\(_2\) sacrificial layer, \( H \) and \( L \) in released and transferred TiO\(_2\) NM was identical with those in TiO\(_2\) substrates and films in as-grown heterostructures; these strain-free TiO\(_2\) layers with precisely controlled thickness are released and transferred onto a Si substrate without modification of the lattice parameters and crystallinity (Supplementary Fig. 7a).

Furthermore, surfaces of the released and transferred TiO\(_2\) NM are uniform and intact without any defective boundaries\(^{31}\). Figure 2d shows that the entire area of TiO\(_2\) films with lateral dimension of millimeter-scale and nanometer thickness was fully released from the VO\(_2\)/TiO\(_2\) substrates after this etching process. Optical microscope (OM) images of transferred TiO\(_2\) NM on the carbon TEM grid exhibit crack-free layers with natural wrinkles (Fig. 2e and Supplementary Fig. 8a). Both scanning electron microscope (SEM, Supplementary Fig. 8b) and atomic force microscope (AFM, Fig. 2f) images confirmed

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**Fig. 3 STEM analysis of freestanding single-crystal TiO\(_2\) nanomembrane (NM).**  
**a** HAADF-STEM, **b** ABF-STEM, and **c** SADP images from the plane-view observation on 20-nm-thick freestanding TiO\(_2\) NM. The white spots in HAADF-STEM, which are identical to Ti atoms, are consistent with cation sites of [001]\(_R\)-projected rutile structure. The atomic arrangement of ABF-STEM, visualization of oxygen atoms, was also identical to anion sites of rutile structure; the results indicate that atomic arrangement of freestanding TiO\(_2\) NM was identical to the single-crystal rutile structure without defective features. **d, e** are the cross-sectional ABF-STEM images of TiO\(_2\) NM, the quality of which is crystallographically high with perfect registry of Ti (orange color in e) and O (red color in e) atoms in rutile structure.
uniform and flat surface of both released and transferred TiO$_2$ NM without surface cracks or residues: the arithmetic average surface roughness of transferred TiO$_2$ NM (R$_a = 0.06$ nm) was comparable to that of originally grown TiO$_2$ films on VO$_2$/TiO$_2$ substrates (R$_a = 0.04$ nm), representing residue-free VO$_2$ removal by H$_2$O$_2$ etching and subsequent surface cleaning (Fig. 2f and Supplementary Figs. 9, 10).

High-resolution scanning transmission electron microscopy (STEM) confirms the local atomic structure of freestanding single-crystal TiO$_2$ NM. First, the released TiO$_2$ NM was transferred onto a TEM grid for STEM observation (Fig. 2e and Supplementary Fig. 11); the high-angle annular dark-field (HAADF) and the annular bright-field (ABF) STEM were applied for the plane-view observation. The HAADF-STEM image shows a square pattern of four titanium atoms (orange, dotted square) without a lattice distortion or defects (Fig. 3a). More interestingly, the ABF-STEM image shows the contrast tails from the titanium atom with contribution by the oxygen atoms and the pattern exactly matched the atomic structure of the rutile TiO$_2$ with the [001] zone axis (Fig. 3b). The selected-area diffraction pattern (SADP) provided that the in-plane lattice parameters of TiO$_2$ NM were 0.46 nm (Fig. 3c), which confirms the freestanding TiO$_2$ film was perfectly transferred. After the TiO$_2$ NM (~60 nm) was transferred to the SiO$_2$/Si substrate, cross-sectional STEM observation was performed with the [100] zone axis to visualize the structural coherency of the freestanding oxide NM, as shown in Fig. 3d, e. The low magnification ABF-STEM image shows that the TiO$_2$ NM is free of defects even after its transfer process from the wide field of view (Fig. 3d); the high magnification ABF-STEM image again verifies the perfect registry of Ti (orange) and oxygen (red) atoms in the rutile structure (Fig. 3e).

Heterogeneous integration of single-crystalline VO$_2$ films on the TiO$_2$-NM-templated Si substrates. After transfer to the (SiO$_2$-coated) Si substrates, the single-crystalline TiO$_2$ NMs served as templates for the epitaxial growth of high-quality VO$_2$ thin films on Si substrates (Fig. 1e). As observed in symmetric 2θ – ω scans, the intense (002)$_R$ VO$_2$ peak appeared at ~2θ = 51.65° along with peaks related to the TiO$_2$ template (~2θ = 49.54°) and Si substrates (~2θ = 54.34°) for the VO$_2$ films on the TiO$_2$-templated Si substrates (red line in Fig. 4a), compared to the absence of related peaks for the VO$_2$ films directly grown on Si substrate (black line in Fig. 4a); this result reveals that lattice-matched single-crystal templates facilitate the formation of epitaxial VO$_2$ films on Si substrates. Single-crystallinity of VO$_2$ films on TiO$_2$/Si was again verified by identical fourfold symmetry with TiO$_2$ NM templates in asymmetric ϕ-scans of the (112)$_R$ plane (Fig. 4b). While the out-of-plane strain state of the TiO$_2$ NM did not change after the growth of VO$_2$ films, the out-of-plane lattice parameters of VO$_2$ films (2.838 Å) were reduced compared to those of bulk VO$_2$ (2.88 Å). Indeed, an RSM near the (112)$_R$ reflection of the TiO$_2$ NM confirms that the peaks from the VO$_2$ films and TiO$_2$ NM showed identical H (i.e., in-plane reciprocal space unit) (Fig. 4c), which indicates that a 10-nm-thick VO$_2$ film remains coherently strained to the TiO$_2$ NM along the in-plane direction.

Low magnification ABF- and high magnification HAADF-STEM images (Fig. 4d, e) confirm that the epitaxial growth of 10-nm-thick VO$_2$ on TiO$_2$ NM can realize heterogeneous integration of single-crystal VO$_2$ films on a Si substrate. In particular, VO$_2$ and TiO$_2$ are coherently matched and the interface can be visualized due to the slight contrast difference between VO$_2$ and TiO$_2$, as indicated by the arrow (Fig. 4e); the atomic resolution image implicates that the VO$_2$ layer is tightly constrained from the underlying TiO$_2$ NM, and thus

Fig. 4 Heterogeneous integration of rutile oxide epitaxial VO$_2$/TiO$_2$ heterostructures on Si substrates. a) Symmetric 2θ – ω scan, b) asymmetric ϕ scan, and c) reciprocal space mapping around (112) reflection of TiO$_2$ NM on Si substrates before (blue in a, b, and left in c) and after (red in a, b, and right in c) the growth of VO$_2$ films, implying single-crystallinity of coherently strained VO$_2$ films on TiO$_2$ NM/Si. d) The cross-sectional ABF-STEM images of the heterogeneous VO$_2$/TiO$_2$ NM on SiO$_2$/Si. The atomic-scale HAADF-STEM image at the area indicated by the yellow square in d is shown in e (zone axis: [001] in TiO$_2$).
the resistivity ratio were significantly improved in the VO$_2$ films with TiO$_2$ NM (i.e., 8.70 and 3.3 K for $\Delta H$ and $\Delta T_c$, respectively) compared to those without TiO$_2$ NM (i.e., 17.94 and 14.54 K for $\Delta H$ and $\Delta T_c$, respectively). The sharpened phase transition is attributed to the single-crystalline nature of the VO$_2$ films perfectly aligned with the underlying single-crystal TiO$_2$ NM templates. Moreover, the transferred single-crystal TiO$_2$ NM forms coherently tensile-strained VO$_2$ films; this epitaxial strain leads to a $T_{MI}$ shift close to room temperature in VO$_2$ films on TiO$_2$ NM/SiO$_2$/Si compared to relaxed VO$_2$ films on SiO$_2$/Si substrates$_{27,28,32}$. Along with steep MIT under temperature, these single-crystal VO$_2$ films on TiO$_2$ NM/Si show high endurance during thermal and electrical cycling. Both thermally induced MIT and electrically induced MIT ($T_{MI}/H_{MT} > 10^5$) were consistently observed without any drift during the multiple cycles of thermal switching (Supplementary Fig. 14) and electrical switching (Supplementary Fig. 15), respectively.

**Discussion**

It should be noted that the integration of VO$_2$ films with excellent electrical properties on a Si substrate has proved challenging due to fundamental limitations. A representative set of data of MIT properties from VO$_2$ thin films on Si (or oxide-coated Si or buffered Si) substrates was compiled to allow for a direct comparison with those from our films (Fig. 5c, Supplementary Table 1, and Supplementary Fig. 16). Despite previous attempts to directly grow VO$_2$ thin films on Si substrates using various deposition techniques, $\Delta\rho/\rho$ across the $T_{MI}$ deteriorated due to the formation of polycrystallinity of the films. Notably, a further reduction in $\Delta\rho/\rho$ was found to occur with decreasing film thickness, likely due to the formation of defective interfacial layers (e.g., by thermodynamic reaction of VO$_2$ with Si (or SiO$_2$)); the cation-to-anion stoichiometry was not maintained in the VO$_2$ films near the interface$_{33,34}$. If this compositional variation (i.e., off-stoichiometry) contains a significant fraction of the films, the resistivity ratio and transition sharpness will significantly degrade in the regime of an ultrathin thickness (<40 nm), as observed in our 10-nm-thick VO$_2$ films on SiO$_2$/Si and Al$_2$O$_3$-buffered Si (Supplementary Figs. 13, 16); steeper transition cannot be engineered simply by direct deposition of thin VO$_2$ films on Si substrates due to the existence of interfacial layers and the substantial density of defects.
However, the TiO2 template NM on Si substrates permits epitaxy with VO2 thin films due to its identical crystal structure (P4_2mm) and small lattice mismatch (\(\gamma \approx 0.86\%\)). The transferred NM could play a crucial role as a seed layer for epitaxy, and artificially allows the first demonstration on heterogeneous integration of single-crystalline VO2 on Si substrates, which are commonly employed in electronic devices. Furthermore, the TiO2 NM is likely to prevent subsequent reaction between VO2 and the Si substrate, and allows excellent control over the V-oxidation states without any extended defects.7,34 Thus, epitaxial growth of ultrathin VO2 films guided by transferred TiO2 NM enables integration of correlated oxides with unprecedented modulation of the resistivity ratio (\(\Delta \rho / \rho > 10^4\)) across the MIT in the regime of an ultrathin thickness (5–10 nm) on Si substrates (see red stars in Fig. 5c).

In summary, heterogeneous integration of a freestanding single-crystalline rutile oxide NM was achieved by exploiting selective oxidation and dissolution of isostructural sacrificial layers. Despite a mild pH condition under a dilute H2O2 solution at room temperature, VO2 sacrificial films are spontaneously oxidized by H2O2 and transformed to layered crystals, which in turn could be exfoliated and dispersed in solution to release and transfer the millimeter-scale TiO2 NM with controlled thickness on oxide-coated Si substrates. Owing to the nearly perfect single-crystallinity of the transferred rutile TiO2 NM, this lattice-matched single-crystal template permits heterogeneous integration of epitaxial VO2 films on Si substrates; exceptional MIT characteristics in terms of transition sharpness (\(\Delta T_\text{h} \sim 2.85\) K and \(\Delta T_\text{f} \sim 3.3\) K) and resistivity ratio (\(\Delta \rho / \rho > 10^4\)) were realized in ultrathin VO2 films integrated on Si substrates, benefiting from the superior quality of epitaxial oxide films.

Our strategy to release and transfer a freestanding epitaxial rutile oxide NM for a MIT will provide an unprecedented platform using emergent phenomena in epitaxial oxide heterostructures to be integrated with current state-of-the-art Si-based technology (e.g., integrated electronics6,36 and photonics13,35 on Si). For example, our epitaxial oxide NM with steep phase transition could deliver a hybrid optical modulator with a high extinction ratio, low loss, and high modulation speed integrated on Si waveguides13,35,36. Moreover, our approach for single-crystalline oxide NMs with high thermal stability are generally applicable for heterogeneous integration of high-quality oxide NM with any rutile crystal structures on Si substrates (e.g., epitaxial growth of metallic RuO2 single-crystalline NMs on transferred TiO2 NM/Si or direct transfer of metallic RuO2 single-crystal NMs on Si, Supplementary Figs. 17–20); our study enables us to extend the materials spectrum for freestanding single-crystalline rutile oxide NM by developing a new combination of sacrificial layer and etchant. It also offers a unique opportunity for new types of artificial heterostructures by stacking multi-functional oxide NMs with other 2D/3D single-crystalline NMs (e.g., III–V, exfoliated 2D layered materials, complex oxides10,17) or by controlling twisted angle between two misaligned sheets of oxide NMs (similar to twisted bilayer graphene heterostructure with atomic and electronic reconstruction)37,38 for novel interfacing physics and a new generation of emergent devices.

\section*{Methods}

\textbf{Epitaxial film growth.} The epitaxial VO2 thin films (~17 nm) were grown on (001) TiO2 single-crystal substrates, followed by the growth of TiO2 films (10–70 nm) by PLED. First, (001) TiO2 single-crystal substrates (Shinkosha CO. LTD.) with a lateral size of up to 5 mm × 5 mm were loaded into the PLED chamber, which was then evacuated to a base pressure of ~1 × 10⁻⁶ Torr. The rotating VO2 and TiO2 targets were then ablated by focusing a KrF excimer laser (Coherent Complex Pro 102 F, λ = 248 nm) with a fluence of 1 J/cm² and a repetition rate of 1 Hz. The growth of VO2 films was performed at fixed \(P_{\text{Ar}} = 15\) mTorr and \(T_\text{PLD} = 300\) °C, which were selected to induce a steep MIT near room temperature from coherently tensile-strained VO2 films. Subsequently, TiO2 films were grown on VO2 templates under \(P_{\text{Ar}} = 28\) mTorr and \(T_\text{PLD} = 300\) °C. After the growth of heterostructure, the samples were cooled to room temperature at a rate of 20 °C/min. The epitaxial VO2 film (5–10 nm) was grown on the transferred TiO2 NM/Si with an identical growth condition of that of VO2 sacrificial layers on the (001) TiO2 substrate.

\textbf{Release and transfer of freestanding TiO2 NMs.} To release the freestanding VO2 NM from the VO2/TiO2 substrates, the surface of the grown heterostructure was adhered onto a rigid supporting layer (e.g., polydimethylsiloxane, thermal release tape (Haeun Chemtec, RP70NS)). The structure was immersed in a dilute \(\text{H}_2\text{O}_2\) solution until the sacrificial VO2 layer was completely dissolved. To transfer the ultrathin TiO2 NM to other substrates, TiO2 NM was placed onto an oxide-coated silicon substrate and exposed to an appropriate temperature. Finally, the freestanding NM remained on the silicon substrate after peeling off the rigid supporting layer slowly. The structure was immersed in a dilute 10% \(\text{H}_2\text{O}_2\) solution (i.e., 30 ml of 35% \(\text{H}_2\text{O}_2\) + 150 ml of \(\text{H}_2\text{O}\)) at room temperature until the sacrificial VO2 layer was completely dissolved, with the freestanding NM left on the rigid supporting layer. After dissolving the VO2 layers in \(\text{H}_2\text{O}, \text{H}_2\text{O}_2\) residue on the released TiO2 surface was evaporated in a vacuum desiccator for 10 min. To transfer the released TiO2 NM to other substrates (such as thermally grown \(\text{SiO}_2\)-coated silicon), the TiO2 NM/rigid supporting layer was attached to a oxide-coated silicon substrate and heated to 60–80 °C for 10 min. Finally, the freestanding NM remained on the silicon substrate after peeling off the rigid supporting layer slowly.

\textbf{SEM, EBSD, and AFM measurements.} OM images were recorded using BX53M (Olympus, Tokyo, Japan) microscope, equipped with an objective MPlanFl N (Olympus) and i-solution IMT cam CCD camera. The SEM and EBSD measurements were performed using an XL30FEG and FEI Helios Nanolab 650 equipped with an EBSD detector, respectively. The EBSD pattern was acquired by an EDAX Hikari EBSD camera while the sample was tilted at 70° and scanned with an electron beam of 25 nA at 20 kV. The measured data were analyzed using TSL OIM AnalySIS7. The AFM images were obtained using a Veeco Dimension 3100 in tapping mode.

\textbf{X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).} High-resolution x-ray scattering was performed by using synchrotron radiation at the 3D XRS (\(\lambda = 0.12398\) nm, energy ~10 keV at Si (111)) beamline of Pohang Light Source II (PLS-II, Pohang, Republic of Korea), and using an in-house HRXRD (Bruker Discover 8 X-ray diffractometer) with Cu Kα radiation (\(\lambda = 0.15406\) nm). The detailed information on in-plane and out-of-plane lattice parameters and strain states of each NMs on Si, VO2 films and NM was obtained by using both symmetric 2θ-scan and asymmetric RSM around the (112) reflection. X-ray absorption spectroscopy (XAS) was performed using the 2 Å MS beamline at PLS-II. The total electron yield mode with an energy resolution of ~0.1 eV was used for measurement at a base pressure of 5 × 10⁻¹⁰ Torr in the analysis chamber by measuring the sample current (I₁) divided by the beam current (I₂) to remove the variation of the beam intensity.

\textbf{Scanning transmission electron microscopy (STEM).} Two sample types were prepared for plane-view STEM imaging of transferred TiO2 NM on a carbon TEM grid and cross-sectional STEM imaging of transferred TiO2 NM and VO2/TiO2 hetero-NM on SiO2/Si. For the plane-view observation, the TiO2 film was directly transferred onto the carbon TEM grid; TiO2/VO2/TiO2 epitaxial heterostructure was physically attached to the PDMS with the carbon TEM grid and immersed in a dilute \(\text{H}_2\text{O}_2\) solution. After selective oxidation and dissolution of the VO2 sacrificial layer, the single-crystal TiO2 NM was naturally released and attached to the carbon TEM grid (Supplementary Fig. 4). For the cross-sectional observation, the transferred TiO2 NM and VO2/TiO2 hetero-NM on SiO2/Si substrates were prepared by a focused ion beam (FIB) system (Helios G3, FEI), in which the samples were thinned by a Ga ion beam. The atomic structures were observed using a STEM (JEOL ARM 200 F, JEOL Ltd., Japan) with a fifth-order aberration corrector (ASCOR, CEOS GmbH, Heidelberg, Germany); the probe diameter and convergence angle of the beam were ~0.7 Å and ~27 mrad under an acceleration voltage of 200 kV, respectively. The collection semi-angles of the detectors for HAADF imaging were 54–210 mrad, and those for ABF imaging were 8–16 mrad to detect light elements (i.e., oxygen). The obtained STEM images were local difference filtered to reduce background noise (HREM Research Inc., Japan).

\textbf{Resistivity measurements.} The resistivity (\(\rho\)) was measured in the van der Pauw geometry during heating and cooling from 260 to 380 K by using a chamber probe station equipped with a Hall measurement system and a temperature control system. The resistivity change over the MIT (\(\Delta\rho / \rho\)) was defined as \(\Delta\rho / \rho = (\rho_{\text{TiO2}} - \rho_{\text{VO2}}) / \rho_{\text{TiO2}}\). The fitting of the derivative of log10 (\(\rho\)) as a function of temperature (K) was performed based on the Gaussian function. \(T_\text{h}\) and \(T_\text{f}\) were then defined at the peak position of the Gaussian and the transition width was calculated from the difference (\(\Delta T = T_\text{h} - T_\text{f}\)). The transition sharpness \(\Delta T_\text{h}\) and \(\Delta T_\text{f}\) was estimated from the full-width at half-maximum of the Gaussian peak.

\textbf{Data availability} All relevant data within the article are available from the corresponding authors on reasonable request.
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Author contributions

J.S., D.K.L., and Y.P. conceived the idea and designed the study with assistance from C.-B.E.; D.K.L. and Y.P. developed the fabrication process of freestanding nanomembranes, performed the growth of heterostructures, XRD, XAS, SEM, EBSD, AFM, and electrical transport measurement with assistance from J.P. and Y.K.; H.S., G.-Y.K., and S.-Y.C. characterized the nanomembranes by STEM; Y.K. assisted synchrotron spectroscopy measurement; J.S., D.K.L., Y.P., S.-C.Y., and H.S. wrote the manuscript and all authors commented on it; J.S. directed the overall research.

Competing interests

The authors declare the following competing financial interest(s): D.K.L., Y.P., H.S., S.-Y.C., and J.S. are co-inventors on a patent application based on the results of this work filed by Pohang University of Science and Technology.

Supplementary information

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