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Rolled-up single-layered vanadium oxide nanomembranes for microactuators with tunable active temperature

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Abstract  
Multilayer vanadium dioxide (VO\textsubscript{2}) actuators are a widespread concern as these micro/nano-actuators present a fast and efficient dynamic response when VO\textsubscript{2} occurs in metal–insulator transition (MIT) at 68 °C. By tuning the O\textsubscript{2} flow rate during oxide deposition and rolled-up nanotechnology, a microactuator based on a single-layered vanadium oxide nanomembrane with vertical component gradient is fabricated. Upward bending of the nanomembrane is driven by the release of the compressive strain gradient which is revealed through the difference in Raman shift of the vibration mode. Combining strain engineering, the initial curvature of microactuators is tuned in a wide range by the thickness of the nanomembranes. The actuation behavior from low curvature to high final curvature across the MIT is observed which depends on the nanomembrane thickness. Initial compressive strain distribution of the rolled-up nanomembrane decreases the MIT temperature simultaneously. Thus, taking advantage of the tunable MIT and reversible shape transformation, micro/nano-actuators with tunable triggering temperature, controllable initial curvature and large-displacement actuation are fabricated for curvature engineering in micromechanical systems.  

Keywords: microactuator, vanadium dioxide, rolled-up nanotechnology, metal–insulator transition  

(Some figures may appear in colour only in the online journal)

1. Introduction  
Microactuators, transforming external stimuli to mechanical motion, have a wide range of applications including biomimetic robots \cite{1}, artificial muscle \cite{2, 3}, and microelectromechanical systems \cite{4}. Fast response, large displacement, good flexibility, and low triggering threshold are most concerned in a microactuator. However, general microactuators are based on organic or organic/inorganic composite materials, which are difficult to meet these issues. For example, the response time of microactuators based on an ionic electroactive polymer or thermally active polymer is more than 0.1 s, and triggering threshold is over 1 kV or 200 °C that limited the range of applications \cite{5, 6}. Therefore, a material with low triggering temperature, below milliseconds of response time and easy to fabrication is desired to be designed for microactuators.  

Vanadium dioxide (VO\textsubscript{2}) is a strongly correlated electronic material with intriguing metal–insulator transition (MIT). The triggering temperature of VO\textsubscript{2} is 68 °C and response time can reach 10 ms. The phase transition of VO\textsubscript{2} generates 1%–2% compressive strain during transition
process from insulator phase to metal phase which can serve as microactuators [7] to be applied in micro/nano-electro-
mechanical systems [8], microrobots [9] and biomimetics [10, 11]. Recently, various microactuators have been inves-
tigated based on bilayer structures. These microactuators were generally constructed by depositing a structural layer on a
VO2 film, followed by an etching process to define the anchor and pattern [12]. The initial state of these microactuators was
altered by the deposited materials with tunable properties and internal strain [13]. Unfortunately, the active layer in these
microactuators can only be set as the bottom layer. Moreover, deposition of VO2 requires a high temperature [7–13], which
means few materials of underlayer materials with VO2 can be
chosen as strain layer for a VO2 microactuator. So the shrinking of the VO2 layer results in downward bending
during actuation or unfolding behavior to a bended micro-
actuator. These limitations hamper the potential of VO2-based
microactuators to be applied in a general situation, especially
in an on-chip system in which a downward bending is not
allowed. Moreover, the introduction of external materials will
cause unexpected side effects [8, 14–16].

Rolled-up nanotechnology, through which 3D micro-
structures are fabricated by strain engineering in 2D patterned
nanomembranes, have proved their capability among on-chip
opto-electronics [17, 18] and off-chip micromachines
[19, 20]. Benefiting from the compatibility and designability
in materials and structures, primary demonstrations on
microactuators constructed by rolled-up nanotechnology have
been demonstrated with stimuli-responsive materials [21, 22].
Here, we fabricated a single-layered vanadium oxide nano-
membrane consisting of VO2 and VO2 hierarchical compo-
ants by tuning the oxygen flow rate during deposition. The
hierarchical components generate an internal strain gradient,
leading to the rolling of the single-layered nanomembrane
after the etching of sacrificial underlayer. The diameter of the
curved nanomembrane can be manipulated by altering the
thickness, which provides capability in structure design of
microactuators. The actuation behavior in which the nano-
membrane rolled upwards into a tighter state was established
on the shrinking of upper VO2 component due to its MIT
triggered by heat. Furthermore, the active temperature is tuned
by the redistribution of compressive strain inside VO2 that the
temperature decreases with rising initial curvature. This work
proposed a VO2-based microactuator with a simple one-step
deposition process. This designable microactuator with tunable
active temperature would provide great potential in phase
transition-based electronics, photonics and micromechanics.

2. Experimental detail

2.1. Growth and characterization of vanadium oxide
nanomembranes
Firstly, SiO2 coated Si substrate was cleaned by ultrasonica-
tion in acetone, ethanol and deionized water for 5 min. After
cleaning, VO2 component was grown on SiO2/Si substrates
by direct-current magnetron sputtering at 300 °C. The growth
pressure, Ar/O2 gas flow, and deposition time were 10.41 mTorr,
55/45 sccm, and 4 min, respectively. Afterwards, the temperature
was increased to 500 °C to deposit VO2 component on VO2,
Ar/O2 gas flow is 60/40 sccm. The pressure is 11.18 mTorr, and
growth time is 30 min. The structure of nanomembrane was
characterized by x-ray diffraction (XRD). The angle of incidence
was fixed at 0.6°, and the measurement was taken using a 2θ
scan geometry. The nanomembrane was also characterized by
micro-Raman scattering spectroscopy (Horiba JY HR-800) with
514 nm Ar laser and transmission electron microscopy (TEM,
FEI TECNAI G2 S-TWIN F20). Before the characterization by
TEM, the sample preparation was conducted via focused ion
beam (FIB, FEI Helios NanoLab 600). The electrical properties
of nanomembrane were measured using a Keithley 4200 semi-
conductor characterization system.

2.2. Fabrication of single-layered vanadium oxide
microactuators
In the first step, thinning of vanadium oxide nanomembrane
was realized by reactive ion etching (RIE) with 10 sccm CF4
flow rate, 30 sccm Ar flow rate, 300 mTorr chamber pressure,
and 100 W power. Vanadium oxide nanomembranes with
various thicknesses of 20, 25, and 35 nm, were fabricated by
altering the etching time from 15 to 7 s. Then, a layer of
photoresist (AZ-5214, Micro-chemicals GmbH, Germany)
with about 1 μm thickness was spin-coated and etching
windows were patterned by photolithography. Thirdly,
exposed part of the sample was etched by RIE for 30 s in
same condition as described above. After that, patterned
nanomembrane was released from the substrate by selectively
etching SiO2 sacrificial layer using 40% HF (hydrofluoric
acid) solution at room temperature. Finally, critical point
drying (CPD030 Critical Point Dryer from Bal-Tec AG) was
applied to dry the rolled-up single-layered vanadium oxide
microactuators without structural collapse.

2.3. Characterization of single-layered vanadium oxide
microactuators
The morphological properties of single-layered vanadium
oxide microactuators were characterized via scanning electron
microscopy (SEM, JEOL JSM-6701F). Additionally, micro-
Raman scattering spectroscopy (Horiba JY HR-800) with
514 nm Ar laser was utilized to analyze the strain distribution
in microactuators with different initial diameters. Eventually,
the actuation ability of the microactuators was triggered by
heating and cooling, and recorded by an optical microscopy
with CCD camera.

3. Results and discussion
The TEM image in figure 1(a) presents the hierarchical
components consisting of VO2 and VO2 in the single-layered
vanadium oxide nanomembrane. There is a clear boundary
Figure 1. Characteristics and MIT of single-layered vanadium oxide nanomembrane with hierarchical components. (a) TEM image from the cross section of vanadium oxide nanomembrane and corresponding elemental mapping of silicon, oxygen and vanadium, respectively. (b) High-resolution TEM image of the VO₂ component in the nanomembrane. (c) X-ray diffraction pattern of the VO₂ component. (d) Raman spectrum of VO₂ component. (e) Temperature-dependent resistance of the VO₂ component with MIT. The inset is corresponding differential resistance related to temperature. (f) Raman spectrum of vanadium oxide nanomembrane evolving with temperature.
between these two components, where textured polycrystalline VO2 with 160 nm is shown in upper part and amorphous VO2 with 10 nm is shown in lower part. The elemental compositions of Si, O and V were evidenced by the energy-dispersive x-ray elemental mapping as shown in right panels of figure 1(a). It is clearly observed that, compared to the VO2 component, the VO2 component grown by magnetron sputtering with higher oxygen flow rate contains a higher ratio of oxygen. High crystal quality of VO2 part was observed in high-resolution TEM image as shown in figure 1(b) and the lattice spacing of 0.623 nm is corresponding to the (100) plane. XRD pattern of polycrystalline VO2 is shown in figure 1(c). Two peaks near 27.98° and 55.65° are attributed to (011) and (220) planes of VO2, respectively. In figure 1(d), Raman spectrum taken with 514 nm laser excitation displays a set of peaks ranging from 137 to 612 cm\(^{-1}\), confirming the existence of standard monoclinic insulating phase of VO2. Here, the A\(_2\) and B\(_2\) are two Raman modes which are Raman vibrations in the low-temperature M phase of VO2 [23]. Besides, two low-frequency phonons \(\omega_{V1} (189.0 \text{ cm}^{-1})\) and \(\omega_{V2} (218.9 \text{ cm}^{-1})\) correspond to V–V lattice motion, and other Raman peaks are attributed to V–O vibration modes [24, 25]. To test the MIT of the upper VO2 component in the single-layered vanadium oxide nanomembrane, electrical resistance related to temperature was measured in figure 1(e). A dramatic decrease in resistance with increasing temperature was obtained, elucidating successful MIT through the nanomembrane. A derivative analysis on resistance was applied as shown in the inset of figure 1(e) to define the MIT temperature and transition slope temperature, that is, the center of the peak is the MIT temperature and the full width at half maximum is the transition slope temperature. Hence, MIT temperature and transition slope temperature are 68.76 °C and 6.83 °C, respectively. The MIT was further clarified through Raman spectrum as present in figure 1(f). All modes of M phase decrease with increasing temperature. When the temperature rises to the phase transition point, all Raman peaks of VO2 disappear owing to the complete transformation of M phase into metallic R phase. Phase transition temperature obtained by Raman is in agreement with the one obtained by electrical resistance examination. These results indicate the successful fabrication of single-layered vanadium oxide nanomembrane with hierarchical components through controlling parameters in the process of magnetron sputtering. And MIT of this nanomembrane is established in the upper VO2 component of which the temperature was kept at 68 °C as is in initial VO2.

For the hierarchical component vanadium oxide nanomembrane, different oxygen ratio between VO2 and VO\(_x\) component generates strain gradient in the nanomembrane for rolling into microactuators with different diameters. Figure 2(a) shows the schematic of microfabrication process as aforementioned. Driven by strain gradient, free-standing vanadium oxide nanomembrane bent into a microtube as shown in figure 2(b). To construct a rolled-up microactuator rather than a microtube, the length of released vanadium oxide was decreased. Figure 2(c) shows the average curvature of single-layered vanadium oxide microactuators. The microactuators I, II and III are rolled-up from vanadium oxide nanomembrane of which the thickness is tuned as 20, 25 and 35 nm while the thickness of VO\(_x\) keeps 10 nm. It is observed that the curvature decreases with rising thickness. To quantitatively describe the curvature variation as a function of strain and nanomembrane thickness, we refer the linear strain theory model used for bilayer systems [26]. According to this theory model, we divide the nanomembrane into two regions. The VO\(_2\) component is a relaxed layer which is close to the interface of the deposited layer/sacrificial layer, as well as the upper VO\(_2\) region is a strained layer. We assume that the elastic coefficients are equal in the two regions. The curvature
K of rolled-up microstructure can be calculated by [26]

\[ K = \frac{6\varepsilon(1 + \nu) d_{strain} d_{relax}}{(d_{strain} + d_{relax})^3} \]  

where \( \varepsilon = 0.0174\% \) is the strain in VO\(_2\) component of unrolled nanomembrane calculated by Raman frequency shift in the figure 3(a) and the \( \nu \) is the Poisson ratio (0.3) [27]. VO\(_2\) component \( d_{relax} \) is kept in constant as 10 nm and the thickness of VO\(_2\) component \( d_{strain} \) ranges from 10 to 25 nm. The solid line of calculated curvature in figure 2(c) indicates that the model agrees well with the experimental results.

To clarify the strain distribution in rolled-up nanomembrane, figure 3(b) shows the Raman spectra for rolled-up microstructures with various curvature. As the laser illuminated the upper surface of single-layered vanadium oxide nanomembrane, the excited signal mainly generated from VO\(_2\) component. The peak position at 189 and 219 cm\(^{-1}\) is attributed to the low-frequency phonons (\( \omega_{V1} \) and \( \omega_{V2} \)) of V–V lattice motion, which is calculated by isotope substitution and density functional theory [28].

The \( \omega_{V1} \) and \( \omega_{V2} \) phonons, with more significant Raman modes shifts, possess higher sensitivity to strain variation than other phonons [29]. The Raman signal of low-frequency phonons (\( \omega_{V1} \) and \( \omega_{V2} \)) collected from microactuators shows associated intensity increase and a slight spectral shift comparing to the unrolled vanadium oxide nanomembrane. Simultaneously, Raman intensity is a positive correlation to the thickness of vanadium oxide nanomembrane in microactuators, and the intensity of the rolled-up nanomembrane is higher than the one of unrolled nanomembrane.

With increasing thickness of microactuators from I to III and unrolled nanomembrane, the \( \omega_{V1} \) phonon presents a redshift from 192.84 to 189.16 cm\(^{-1}\) and the redshift of \( \omega_{V2} \) phonon is from 221.56 to 219.05 cm\(^{-1}\). These shifts of \( \omega_{V1} \) and \( \omega_{V2} \) phonons caused by compressive strain can be determined by [30]

\[ \Delta \omega_{\text{alloy}} = \frac{1}{2\omega_0} (p + 2q) \cdot \varepsilon, \]  

where \( \varepsilon \) is the strain distribution in VO\(_2\), \( \omega_0 \) refers to original \( \omega_{V1} \) (189 cm\(^{-1}\)) and \( \omega_{V2} \) (218.96 cm\(^{-1}\)) of unstrained VO\(_2\). The \( p \) and \( q \) are linear interpolations between the value of V–V that are extrapolated from [29]. In our case, \( (p + 2q)\omega_{V1} \) is equal to 3.49 \times 10\(^5\) \pm 0.15 \times 10\(^5\) s\(^{-2}\) and \( (p + 2q)\omega_{V2} \) is equal to 2.49 \times 10\(^5\) \pm 0.18 \times 10\(^5\) s\(^{-2}\). The strain of microactuators I, II and III were calculated by shift of \( \omega_{V1} \) (\( \omega_{V2} \)) phonon as 0.42\% (0.45\%), 0.32\% (0.31\%), and 0.16\% (0.12\%), respectively.

As aforementioned, the phase transition of VO\(_2\) will generate 1%–2% compressive strain during the transition which supplies the possibility to make VO\(_2\) as a heat-driven microactuator. Figure 4(a) presents the actuating behavior of the microactuator II in a heating-cooling cycle. The dark part is the microactuator, whose area decreases with increasing temperature, reflecting an upward bending of microactuator. The actuation behavior from small to large final curvature owes to the phase transition of VO\(_2\), leading to additional compressive strain in upper part of microactuator. Then the system starts to cool to room temperature. VO\(_2\) suffers from an opposite transition so that the microactuator returns to initial curvature. Thus, the curvature increases in heating and reduces in cooling, opposite to reported microactuators in which VO\(_2\) serves as the bottom layer. The variation in curvature of microactuators I, II and III during heating and cooling are present in figure 4(b). As the initial curvature is different with the thickness of nanomembrane as discussed in figure 2(c), we normalized the initial curvature of microactuator with different nanomembrane thickness to comfortably compare their curvature changes during the phase transition. The great change in curvature is attributed to the low bending stiffness of ultra-thin vanadium oxide nanomembrane, leading to lower requirement of actuating energy. Besides, it represents that with reduction of the vanadium oxide nanomembrane thickness, the range of curvature changes during actuation is wider, which owes to the decreasing bending stiffness in thinner nanomembrane. Here,
the capability of these microactuators can be described by volumetric work density which is given by $E \times \Delta \varepsilon^2/2$, where $E$ is the Young’s modulus of the VO$_2$ (∼140 GPa) and the $\Delta \varepsilon$ is calculated by equation (1). The maximum work density was estimated to reach 0.031 J cm$^{-3}$, which is much higher than human muscle (∼0.008 J cm$^{-3}$) [3]. Moreover, figure 4(c) shows differential analysis of curvature, reflecting that the temperature of phase transition moves to lower area in thinner microactuators. This variation is considered as a consequence of compressive strain redistribution in rolled-up microactuators. The phase transition temperature turns to 60.19 °C in microactuator I corresponding to 0.43% strain calculated by Raman spectrum. With different thickness of single-layered vanadium oxide microactuator, the MIT temperature can be tuned by different strain states.

4. Conclusion

In summary, we demonstrated a novel and simple approach to fabricate a tunable single-layered vanadium oxide microactuator based on rolled-up nanotechnology. Different layer components in the microactuator were deposited by controlling the oxygen flow rate in magnetron sputtering which generate a strain gradient to drive the nanomembrane bending upwards. The thickness controlled by further thinning process of the nanomembrane offers tunability in initial curvature of rolled-up nanomembrane. Benefiting from MIT in upper VO$_2$ component, the single-layered vanadium oxide nanomembrane suffers a great curvature increase into a tighter rolling state with heat stimulus. As the initial curvature decreases in the thinner nanomembrane, compressive strain redistribution in the VO$_2$ layer component increases leading to a lower MIT temperature, so that the actuation behavior can be controlled by the fabrication process. When the nanomembrane thickness decreases from 35 to 20 nm, the MIT temperature of the microactuator decreases from 68.71 °C to 60.19 °C with enhanced curvature change. Such microactuator driven by MIT requires a small quantity of actuation energy with a rapid response to heating or cooling. Such microactuators with controllable initial curvature, large-displacement actuation, controllable phase transition temperature and simple fabrication method could envision a wide range of micro- and nanoscale applications such as micromanipulation, optomechanical and electromechanical switch, microfluidic valving and pumping, drug delivery, heat regulation, and artificial muscle.

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