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Effect of Lanthanum Doping on Modulating Thermochromic Properties of VO$_2$ Thin Films

Ning Wang,$^{a}$ Nigel Tan Chew Shun,$^{a}$ Martial Duchamp,$^{b}$ Rafal E Dunin-Borkowski,$^{b}$ Zhong Li,$^c$ and Yi Long$^a$

Lanthanum (La) doped vanadium dioxide (VO$_2$) thin films were fabricated through a facile sol-gel technique. The La doping was found to be effective in reducing the phase transition temperature ($T_c$) of VO$_2$ below the 4 at.% doping level, with a reducing rate of -1.1 °C/at.%. In addition, below the 3 at.% La doping level, the band gap ($E_g$) decreased steadily with the increasing addition of La dopants. The 5 at.% La doping can enhance both integrated visible transmission ($T_{\text{vis}}$) and solar modulating ability ($\Delta T_{\text{sol}}$) simultaneously. The combination of $T_{\text{vis}}$=50.1% and $\Delta T_{\text{sol}}$=10.3% represents the best value for VO$_2$ continuous thin films.

Introduction

Vanadium dioxide (VO$_2$) is an interesting phase transition material at a critical temperature ($T_c$) around 68 °C, accompanied by a reversible metal to insulator transition (MIT). With regard to the pure VO$_2$, the insulating phase ($T_c$=68 °C) with a monoclinic $P 2_1/c$ crystal system shows strong transmission at the infrared (IR)/near infrared (NIR) range, while the metallic counterpart ($T_c$=68 °C) with a tetragonal $P 4_1/mmm$ crystal system exhibits depressed transmission across IR/NIR. The thermal modulating abilities in IR/NIR and electrical conductivity contrast across $T_c$ make VO$_2$ a promising candidate in thermochromic smart window and various smart sensor applications. Especially for the smart window, the IR/NIR light can be transmitted ($t<T_c$) or absorbed ($t>T_c$) automatically according to the out-door temperature, maintaining the comfortable indoor environment, which meets the nowadays energy-saving requirements.

However, the high $T_c$, low visible transmission ($T_{\text{vis}}$) and the low solar modulating abilities ($\Delta T_{\text{sol}}$) of pure VO$_2$ are three main drawbacks to be overcome. Moreover, there is always a trade-off between enhancing both $T_{\text{vis}}$ and $\Delta T_{\text{sol}}$ simultaneously. With respect to $T_c$, the extra strain energy$^{13-15}$ and doped by metal cations with large ion radii/large valence state$^{18-20}$ have been proved to be effective in reducing $T_c$. As for $T_{\text{vis}}$, the microroughness,$^{21}$ widening band gap ($E_g$)$^{17}$ and porous morphology$^{16-21}$ have been reported to be useful to increase $T_{\text{vis}}$. Lastly, the $\Delta T_{\text{sol}}$ is always believed to be correlated to the solid contents of VO$_2$ and/or surface plasmon resonance (SPR). In some special surface/interface conditions.

Rare earth (RE) elements are characterized with large ion radii and abundant valence electrons, which always contribute to the enhancement of physical properties as dopants.$^{24-26}$ Europium cation (Eu$^{3+}$) has been found to be effective in reducing $T_c$ of VO$_2$ with a rate of -6.5 °C/at.%, and a moderate combination of $T_{\text{vis}}$=54%, $\Delta T_{\text{sol}}$=6.7% was achieved.$^{11}$ Terbium cation (Tb$^{3+}$) was reported to be helpful in increasing the $T_{\text{vis}}$ from ~45% to ~79%, but only a relative low $T_c$ reducing rate (~1.5 °C/at.%) could be obtained.$^{27}$ As predicted by Chaos Sun et al. using the density functional theory (DFT) calculation,$^{28}$ the doping of lanthanum cation (La$^{3+}$) could cause the V-V distance change and great V-V dimer distortion, which may result in a decrease of $T_c$. In this paper, La$^{3+}$ cations were firstly doped into VO$_2$ lattice at different doping levels experimentally from 1 to 5 at.%. It was found that the $T_c$ of MIT could be reduced in a rate of -1.1 °C/at.% and a combination of $T_{\text{vis}}$=50%, $\Delta T_{\text{sol}}$=10.3% could be achieved at the 4 at.% doping level.

Experimental section

All of the chemicals V$_2$O$_5$ (99.6%, Alfa Aesar), La$_2$O$_3$ (99.9%, Alfa Aesar) and H$_2$O (30 wt.%, Sigma-Aldrich) were used as received without any further purification.

Precursor preparation. 182 mg V$_2$O$_5$ and weighed La$_2$O$_3$ powder were added into 5 mL hot H$_2$O (30 wt., 90 °C) solution under vigorous stirring. After a violent evaporation and cooling down to room temperature, another 15 mL H$_2$O (30 wt.%) was added into the suspension, and a clear brown liquid color precursor solution was obtained after stirring for 4 minutes. Then the precursor was moved to do the dip coating at once. It should be noted that the reaction should be done in a 300 mL beaker due to the strong heat release during the reaction between V$_2$O$_5$ and hot H$_2$O.

VO$_2$ thin film fabrication. A fused silica substrate with the dimension 15×15×0.5 mm$^3$ was dipped into the precursor solution at a rate 50 mm/min. After immersing for 20 seconds, the substrate was lifted up vertically at a withdrawing rate 200 mm/min. After drying in air, a brown thin film with the thickness ~60 nm/side was got on the substrate. Then the thin film was moved into a tube furnace and annealed at 550 °C for 2h in an Ar flow (200 mL/min).

Characterization. The phase of the products was characterized with a Shimadzu XRD-6000 X-ray diffractometer (Cu-Ka, $\lambda = 0.15406$ nm) using a voltage of 40 kV and a current of 30 mA at an X-ray grazing angle of 1°. Their morphology and La doping level were determined using a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan) with an INCA EDX detector at an accelerating voltage of 5 kV and 20 kV, respectively. For conventional transmission electron microscopy (TEM) studies, i.e., using selected area electron diffraction (SAED), bright field (BF) imaging, an JEOL 2010 (JEOL Company, Japan) microscope was used at an accelerating voltage of 200 kV. Transmittance spectra in the range 250-2500 nm were measured using a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) equipped with a Linkam PE120 system Peltier heating & cooling stage. The integrated visible transmittance ($T_{\text{vis}}$) 380-780 nm and solar/IR transmittance ($T_{\text{sol}}$) 280-2500 nm; $R_{\text{sol}}$ 780-2500 nm were calculated based on the recorded %T spectra using the expression...
where \( T(\lambda) \) is the recorded film transmittance, \( \Phi_{\text{lum}} \) is the standard luminous efficiency function for the photopic vision of human eyes, and \( \Phi_{\text{sol}} \) is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon). The hysteresis loop of %T at a wavelength of 2000 nm was measured at temperatures ranging from 20 to 100 °C. In order to attain the phase transition temperature \( \tau_c \), the temperature-dependent heating and cooling %T(\tau) data were fitted using a sigmoidal function of the form:

\[
%T(\tau) = \frac{A_2 + (A_1 - A_2) / [1 + \exp(\tau - \tau_c)/B]}{2}
\]

where \( \tau \) is the temperature in °C and \( A_1, A_2, \tau_c \), and \( B \) are fitting parameters. Two phase transition temperatures \( \tau_{c,h} \) and \( \tau_{c,c} \) were obtained in the heating and cooling cycles, respectively and the average phase transition temperature was defined as \( \tau_c = (\tau_{c,h} + \tau_{c,c})/2 \).

Results and discussion

Synthesis of La doped VO\(_2\) thin films

Figure 1a shows the XRD patterns of the pristine and La doped VO\(_2\) thin films. The bump around 20° (28) in the XRD patterns should be ascribed to the diffraction of the amorphous fused silica substrates. All of the thin films exhibit the characteristic (011) XRD peak of VO\(_2\) ( monoclinic, P 2\(_1\)/c, JCPDS #82-661) around 28° (28), and no other impurity phase can be found, indicating the successful synthesis of VO\(_2\) phase. Compared with the pristine VO\(_2\), the (011) peak position in the 5 at.% La doped sample is left-shifted by 0.2° from 28.0° to 27.8°, which indicates the lattice expansion arising from the replacement of V by La with relatively larger ionic radius (1.032 Å v.s. 0.58 Å) in accord with the DFT calculation.

The La doping levels were further confirmed by EDX analysis with a 10% derivation. As depicted in Figure 1b, the EDX results agree well with the expected doping levels.

Fig. 1 (a) XRD patterns of the pristine and La doped (1-5 at.%) VO\(_2\) thin films. (b) La doping levels determined by EDX characterization with a 10% derivation.

Figure 2 shows the morphology evolution of the pristine and La doped VO\(_2\) thin films tested using FESEM. All of the samples show nanograin packed morphology, and the average grain size for the 0-5 at.% La doped samples is 61, 72, 84, 79, 62 and 73 nm, respectively, which shows that the La doping gives rise to a slight increase of the grain size. The roughness and thickness of the thin films have been detected using AFM under tapping mode, which have been tabulated in Table 1. The thickness of the La-doped samples shows a derivation compared to the pristine VO\(_2\) thin film by ~14 nm, while the roughness exhibits a slight increase by 1.1-5.6 nm. The TEM characterization of the 3 at.% La doped sample has been shown in Figure 3. As shown in Figure 3a-b, the bright-field TEM images reveal that the average grain size of the sample is ~80 nm, consistent with the SEM result (Figure 2). The SAED as shown in Figure 3c exhibits diffraction rings that can be indexed by (011), (200), (021) and (022) faces of VO\(_2\), which indicates the polycrystalline nature of the La doped VO\(_2\) thin film. The doping of La was further investigated through STEM. As shown in Figure 3d, the atom replacement of V by La could be clearly observed in the high resolution STEM image, where the La atoms with larger atomic number are brighter than the V atoms, arising from their different contributions to the elastic scattering signals collected by the detector. In addition, the STEM-EDX elemental mapping (Figure 3f) related to the view of HAADF (high angle annular dark field) shows that the La atoms are incorporated in the VO\(_2\) lattice as the distribution of La signal matches the lattice plane arrangement.
Fig. 2 FESEM images for the pristine (a) and La doped (1-5 at.%, b-f) VO₂ thin films. The scale bar in the images is 500 nm.
Fig. 3 TEM (a) and the enlarged TEM image (b) of the 3 at.% La doped VO$_2$ grains. (c) SAED pattern of the polycrystalline 3 at.% La doped VO$_2$ grains. (d) STEM image of the 3 at.% La doped VO$_2$ grain. (e) HAADF image of the doped sample. (f) The La element mapping related to (e).

Thermochromic properties

Figure 4a shows the transmittance (%T) spectra (250<λ<2500 nm) of the samples at the temperature 20 and 90 °C, respectively. Upon heating from 20 to 90 °C, a large %T contrast in the IR range could be observed for all of the samples, which should be ascribed to the MIT. The integrated $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$ were tabulated in Table 1 and Figure 4b shows the doping level dependent average $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$. It can be observed that the best combination of $T_{\text{lum}}=50.1\%$, $\Delta T_{\text{sol}}=10.3\%$ was achieved at the La doping level 4 at.%, which represents the best value for RE-doped VO$_2$ thin films, and is comparable to other doping cases without RE. It is of interest that both of average $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$ at the La doping level 5 at.% are higher than that of pristine VO$_2$ (69.2 %, 9.0 % v.s. 64.8%, 7.3 %), which should be due to a surface plasmon resonance peak around 1250 nm arising from the La doping. The %T hysteresis loop was recorded at the wavelength 2000 nm in a temperature range 20-100 °C. As shown in Figure 4c, after doping with La, the MIT tends to move toward lower temperature until the doping level of 4 at.%, which is similar to the case of Eu doping. Plots of doping level dependent $\tau_c$ were shown in Figure 4d, and a $\tau_c$ reducing rate of 1.1 °C/at.% could be attained below the doping level of 4 at.%. This is the first experiment to prove the efficiency of La doping in reducing $\tau_c$ as indicated in simulation work using DFT calculation. With respect to the $\tau_c$ reduction mechanism, besides the lattice distortion from the substitution of large La atoms calculated by DFT, the increase of hole carrier density ($n^+$) from $V_{\text{5+}}^+$ propagating caused by La doping ($V_{\text{4+}}^{\text{La}}V_{\text{4+}}^{\text{La}}V_{\text{5+}}^{\text{La}}O_2$) should also contribute to the adjustment of $\tau_c$. The competition between these two mechanisms should be the reason why $\tau_c$ starts to increase at higher La doping level.
Fig. 4 (a) UV-Vis-NIR spectra of the pristine and La doped (1-5 at.%) VO$_2$ thin films under the temperature 20 and 90 °C. (b) Average $T_{lum}$ and the $\Delta T_{sol}$ of the VO$_2$ thin films with different La doping levels. (c) %T hysteresis loop of the pristine and La doped (1-5 at.%) VO$_2$ thin films. (d) Plots of $\tau_c$ v.s. La doping level.

As listed in Table 2, compared to other two reported rare earth dopants Eu$^{3+}$ and Tb$^{3+}$, the La$^{3+}$ cation has the largest ionic radius. The average $T_{lum}$ of the RE-doped VO$_2$ thin films decrease with the ascending ionic radius of dopants and this is consistent with the fact that larger ions result in greater electronic polarization and slower velocity of light, leading to a larger refractive index. From Tb$^{3+}$ to Eu$^{3+}$ dopant, the ionic radius increases from 0.92 to 0.95 Å and the $\tau_c$ reducing rate is increased from 1.5 to 6.5 °C/at% which should be due to the larger lattice distortion. However, the largest size La$^{3+}$ doping shows the lowest $\tau_c$ reducing rate and the reason remains unknown, but some dot defects in the form of La insertion in the seriously distorted lattice may be partially attributed to this phenomenon. In addition, compared to the previous reported W-/Mg-doped VO$_2$ continuous thin films (Table 2), the La-doped thin film shows the best combination of $T_{lum}$ (50.1%) and $\Delta T_{sol}$ (10.3%).

Figure 5a shows the %A and %R spectra of the pristine and La doped VO$_2$ thin films. It can be found that the %A and %R could be changed by the La doping, where the 5 at.% and 4 at.% La doped samples exhibit the lowest and highest %A / %R, resulting in their highest and lowest %T, respectively. In order to further investigate the La doping effects on the optical properties, the direct bandgap ($E_g$) of the VO$_2$ thin films was calculated by fitting the linear part of $(\alpha \nu \omega)^2$ v.s. $E$ curves (Figure 5b) based on the equation $(\alpha \nu \omega)^2 = A(\nu \omega - E_g)$, where $\alpha$ is the absorption coefficient ($\alpha d = \ln(T/1-R)$), $A$ is a constant and $\nu \omega$ is the photon energy. As depicted in the inset of Figure 5b, the $E_g$ of the VO$_2$ thin films is gradually declined upon doping with La and the lowest value 2.42 eV is got at the doping level of 3 at.%, then it returns back with further doping. The decrease of $E_g$ below the doping level 3 at.% is similar to the case under tungsten (W) doping arising from the larger ionic radius, and the following $E_g$ widening should be due to the competition between the effect of large ionic radius and $h^+$ carrier density. Since the change of band gap is of electronic nature, the $E_g$ narrowing of La doped VO$_2$ thin films below 3 at.% doping should be also related to the change of band structure resulted from the La doping in the lattice.
Fig. 5 (a) %A and %R spectra of the pristine and La doped (1-5 at.%) VO$_2$ thin films at room temperature. (b) Curve of $(\alpha \omega \nu)^2$ v.s. E and the band gap $E_g$ (inset) under different La doping levels.

<table>
<thead>
<tr>
<th>Doping level/at.%</th>
<th>Thickness/nm</th>
<th>$R_a$/nm</th>
<th>$T_{lum}(20\degree C/90\degree C)/%$</th>
<th>$\Delta T_{sol}/%$</th>
<th>$\tau_c$(heating/cooling)/°C</th>
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<tr>
<td>0</td>
<td>74</td>
<td>3.0</td>
<td>64.8/64.8</td>
<td>7.3</td>
<td>79.9/57.1</td>
</tr>
<tr>
<td>1</td>
<td>83</td>
<td>4.4</td>
<td>61.1/61.3</td>
<td>9.1</td>
<td>76.1/52.4</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>8.6</td>
<td>67.5/67.7</td>
<td>6.2</td>
<td>79.6/54.2</td>
</tr>
<tr>
<td>3</td>
<td>72</td>
<td>4.4</td>
<td>55.8/56.6</td>
<td>8.4</td>
<td>76.2/54.9</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>4.1</td>
<td>49.9/50.4</td>
<td>10.3</td>
<td>75.9/49.2</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>5.5</td>
<td>69.5/68.9</td>
<td>9.0</td>
<td>80.2/55.2</td>
</tr>
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$^a$ $R_a$ is the average roughness; $^b$ $\Delta T_{sol} = T_{sol}(20\degree C) - T_{sol}(90\degree C)$.

Table 2. Doping effects on the thermochromic performance of VO$_2$ continuous films.

<table>
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<tr>
<th>RE doping</th>
<th>Ionic Radius/Å</th>
<th>Doping /at.%</th>
<th>Ave. $T_{lum}/%$</th>
<th>$\Delta T_{sol}/%$</th>
<th>$\tau_c$/d at.%</th>
<th>Ref.</th>
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<tr>
<td>Eu$^{3+}$</td>
<td>0.95</td>
<td>4</td>
<td>54</td>
<td>6.7</td>
<td>-6.5</td>
<td>13</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>0.92</td>
<td>4</td>
<td>65.9</td>
<td>4.6</td>
<td>-1.5</td>
<td>27</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>1.03</td>
<td>4</td>
<td>50.1</td>
<td>10.3</td>
<td>-1.1</td>
<td>This work</td>
</tr>
<tr>
<td>Other dopings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W$^{6+}$</td>
<td>0.6</td>
<td>2</td>
<td>45.1</td>
<td>6.9</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>0.605</td>
<td>1</td>
<td>40</td>
<td>4.6</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.72</td>
<td>5</td>
<td>82.1</td>
<td>4.8</td>
<td>1.4</td>
<td>10</td>
</tr>
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</table>

Notes: The thickness, roughness and grain size of the RE-doped VO$_2$ thin films are at the same level.
Conclusions
In summary, a series of La doped VO$_2$ thin films were prepared through a facile sol-gel method, and the thin films exhibited high visible transmission and large solar modulating abilities. Especially, the 4 at.% La doped sample shows the best combination of $T_{\text{sum}}=94.1\%$ and $\Delta T_{\text{sol}}=10.3\%$ compared with other reported VO$_2$ continuous thin films. Compared with pristine VO$_2$, 5 at.% La doped sample can increase $T_{\text{sum}}$ and $\Delta T_{\text{sol}}$ simultaneously. La doping was firstly proved to be able to reduce the $\tau_c$ of MIT in experiment which is consistent with the simulation work, and it followed a reducing rate of -1.1°C/at.% below the doping level of 4 at.%. A narrowing down of band gap was observed below the doping level of 3 at.%, which should be ascribed to the change of band structure caused by the doping in VO$_2$ lattice with large La atoms. This investigation of La doping effects on thermochromic properties of VO$_2$ thin films should be useful for other element doping researches with large ionic radius and low valence state.

Acknowledgements
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Notes and references