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Effect of magnetic field on the visible light emission of V$_2$O$_5$ nanorods

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V$_2$O$_5$ nanorods with remarkable visible light emission were synthesized by heating a V$_2$O$_3$ thin film in air at $\sim$530 °C due to the involvement of oxygen defects. The density of defects in the nanorods can be decreased by applying a magnetic field of 5 T during this transition, resulting in drastic decrease in the intensity of the photoluminescence of the V$_2$O$_5$ nanorods. The dependence of the defect removal on the magnetic field and the mechanism for this influence were also investigated.

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Due to its outstanding properties, such as photochromic, catalytic, chemical sensing properties, etc., vanadium pentoxide (V$_2$O$_5$) has been applied in various fields, e.g., electronic information displays, electrochromic/color memory devices, optical-electrical switch, etc. Thus lots of efforts have been focused on the synthesis and properties of the family of vanadium oxides in the past years. Recently, the synthesis of nanostructures of vanadium oxides has attracted a thermal oxidation process reported earlier, and then an-

An alternative approach to produce single crystalline V$_2$O$_5$ nanorods is by oxidizing a V$_2$O$_3$ film in air at $\sim$500 °C. By this method V$_2$O$_5$ nanorods were grown from the film during the oxidation of V$_2$O$_3$→V$_2$O$_5$. The nanorods exhibited photoluminescence (PL) in the visible range due to the involvement of oxygen defects. This is interesting as V$_2$O$_5$ has not been considered as a candidate material for light emitting before. Thus it is of interest to study the defect-property relationship of V$_2$O$_5$ nanorods and devise ways to control the defects in the nanorods to adjust the light-emitting properties.

In this letter, we report our investigation on the influence of a strong magnetic field on the nanorod growth and defect involvement during the V$_2$O$_3$→V$_2$O$_5$ transition by the above approach. Our study revealed that applying a strong magnetic field during the growth could be an effective way to control the defects in nanomaterials. The substrates used in this study were Si (001) wafers. These were supersonically cleaned in acetone, alcohol, and de-ionized water baths in sequence and then dried with a gentle nitrogen blow. Films of V$_2$O$_3$ with a thickness of $\sim$300 nm were first deposited on the silicon substrates using a thermal oxidation process reported earlier, and then annealed in air at 530 °C for 1 h, during which V$_2$O$_5$ films were oxidized further and transformed into single crystalline V$_2$O$_5$ nanorods. To investigate the effect of magnetic fields on V$_2$O$_5$ nanorod growth, a static field of 5 T generated by a superconducting magnet system (JMTD-10T150) was applied in the oxidation processing, along directions set at 0°, 20°, 40°, 60°, and 90° from the surface normal of the substrate. The morphology and structure of the as-deposited V$_2$O$_5$ films and those after further oxidation were examined by scanning electron microscope (SEM) and transmission electron microscope (TEM), Raman spectrometer, and x-ray diffraction (XRD), respectively. The PL property of these samples was also evaluated using a Raman spectrometer.

The as-deposited films were consisted of pyramid-shaped V$_2$O$_3$ particles with a size of several hundred nanometers [see Fig. 1(a) and the inset of Fig. 1(b)]. After thermal annealing in air at 530 °C for 1 h, the V$_2$O$_3$ particles were further oxidized into V$_2$O$_5$ and transformed into nanorods, $\sim$1 µm long and several hundred nanometers in diameter [see Fig. 1(a) and the inset of Fig. 1(c)]. The XRD patterns shown in Fig. 1(a) were taken with a Rigaku x-ray diffractometer using the Cu Ka radiation. PL measurements indicated that the V$_2$O$_3$ particles did not emit any light when excited by a 514 nm Ar$^+$ laser, while the V$_2$O$_5$ nanorods emitted stably strong visible light [see Figs. 1(b) and 1(c)]. The PL spectrum of the V$_2$O$_5$ nanorods can be well fitted by two Gaussian peaks centered at $\sim$650 nm (1.82 eV) and $\sim$730 nm (1.68 eV), respectively [see Fig. 1(c)]. As the band gap of V$_2$O$_5$ is $\sim$2.24 eV, the emissions were believed to be caused by some oxygen defects that got involved during the nanorod growth.

Applying a strong static magnetic field during the oxidation of V$_2$O$_3$→V$_2$O$_5$ did not influence greatly the V$_2$O$_5$ nanorod growth. Figures 2(a)–2(f) show SEM and TEM images of V$_2$O$_5$ nanorods grown from the V$_2$O$_3$ films under a 5 T magnetic field along directions of 0°, 20°, 40°, 60°, and 90° from the surface normal of the substrate, respectively. One sees that as we observed without the magnetic field [see Fig. 1(c)], V$_2$O$_5$ nanorods were grown from the V$_2$O$_3$ films in all cases. The only visible effect of the magnetic field is the slight change of the dimension of the nanorods, i.e., the size of the nanorods got reduced when the magnetic field direction (H) was off the surface normal of the substrate (n). For comparison, at an angle of 0° or H∥n, the V$_2$O$_5$ rods were

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\[ \text{\(5 \text{ cm} \) long and \(0.5 \text{ cm} \) in diameter} \]

\[ \text{\( \theta = 90^\circ \) or \( \hat{n} \), the rods were \(1 \text{ cm} \) long and \(200 \text{ nm} \) in diameter} \]

\[ \text{see Fig. 2} \]

\[ \text{a} \]

\[ \text{ta} \]

\[ \text{n} \]

\[ \text{similar to those nano-rods grown without the magnetic field.} \]

\[ \text{Selected area diffraction} \]

\[ \text{SAD} \]

\[ \text{analysis} \]

\[ \text{see insets of Figs. 2} \]

\[ \text{b} \]

\[ \text{e} \]

\[ \text{, similar to those nano-rods grown without the magnetic field.} \]

\[ \text{Raman} \]

\[ \text{spectroscopy analysis of the nanorods} \]

\[ \text{see Fig. 3} \]

\[ \text{confirmed that they are V2O5 with an orthorhombic structure.} \]

\[ \text{These suggested that applying a magnetic field did not influence the} \]

\[ \text{crystallinity of the V2O5 nanorods.} \]

\[ \text{However, the application of the magnetic field did} \]

\[ \text{change considerably the oxygen defect involvement in the} \]

\[ \text{nanorods and thus influenced greatly their PL properties. Figure} \]

\[ \text{4(a)} \]

\[ \text{compares the PL spectra of V2O5 nanorods grown in} \]

\[ \text{a 5 T magnetic field of different directions. It is noticed that} \]

\[ \text{the visible light emission was suppressed in nanorods grown in} \]

\[ \text{the field with its \( \vec{H} \) close to \( \hat{n} \), while the emission centers} \]

\[ \text{remained almost unchanged} \]

\[ \text{[see Fig. 4(b)]. As these visible light emissions are due to oxygen defects got involved during} \]

\[ \text{the nanorod growth, it suggests that applying a strong} \]

\[ \text{magnetic field could adjust the defect level in the V2O5 nanorods. Figure} \]

\[ \text{4(c)} \]

\[ \text{plots the PL intensity of the nanorods versus the direction of the field, i.e., the angle between \( \vec{H} \) and} \]

\[ \hat{n}. \]

\[ \text{One sees that the intensity got decreased monotonically at} \]

\[ \text{decreased angles, suggesting a close relationship between the} \]

\[ \text{PL and the field direction. To make this relationship clear, we plotted in Fig. 4(d) the intensity of the two emissions as a} \]

\[ \text{function of the value of projected field on} \]

\[ \hat{n} \] 

\[ \text{[i.e.,} \]

\[ \text{\( H_z \)]} 

\[ \text{From the figure one observes that the intensity is reversely related to} \]

\[ \text{\( H_z \), i.e., the larger} \]

\[ \text{\( H_z \)}, \]

\[ \text{the weaker the PL. One may also notice the difference in the two emissions influenced by the magnetic field, i.e., the emission at 730 nm was of a negative} \]

\[ \text{linear relationship with} \]

\[ \text{\( H_z \)}, \]

\[ \text{while the emission at 650 nm} \]

\[ \text{was of a negative nonlinear relationship with} \]

\[ \text{\( H_z \)}, \]

\[ \text{suggesting that the two emissions were caused by different oxygen defects.} \]

\[ \text{It is also suggested that the defects corresponding to} \]

\[ \text{the emission at 650 nm may be easily removed completely by the strong magnetic field, while it is hard to remove} \]

\[ \text{completely those defects corresponding to the emission at} \]

\[ \text{730 nm.} \]

\[ \text{The reason for the effect of the magnetic field on the} \]

\[ \text{defect involvement in V2O5 nanorods is intriguing. It has} \]

\[ \text{been reported that the defect intensity in silicon crystals} \]

\[ \text{grown from the melt was effectively decreased by introducing} \]

\[ \text{a static magnetic field due to the Lorentz force.} \]

\[ \text{The Lorentz force proportional and perpendicular to the magnetic} \]

\[ \text{field was applied.} \]

\[ \text{FIG. 1.} \]

\[ \text{(a) XRD spectra of as-deposited V2O3 films and those after oxidation into V2O5 nanorods; (b) and (c) are PL spectra of the V2O3 film and} \]

\[ \text{V2O5 nanorods, excited by a 514 nm Ar\textsuperscript{+} laser. Insets of (b) and (c) are SEM images of the as-deposited V2O3 particles and the V2O5 nanorods, respectively.} \]

\[ \text{FIG. 2.} \]

\[ \text{(Color online) V2O5 nanorods synthesized in a 5 T magnetic field of different directions. (a), (c), (d), and (e) show SEM images of V2O5 nanorods grown at field directions of 0\(^\circ\), 20\(^\circ\), 40\(^\circ\), and 90\(^\circ\); (b) and (f) show TEM images and corresponding SAD patterns of the V2O5 nanorods grown at field directions of 0\(^\circ\) and 90\(^\circ\), respectively.} \]

\[ \text{FIG. 3.} \]

\[ \text{Raman spectra of the samples synthesized at field directions of 0\(^\circ\), 20\(^\circ\), 40\(^\circ\), 60\(^\circ\), and 90\(^\circ\). All peaks fit well those of V2O5.} \]

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The field could suppress the turbulent fluctuations due to the damping action on the melt flow, thus reducing the number of the nuclei and improving the quality of the silicon crystals grown. This might also be the reason for its influence on the V2O5 nanorod growth observed here. Since the melting points of V2O3 and V2O5 are 1967 and 670 °C, respectively, V2O5 formed on the surface of V2O3 particles may melt at the temperature of 530 °C, as the melting point of nanomaterials could be reduced greatly compared with their bulk state. Thus the V2O5 nanorods were probably grown from the V2O3 melt formed on the V2O3 particles, similar to that observed for the Fe nanorod growth from the melt on submicron-sized Fe grains. In this case the growth of V2O5 nanorods should be influenced by the Lorentz force similar to that observed for silicon crystal growth. Since the Lorentz force is proportional to $H_z$, this influence should become stronger at larger $H_z$. This is exactly what we observed in this study.

In short, we observed that by applying a strong magnetic field during the oxidation of V2O3 into V2O5, the density involved in the V2O5 nanorods can be influenced greatly by increasing the projected field perpendicular to the film plane. The mechanism for the influence of the magnetic field was also discussed. This study provides a possible technique to control the defects involved in nanomaterials and thus to adjust their properties.

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