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Effect of magnetic field on the visible light emission of V_2O_5 nanorods

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V_2O_5 nanorods with remarkable visible light emission were synthesized by heating a V_2O_3 thin film in air at ~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_2O_5 nanorods. The dependence of the defect removal on the magnetic field and the mechanism for this influence were also investigated. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3095502]

Due to its outstanding properties, such as photochromic, catalytic, chemical sensing properties, etc., vanadium pentoxide (V_2O_5) has been applied in various fields, e.g., electronic information displays, electrochromic/color memory devices, optical-electrical switch, etc.[1,2] Thus lots of efforts have been focused on the synthesis and properties of the family of vanadium oxides in the past years.[3,4] Recently, the synthesis of nanostructures of vanadium oxides has attracted great attention as materials at such tiny dimensions could possess properties that are different from their bulk states and attractive to nanodevices, and several approaches have been developed, for instance, the sol-gel reaction method for VO_x nanotubes,[5] the solid-reaction and sol-electrophoretic deposition for V_2O_5 nanofibers/nanorods,[6] the thermal oxidation approach for synthesizing arrays of aligned VO_2 nanorods,[7] etc.

An alternative approach to produce single crystalline V_2O_5 nanorods is by oxidizing a V_2O_3 film in air at ~500 °C. By this method V_2O_5 nanorods were grown from the film during the oxidation of $V_2O_3 \rightarrow V_2O_5$. The nanorods exhibited photoluminescence (PL) in the visible range due to the involvement of oxygen defects.[8] This is interesting as V_2O_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_2O_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 $V_2O_3 \rightarrow V_2O_5$ 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_2O_3 with a thickness of ~300 nm were first deposited on the silicon substrates using a thermal oxidation process reported earlier,[9–11] and then annealed in air at 530 °C for 1 h, during which V_2O_3 films were oxidized further and transformed into single crystalline V_2O_5 nanorods. To investigate the effect of magnetic fields on V_2O_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_2O_3 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_2O_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_2O_3 particles were further oxidized into V_2O_5 and transformed into nanorods, ~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 $K\alpha$ radiation. PL measurements indicated that the V_2O_3 particles did not emit any light when excited by a 514 nm Ar^+ laser, while the V_2O_5 nanorods emitted stably strong visible light [see Figs. 1(b) and 1(c)]. The PL spectrum of the V_2O_5 nanorods can be well fitted by two Gaussian peaks centered at ~650 nm (1.82 eV) and ~730 nm (1.68 eV), respectively [see Fig. 1(c)]. As the band gap of V_2O_5 is ~2.24 eV,[12] the emissions were believed to be caused by some oxygen defects that got involved during the nanorod growth.[8,13]

Applying a strong static magnetic field during the oxidation of $V_2O_3 \rightarrow V_2O_5$ did not influence greatly the V_2O_5 nanorod growth. Figures 2(a)–2(f) show SEM and TEM images of V_2O_5 nanorods grown from the V_2O_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_2O_5 nanorods were grown from the V_2O_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 ($\hat{H}$) was off the surface normal of the substrate ($\hat{n}$). For comparison, at an angle of 0° or $\hat{H} \| \hat{n}$, the V_2O_5 rods were

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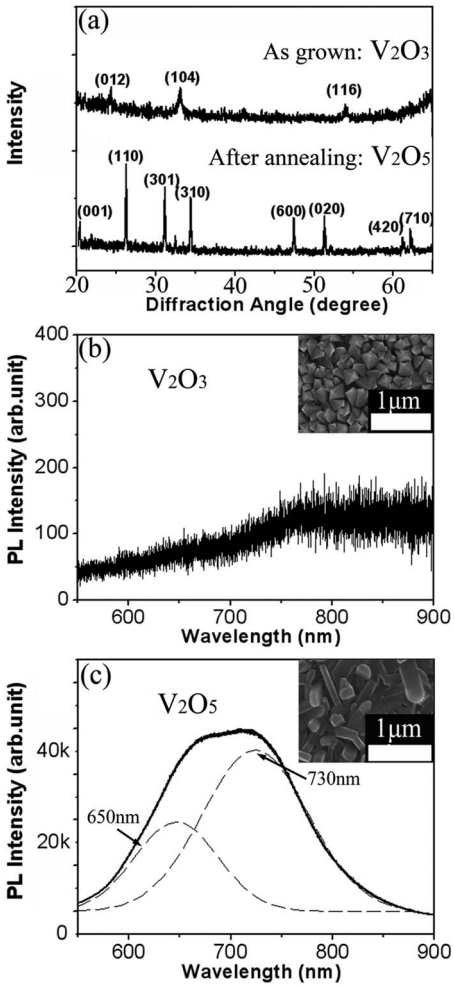

FIG. 1. (a) XRD spectra of as-deposited V_2O_3 films and those after oxidation into V_2O_5 nanorods; (b) and (c) are PL spectra of the V_2O_3 film and V_2O_5 nanorods, excited by a 514 nm Ar^+ laser. Insets of (b) and (c) are SEM images of the as-deposited V_2O_3 particles and the V_2O_5 nanorods, respectively.

~ 5 μm long and ~ 0.5 μm in diameter [see Fig. 2(a)]; at an angle of 90° or $\hat{H} \perp \hat{n}$, the rods were ~ 1 μm long and ~ 200 nm in diameter [see Fig. 2(e)], similar to those nanorods grown without the magnetic field. Selected area diffraction (SAD) analysis [see insets of Figs. 2(b) and 2(f)] indicated that the nanorods are single crystalline V_2O_5. Raman spectrum analysis of the nanorods (see Fig. 3) confirmed that they are V_2O_5 with an orthorhombic structure.[14] These suggested that applying a magnetic field did not influence the crystallinity of the V_2O_5 nanorods.

However, the application of the magnetic field did change considerably the oxygen defect involvement in the nanorods and thus influenced greatly their PL properties. Figure 4(a) compares the PL spectra of V_2O_5 nanorods grown in a 5 T magnetic field of different directions. It is noticed that the visible light emission was suppressed in nanorods grown in the field with its $\hat{H}$ close to $\hat{n}$, while the emission centers remained almost unchanged [see Fig. 4(b)]. As these visible light emissions are due to oxygen defects got involved during the nanorod growth, it suggests that applying a strong magnetic field could adjust the defect level in the V_2O_5 nanorods. Figure 4(c) plots the PL intensity of the nanorods versus the direction of the field, i.e., the angle between $\hat{H}$ and

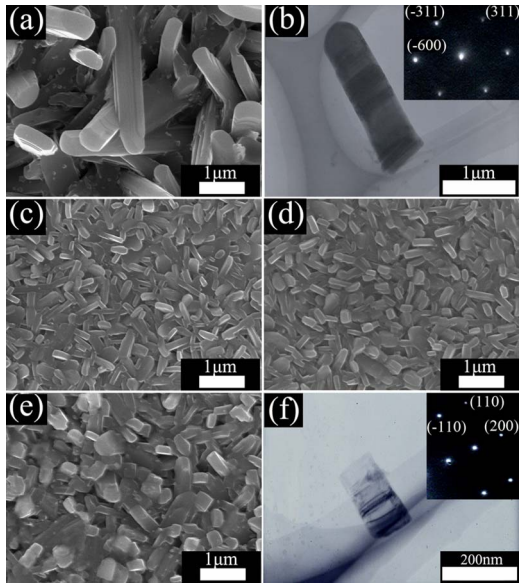

FIG. 2. (Color online) V_2O_5 nanorods synthesized in a 5 T magnetic field of different directions. (a), (c), (d), and (e) show SEM images of V_2O_5 nanorods grown at field directions of 0°, 20°, 40°, and 90°; (b) and (f) show TEM images and corresponding SAD patterns of the V_2O_5 nanorods grown at field directions of 0° and 90°, respectively.

$\hat{n}$. One sees that the intensity got decreased monotonically at decreased angles, suggesting a close relationship between the PL and the field direction. To make this relationship clear, we plotted in Fig. 4(d) the intensity of the two emissions as a function of the value of projected field on $\hat{n}$ (i.e., H_z). From the figure one observes that the intensity is reversely related to H_z, i.e., the larger the H_z, 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 linear relationship with H_z, while the emission at 650 nm was of a negative nonlinear relationship with H_z, suggesting that the two emissions were caused by different oxygen defects. It is also suggested that the defects corresponding to the emission at 650 nm may be easily removed completely by the strong magnetic field, while it is hard to remove completely those defects corresponding to the emission at 730 nm.

The reason for the effect of the magnetic field on the defect involvement in V_2O_5 nanorods is intriguing. It has been reported that the defect intensity in silicon crystals grown from the melt was effectively decreased by introducing a static magnetic field due to the Lorentz force.[15] The Lorentz force proportional and perpendicular to the magnetic

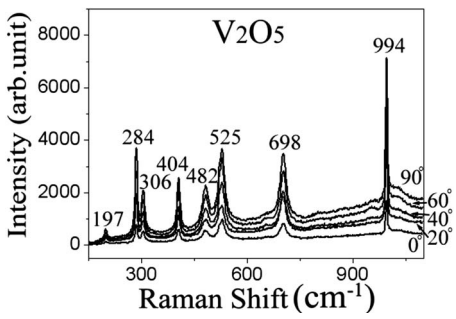

FIG. 3. Raman spectra of the samples synthesized at field directions of 0°, 20°, 40°, 60°, and 90°. All peaks fit well those of V_2O_5.

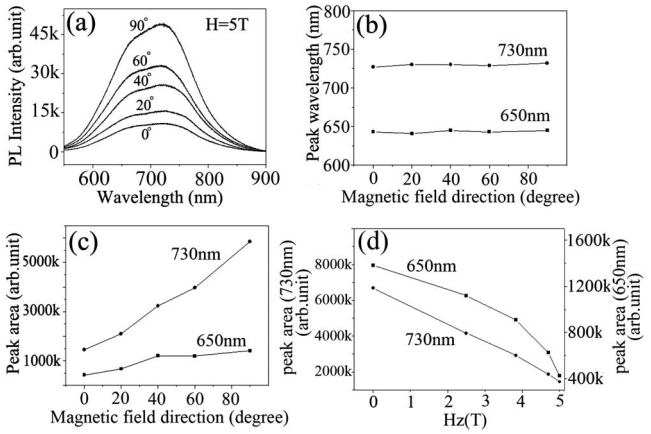

FIG. 4. (a) PL spectra of V_2O_5 nanorods synthesized in a 5 T magnetic field as a function of the field direction; (b) and (c) show, respectively, the position and intensity of the two emissions vs the field direction; (d) shows the intensity of the emissions at ~730 and ~650 nm as a function of H_z.

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.[16] This might also be the reason for its influence on V_2O_5 nanorod growth observed here. Since the melting points of V_2O_3 and V_2O_5 are 1967 and 670 °C, respectively, V_2O_5 formed on the surface of V_2O_3 particles may melt at the temperature of 530 °C, as the melting point of nanomaterials could be reduced greatly compared with their bulk state.[17] Thus the V_2O_5 nanorods were probably grown from the V_2O_5 melt formed on the V_2O_3 particles, similar to that observed for the Fe nanorod growth from the melt on submicron-sized Fe grains.[18] In this case the growth of V_2O_5 nanorods should be influenced by the Lorentz force similar to that observed for silicon crystal growth.[16] 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 V_2O_3 into V_2O_5, the defect density involved in the V_2O_5 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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