

Synthesis and optical properties of V₂O₅ nanorods

Yuquan Wang, Zhengcao Li, Xing Sheng, and Zhengjun Zhang

Citation: *J. Chem. Phys.* **126**, 164701 (2007); doi: 10.1063/1.2722746

View online: <http://dx.doi.org/10.1063/1.2722746>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v126/i16>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

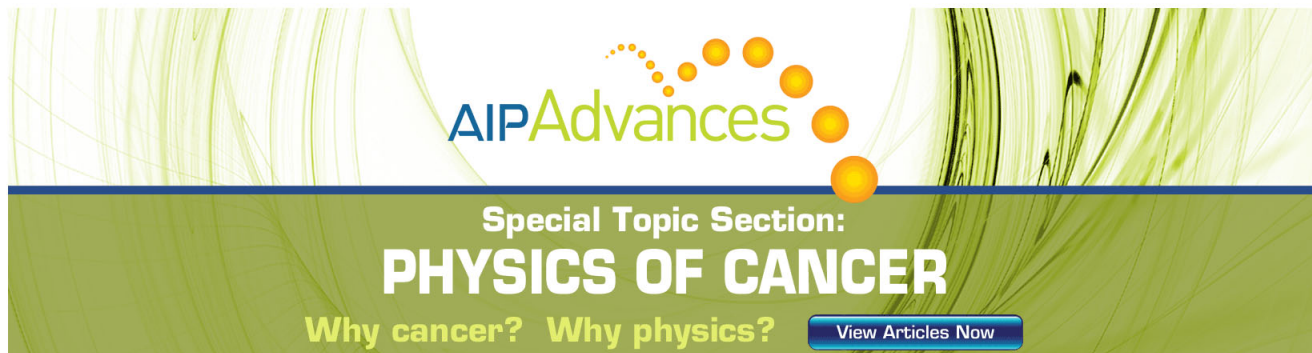
Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Synthesis and optical properties of V_2O_5 nanorods

Yuquan Wang, Zhengcao Li, Xing Sheng, and Zhengjun Zhang^{a)}

Advanced Materials Laboratory, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

(Received 4 December 2006; accepted 13 March 2007; published online 23 April 2007)

A two-step method was proposed in synthesizing V_2O_5 nanorods on planar substrates, i.e., depositing a V_2O_3 thin film at ~ 220 °C (by heating a pure sheet of vanadium in a rough vacuum) and then heating it in air at ~ 400 °C. The V_2O_5 nanorods produced by this technique are single crystalline and could emit intense visible light at room temperature, possibly due to some defects such as oxygen vacancies which got involved during growth. This study provides a simple and low-substrate-temperature route in fabricating V_2O_5 nanorods on planar substrates, which might be also applicable to other metal oxides. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2722746]

Vanadium oxides have attracted tremendous interest due to their excellent properties and applications in a wide range of fields.^{1,2} For example, vanadium pentoxide (V_2O_5) exhibits properties such as chemical sensing, photochromism, and catalysis³⁻⁵ and is a candidate material for applications in electronic information displays, electrochromic devices, optical-electrical switch and color memory devices, etc.^{2,6-8} Since materials having reduced dimensions may possess interesting properties that are very different from their bulk states, efforts have been directed recently to the synthesis of nanostructures of vanadium oxides and to the study of their structure-property relationships.⁹

There are several approaches available for synthesizing nanostructures of vanadium oxides.¹⁰⁻¹⁶ For example, Nesper and co-workers reported the synthesis of VO_x nanotubes by a sol-gel reaction of vanadium oxide trisopropoxide conducted in the presence of the structurally directing hexadecylamine and followed by hydrothermal treatment,^{13,14} Ajayan *et al.* reported the synthesis of V_2O_5 nanofibers by heating a mixture of carbon nanotubes (as template) and V_2O_5 powder in air at ~ 750 °C,¹⁵ and Takahashi *et al.* reported that single crystal V_2O_5 nanorod arrays could be synthesized inside polycarbonate templates by sol electrophoretic deposition.¹⁶

Here, we report a thermal oxidation method to form V_2O_5 nanorods at relatively low substrate temperatures. By heating in air a V_2O_3 thin film deposited on silicon substrates to ~ 400 °C, it was further oxidized into V_2O_5 and started to transform into nanorods. The photoluminescence (PL) property and its relation to the phase transformation of the film upon heating were also investigated.

The substrates used in the present study were Si (001) wafers. These were supersonically cleaned in acetone, alcohol, and de-ionized water baths and placed ~ 20 mm below a sheet of pure vanadium (99.99%, $\sim 5 \times 50 \times 0.7$ mm in size) connected to two copper electrodes in a vacuum chamber. The chamber was pumped to a vacuum level of $\sim 5 \times 10^{-2}$ Torr and then a voltage of ~ 2 V was applied to the

two electrodes, resulting in a current of ~ 50 A passing through the vanadium sheet. The vanadium sheet was heated up rapidly in the rough vacuum, leading to the deposition of vanadium oxides on the silicon substrate. After deposition for 5 min, the temperatures of the vanadium sheet and the silicon substrate were measured to be ~ 900 and ~ 220 °C, respectively. When the deposition was finished, the samples were heated at several temperatures for an hour in air. The growth morphology and structure of the deposits before and after heating was examined with scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and x-ray diffraction (XRD), respectively. Their PL spectra were measured with a Raman spectrometer at room temperature under the excitation of a 514 nm Ar^+ laser.

Figure 1(a) shows a typical SEM image of a thin film as deposited on a silicon substrate at a temperature of ~ 220 °C. The structure of this as-deposited film, as we will see later, is V_2O_3 . The film had a thickness about $1 \mu\text{m}$ and

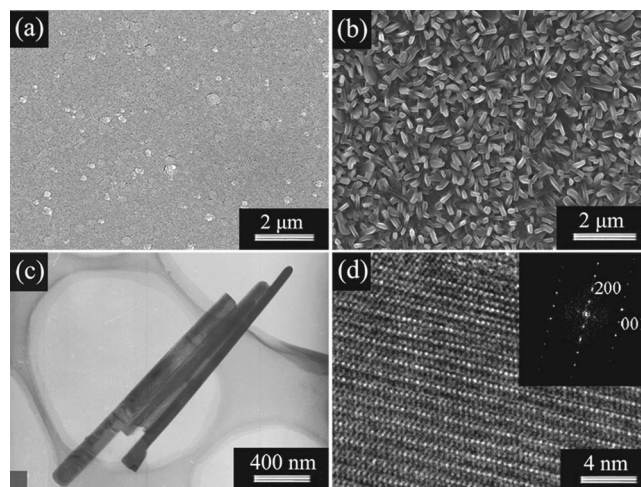


FIG. 1. SEM images of (a) the as-deposited V_2O_3 film and (b) V_2O_5 nanorods grown from the film after heating at 500 °C in air; (c) a low-magnification TEM image and (d) a HRTEM image of the V_2O_5 nanorods. Inset of (d) is the corresponding SAD pattern.

^{a)} Author to whom correspondence should be addressed. Electronic mail: zjzhang@tsinghua.edu.cn

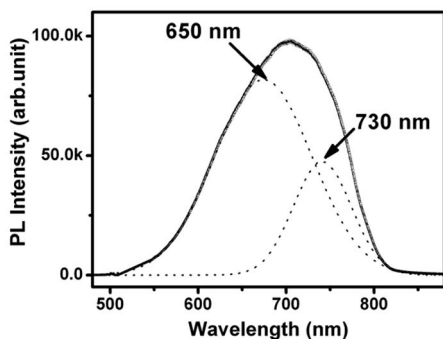


FIG. 2. A room-temperature PL spectrum of the sample after heating at 500 °C in air.

made up of tiny particles which would grow long with the increase of air-annealed temperatures. When the film was heated in air at ~ 500 °C for an hour, interestingly, all the particles finally transform into uniform nanorods. Figure 1(b) shows a typical SEM image of the growth morphology of the nanorods grown from the V_2O_3 thin film. The images were taken with a JOEL-4500 SEM working at 20 kV. Figure 1(c) is a low-magnification TEM image of the nanorods, taken with a JEOL-200CX TEM working at 200 kV. One sees that the nanorods are ~ 2 μm long and have a diameter of ~ 100 nm. Figure 1(d) shows a HRTEM image of a nanorod, the inset of which is the corresponding selected area diffraction (SAD) pattern. The HRTEM image and the SAD pattern were taken with a JEOL-2011 TEM working at 200 kV. It is seen that the nanorods grown from the V_2O_3 thin film (by heating in air at ~ 500 °C) are single crystalline V_2O_5 of an orthorhombic structure.^{17,18} This suggests that V_2O_5 nanorods can be fabricated on silicon substrates simply by heating a V_2O_3 thin film in air. This was also confirmed by XRD analysis shown later.

Figure 2 shows a typical PL spectrum of the sample after heating at ~ 500 °C in air. The spectrum was measured with a Renishaw Raman spectrometer (RM 1000) under the excitation of a 514 nm Ar^+ laser. One sees from the figure that the annealed sample could emit intense visible light at room temperature. As indicated by Fig. 2, the PL spectrum can be fitted by two Gaussian peaks centered at ~ 650 and ~ 730 nm, which corresponds to energies of ~ 1.82 and ~ 1.68 eV, respectively. Since the band gap of V_2O_5 is ~ 2.24 eV, the above visible light emissions, obviously, should not be caused by the band edge transition.¹⁹⁻²¹

To gain an understanding of the visible light emissions, we have investigated the phase transition of the V_2O_3 film upon heating in air, and measured the PL spectra. Figure 3 shows the XRD pattern of the V_2O_3 film upon heating at several temperatures. As indexed in the figure, we note that the as-deposited film is V_2O_3 . It is seen that when the film was heated to 300 °C, it was oxidized into VO_2 , and that when the film was heated to 350 °C, it was oxidized further into V_6O_{13} . SEM analysis (not shown) indicates that there is no observable change in the morphology of the film at this stage. When the film was heated to ~ 400 °C, it was oxidized finally into V_2O_5 and, interestingly, nanorods started to grow from the film. After heating at a higher temperature such as ~ 450 and 500 °C, the film was mostly transformed

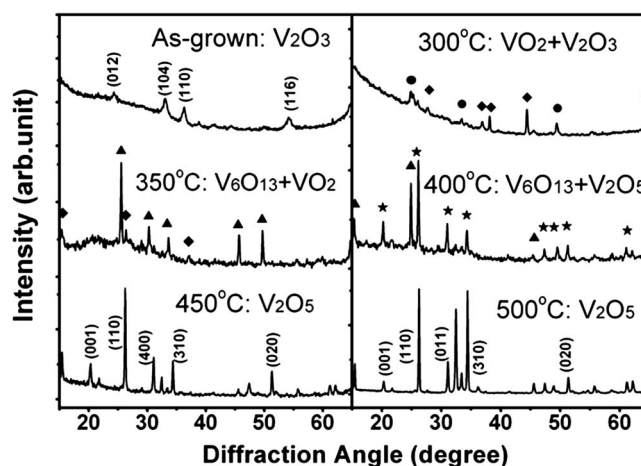


FIG. 3. XRD patterns of the V_2O_3 thin film on silicon substrates after heating at several temperatures in air. The solid circle (●), solid diamond (◆), solid triangle (▲), and solid star (★) stands for the V_2O_3 , VO_2 , V_6O_{13} , and V_2O_5 phases, respectively.

into V_2O_5 nanorods [see Fig. 1(b)]. It is thus clear that there is a critical temperature for the growth of V_2O_5 nanorods by heating a V_2O_3 film in air, i.e., ~ 400 °C.

Figures 4(a) and 4(b) show, respectively, PL spectra of the samples before and after V_2O_5 nanorod growth by heating the V_2O_3 film in air. One sees that the PL intensity from

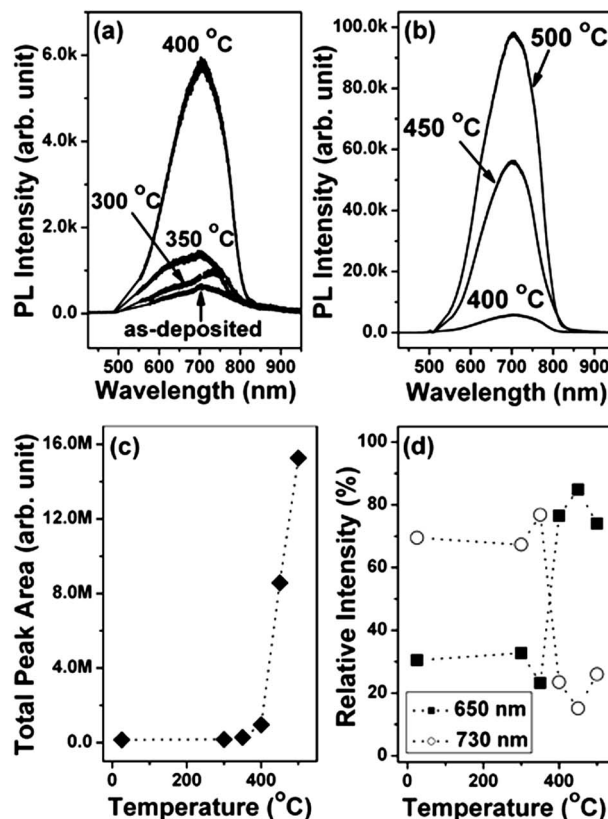


FIG. 4. The room-temperature PL spectra of the samples after heating in air: (a) before V_2O_5 growth and (b) after V_2O_5 growth; (c) the integrated area of the PL spectra and (d) the ratio of the two peaks centered at ~ 650 and 730 nm, respectively, as a function of the heating temperature.

the as-deposited sample and samples heated at ~ 300 and 350 °C is very weak, and that a drastic increase in the PL intensity was observed for the sample heated at ~ 400 °C. Looking at PL spectra of samples heated at ~ 400 , 450 , and 500 °C shown by Fig. 4(b), it is noticed that these spectra are similar in shape though their intensity is different. The three PL spectra can be well fitted by the two Gaussian peaks centered at ~ 650 and ~ 730 nm shown in Fig. 2. Figures 4(c) and 4(d) show, respectively, the total PL intensity and the relative intensity of the two peaks as a function of the heating temperature. It is seen clearly that there exists a critical point for observing intense PL, i.e., ~ 400 °C.

Comparing Figs. 3 and 4, we could find out the relationship between the visible light emission and the structure change of the V₂O₃ film upon heating in air. When the film was heated to < 400 °C in air, it was oxidized gradually into VO₂ and V₆O₁₃ with no obvious PL; when it was heated to ~ 400 °C or higher, the film was further oxidized into V₂O₅ and nanorods started to grow. From this point on, intense visible light emission was observed. This suggests that the above intense visible light emission was due to the formation of V₂O₅ through the oxidation of V₂O₃ upon heating in air. Since the energy of the above emission is much smaller than the band gap of V₂O₅, the visible light emission from V₂O₅ observed here might be due to some defects such as oxygen vacancies that are probably introduced during the oxidation at relatively low temperatures.²²⁻²⁵

In summary, we developed a method to synthesize single crystalline V₂O₅ nanorods on silicon substrates, i.e., simply heating in air a V₂O₃ thin film at a temperature of ~ 400 °C. The V₂O₅ formed by this method could emit intense visible light, which is probably due to some defects which got involved during the oxidation process. This study might provide a simple route in synthesizing and adjusting the properties of nanostructures of metal oxides.

The authors are grateful to the financial support from the National Natural Science Foundation (Grant No. 10675070) and the Ministry of Science and Technology of China, and

that in part by the National Center for Nanoscience and Technology of China.

- ¹C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials* (Elsevier, Amsterdam, 1995).
- ²B. B. Lakshmi, C. J. Patrissi, and C. R. Martin, *Chem. Mater.* **9**, 2544 (1997).
- ³A. Z. Moshfegh and A. Ignatiev, *Thin Solid Films* **198**, 253 (1991).
- ⁴A. Legrouri, T. Baird, and J. R. Fryer, *J. Catal.* **40**, 173 (1993).
- ⁵J. Schoiswohl, G. Kresse, S. Surnev, M. Sock, M. G. Ramsey, and F. P. Netzer, *Phys. Rev. Lett.* **92**, 206103 (2004).
- ⁶X. Liu, C. Taschner, A. Leonhardt, M. H. Rummeli, T. Pichler, T. Gemming, B. Buchner, and M. Knupfer, *Phys. Rev. B* **72**, 115407 (2005).
- ⁷A. Talledo and C. G. Granqvist, *J. Appl. Phys.* **77**, 4655 (1995).
- ⁸V. Petkov, P. Y. Zavalij, S. Lutta, M. S. Whittingham, V. Parvanov, and S. Shastri, *Phys. Rev. B* **69**, 085410 (2004).
- ⁹P. Viswanathamurthi, N. Bhattarai, H. Y. Kim, and D. R. Lee, *Scr. Mater.* **49**, 577 (2003).
- ¹⁰S. Pavasupree, Y. Suzuki, A. Kitiyanan, S. Pivsa-Art, and S. Yoshikawa, *J. Solid State Chem.* **178**, 2152 (2005).
- ¹¹M. Niederberger, M. H. Bard, and G. D. Stucky, *J. Am. Chem. Soc.* **124**, 13642 (2002).
- ¹²N. Pinna, M. Willinger, K. Weiss, J. Urban, and R. Schlögl, *Nano Lett.* **3**, 1131 (2003).
- ¹³F. Krumeich, H. J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, and R. Nesper, *J. Am. Chem. Soc.* **121**, 8324 (1999).
- ¹⁴G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.* **41**, 2446 (2002).
- ¹⁵P. M. Ajayan, O. Stephan, P. Redlih, and C. Colliex, *Nature (London)* **375**, 564 (1995).
- ¹⁶K. Takahashi, Y. Wang, and G. Z. Cao, *Appl. Phys. Lett.* **86**, 053102 (2005).
- ¹⁷R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1964).
- ¹⁸R. Enjalbert and J. Galy, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **42**, 1467 (1986).
- ¹⁹N. Kenny, *J. Phys. Chem. Solids* **27**, 1237 (1966).
- ²⁰C. V. Ramana and O. M. Hussain, *Adv. Mater. Opt. Electron.* **7**, 225 (1997).
- ²¹P. Clauws and J. Vennik, *Phys. Status Solidi B* **66**, 553 (1974).
- ²²Z. J. Zhang, Y. Zhao, and M. M. Zhu, *Appl. Phys. Lett.* **88**, 033101 (2006).
- ²³Y. Zhao, Z. J. Zhang, and Y. H. Lin, *J. Phys. D* **37**, 3392 (2004).
- ²⁴X. Su, Z. J. Zhang, and M. M. Zhu, *Appl. Phys. Lett.* **88**, 061913 (2006).
- ²⁵M. M. Zhu, Z. J. Zhang, and W. Miao, *Appl. Phys. Lett.* **89**, 021915 (2006).