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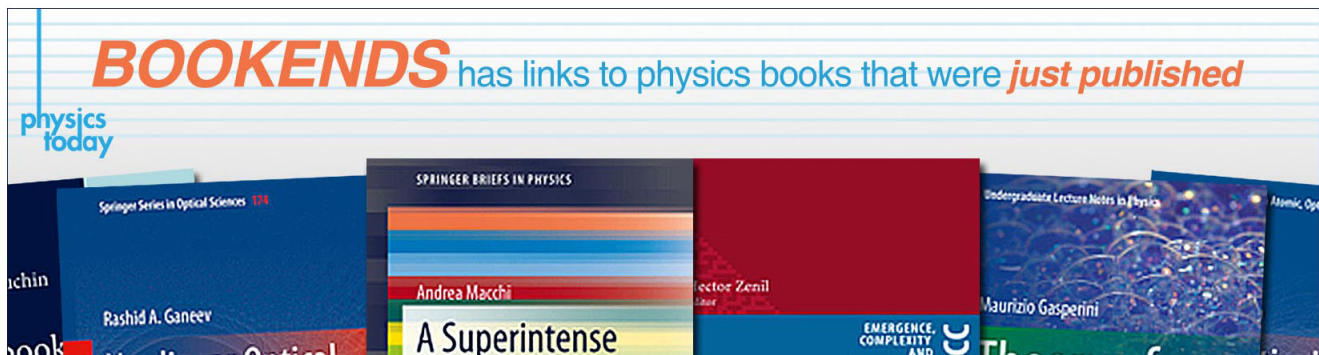
Structural and cathodoluminescence assessment of V$_2$O$_5$ nanowires and nanotips grown by thermal deposition

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V$_2$O$_5$ nanostructures have been grown on 4H-SiC and Si substrates by a thermal deposition method without a catalyst. High aspect ratio nanowires with rectangular cross sections were grown on 4H-SiC. High-resolution transmission electron microscopy observations and cathodoluminescence (CL) spectroscopy measurements reveal the high crystal quality of the grown nanowires. Deposition on Si substrates leads to the growth of V$_2$O$_5$ platelets or rod-shaped crystals ending in arrays of parallel sharp nanotips with apex radius in the 50 nm range. A CL emission band observed centered at about 1.70 eV in spectra from these nanostructures is tentatively attributed to defect centers involving oxygen vacancies. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2799952]

I. INTRODUCTION

Vanadium pentoxide (V$_2$O$_5$) is a key technological material widely used in chemical sensors, catalysis, solid-state batteries, solar cell windows, and electrochromic devices.[1,2] In recent years, great efforts have been focused on the growth of meso- and nanostructured V$_2$O$_5$ in order to optimize the useful properties of this material. Elongated nanostructures, such as nanorods or nanowires, are particularly attractive because they exhibit novel characteristics owing to their small radial dimension while retaining wire-like connectivity. For instance, the high specific surface area of V$_2$O$_5$ nanotubes makes them very attractive as electrodes in Li batteries, while they also show an increased capability for redox reactions.[1] Moreover, hydrated vanadium pentoxide nanotube arrays exhibit excellent field emission properties, as reported by Zhou *et al.*[3] In addition, the nanostructured material has been used in novel applications such as nonlinear optical limiters and nanoactuators.[4]

Recently, different authors have reported on the synthesis and properties of V$_2$O$_5$ nanorods, nanotubes, and other nano- and microstructures with large surface-to-volume ratio. In particular, nanotubes and nanorods of different vanadium oxides have been grown by sol-gel,[5,6] reverse micelle techniques,[7] hydrothermal methods,[8] or electrophoretic deposition.[9] Optical absorption and transmittance of V$_2$O$_5$ films have sometimes been investigated in connection with its electrochromic properties,[10] while reports on the luminescence properties of this oxide are scarce,[11] which is probably due to the low quantum efficiency of this material.

In this work, V$_2$O$_5$ nanostructures have been grown over Si and 4H-SiC substrates by a thermal deposition method without a catalyst using V$_2$O$_5$ powder as the starting material. A similar technique was used previously to grow elongated micro- and nanostructures of other functional oxides.[12–18] The samples have been characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and cathodoluminescence (CL) spectroscopy in the SEM.

II. EXPERIMENTAL

The synthesis of the V$_2$O$_5$ nanostructures was performed using a vapor transport method. The starting material was commercially available V$_2$O$_5$ powder (99.999% nominal purity) with a range of particle size up to about 400 μm. Source samples were prepared by compacting the powder under compressive load to form disks of about 7 mm diameter and 2 mm thickness. These disks were then placed inside a horizontal tube furnace under Ar flow and the reaction product collected on Si or 4H-SiC substrates downstream from the source material. Optimum reaction conditions resulting in the growth of the nanostructures were temperatures between 690 and 710 °C, evaporation times between 15 and 24 h, and Ar flow ≈0.5 L/min.

XRD measurements were performed in a Philips X'Pert PRO MPD diffractometer. Secondary electron and CL observations were carried out in a Leica 440 SEM and a Hitachi 2500 SEM. The CL measurements were carried out at 85 K with a Hamamatsu R928 photomultiplier working in photon-counting mode and an Oriel 74100 monochromator. CL spectra were corrected for system response. HRTEM images and selected area electron diffraction (SAED) patterns were obtained in a Jeol EM-400EX microscope operating at 400 kV. Observation conditions were carefully adjusted in order to avoid electron-beam-induced structural transformations.[19] Nanostructures were released from the substrates by sonicating the samples in ethanol. Drops of the nanostructure solution were then deposited on holey carbon-coated TEM grids.

III. RESULTS AND DISCUSSION

The morphology of the reaction products depends strongly on the material substrate used for deposition, but all the peaks observed in XRD patterns (not shown here) from both the starting material and the different nanostructures grown could be unambiguously indexed to orthorhombic α-V$_2$O$_5$ (JCPDS card 85-0601). Energy-dispersive x-ray microanalysis carried out in the SEM indicates that neither Si nor C from the substrates were incorporated into the nanostructures during the growth process, although it should be

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mentioned that the detection limit of this technique is about 1000 ppm. Temperature was found to be the most critical parameter for V_2O_5 nanostructures grown on SiC substrates. Actually, reaction products containing nanostructures with well-defined morphologies were not obtained for temperatures below 670 °C irrespective of the evaporation time or the Ar flow used. Treatments at 690 °C for 15–24 h lead to the growth of nanowires with lengths up to 150 μm and cross-sectional dimensions in the range 150–250 nm, as shown in Fig. 1(a). Increasing temperature to 700–710 °C increases the density of nanowires [Fig. 1(b)]. In this case, nanowires with well-defined facets and rectangular cross sections grow on the SiC substrates. The average width of these high aspect ratio nanowires is 250 ($\pm$50) nm, with lengths reaching up to 100 μm. It was frequently observed that the nanowires appeared interconnected or grew on top of other nanowires previously formed [Fig. 1(c)]. The structure of individual nanowires was investigated by HRTEM. Figure 2(a) shows a low magnification image of a 220-nm-wide nanowire, while Fig. 2(b) shows a high-resolution image of the area marked in the previous micrograph. Lattice fringes running parallel to the edge of the nanowire can be clearly appreciated. The corresponding SAED pattern, shown in the inset, can be identified as the (001) pattern of orthorhombic α-V_2O_5. This diffraction pattern did not change as the electron beam was moved along the nanostructure, indicating the single-crystalline nature of the nanowire. The spacing between the fringes was measured to be 0.58$\pm$0.01 nm, which corresponds to the spacing of the (200) planes [Fig. 2(c)]. A projection of the unit cell (a=1.15 nm, b=0.36 nm) is marked in the image. Similar results were obtained in all the samples investigated by HRTEM. These observations indicate that our V_2O_5 nanowires grow along the [010] direction.

The luminescence properties of individual nanostructures were investigated by CL spectroscopy in a scanning electron microscope. Figure 3 shows representative CL spectra of the untreated V_2O_5 powder and the nanowires grown on 4H-SiC substrates. Spectra from the starting powder shows a main band peaked at about 1.68 eV and much weaker emission at higher energies, while CL emission from the nanowires appears peaked at about 2.0 eV. Luminescence emission from vanadium oxides has been scarcely investigated. Nishio and Kakihana[11] reported on a broad photoluminescence (PL) band centered at 1.85 eV at room temperature in a study on visible light photochromism in sintered V_2O_5. The PL intensity decreased after strong laser irradiation, but the origin of this luminescence was not addressed. According to absorption measurements, the absorption edge of V_2O_5 single crystals varies between 2.15 and 2.22 eV and depends slightly on the orientation of the sample.[20] The reported values for thin films at room temperature vary between 1.95 and 2.40 eV, depending on the stoichiometry of the samples investigated, which in turn is influenced by the growth method and deposition conditions.[21,22] The layer structure of V_2O_5 leads to the splitting of the V 3d conduction band. Although the direct gap is about 3.3 eV, the split-off localized band lies at about 0.6 eV below the main V 3d band, so that it is located within the main energy gap. The optical band gap for near stoichiometric V_2O_5 corresponds
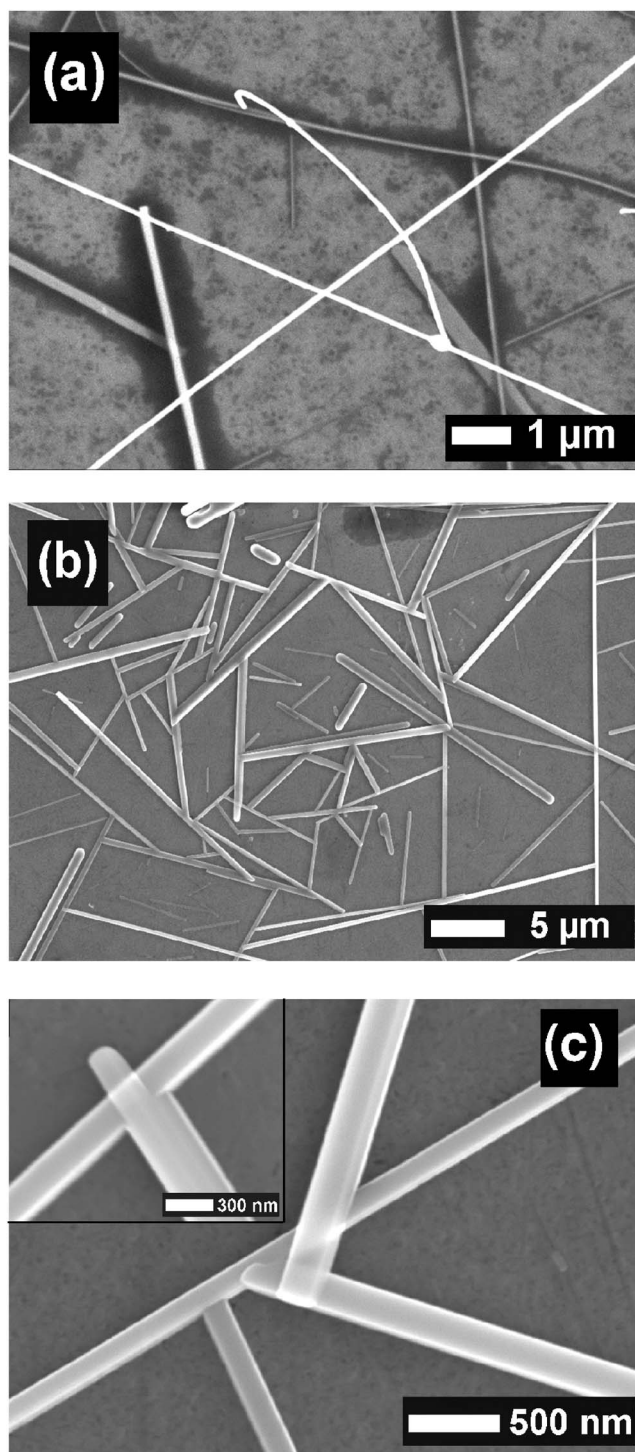

FIG. 1. (a) SEM image of vanadium pentoxide nanowires grown at 690 °C over a 4H-SiC substrate. Deposition time was 24 h. (b) Nanowires grown at 700 °C on a similar substrate. Deposition time was 15 h. (c) SEM image showing joining or superposition (inset) of some nanowires.

then to the energy between the top of the O 2p valence band and the split-off part of the V 3d band.[10,23] Hence, our 2.0-eV CL band can be attributed to the optical gap of the V_2O_5 nanowires. These CL results, together with our TEM observations, are indicative of the better crystalline quality of the grown nanowires, as compared with the as-received V_2O_5 powder.

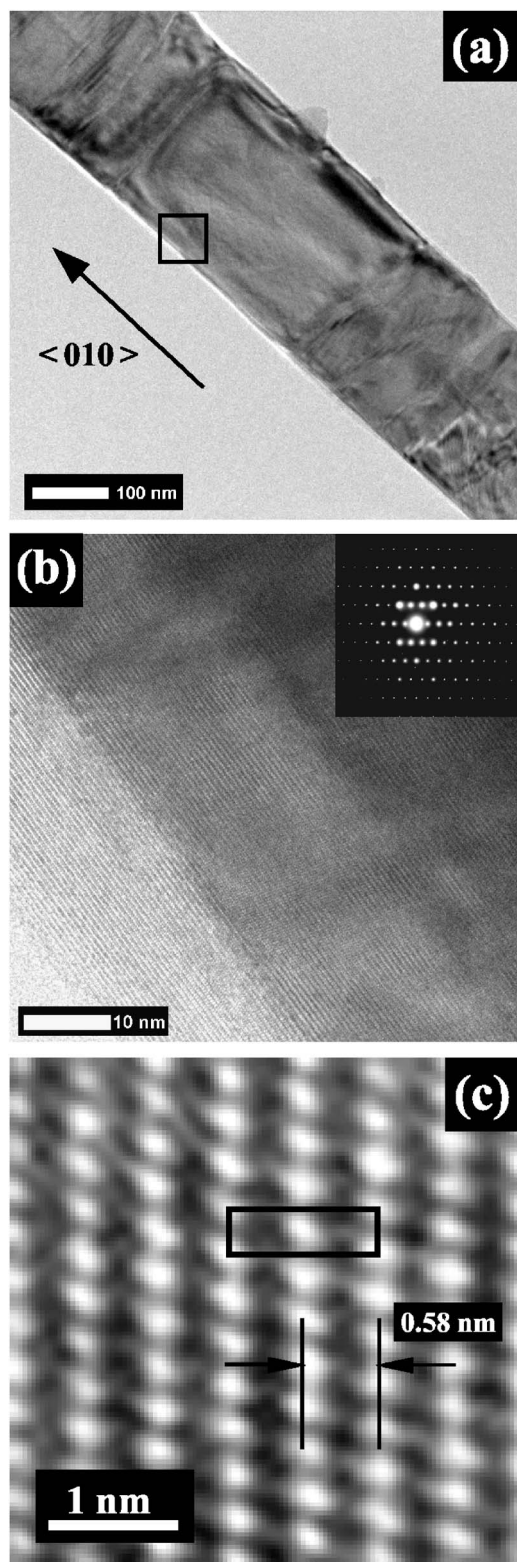The morphology of the nanostructures grown on Si sub-

FIG. 2. (a) Low magnification TEM micrograph of a nanowire grown at 700 °C on a 4*H*-SiC substrate. (b) HRTEM image of the area marked in the previous micrograph showing (200) lattice fringes running parallel to the edge of the nanowire. The corresponding SAED pattern, shown in the inset, can be identified as the (001) pattern of orthorhombic V_2O_5. (c) HRTEM micrograph of the same nanowire. A projection of the unit cell ($a = 1.15$ nm, $b = 0.36$ nm) is inserted in the image.

strates (Fig. 4) is completely different from that of the nanowires grown on 4*H*-SiC. In this case, both temperature and evaporation time are critical parameters. Optimum reaction
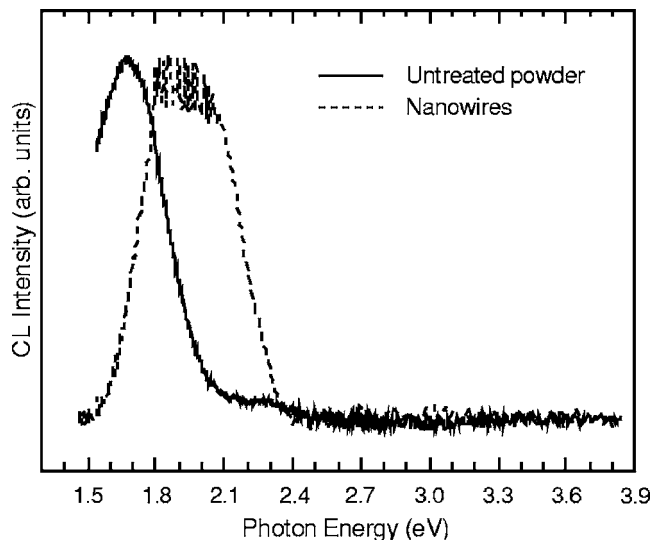

FIG. 3. CL spectrum (85 K, 12 kV, 0.5 nA) of the untreated V_2O_5 powder (solid line) and representative spectrum (obtained using the same excitation conditions) of one of the nanowires shown in Fig. 1(b).

conditions for the formation of vanadium pentoxide nanostructures on Si were found to be 705 °C and 24 h evaporation time. An increase of the deposition time leads to a rather uniform coverage of the Si substrate with a thick V_2O_5 layer but no nanostructures on it. Figures 4(a) and 4(b) show platelets 2–4 μm wide ending in sharp nanotips 1–5 μm long with diameters ranging from 100 to 400 nm and apex radius smaller than 50 nm. These platelets appear uniformly distributed on the substrate, although rod-shaped crystals ending in arrays of parallel nanotips [Fig. 1(c)] were also observed. TEM measurements (not shown) revealed the single-crystalline nature of the nanotips.

The present results demonstrate the growth of vanadium pentoxide nanostructures by a thermal deposition method without the use of a catalyst. The process leads to nanostructures, such as the above-described nanotip arrays or nanowires with rectangular cross sections, which are not normally
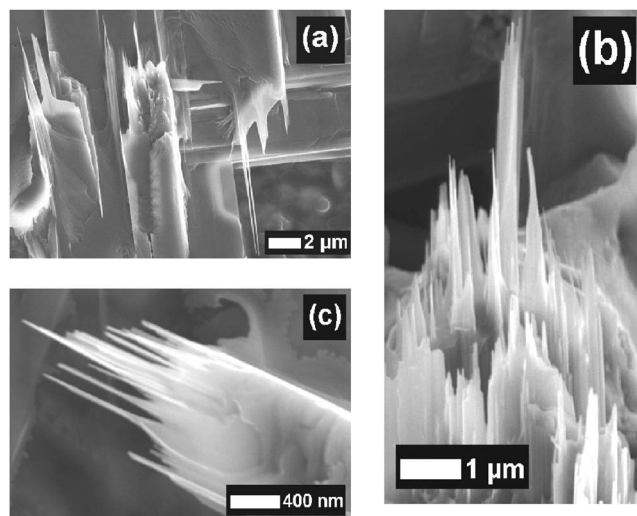

FIG. 4. (a,b) SEM images of V_2O_5 platelets ending in sharp nanotips deposited on Si substrates after treatment at 705 °C for 24 h. (c) Array of parallel nanotips stemming from the top of a platelet.
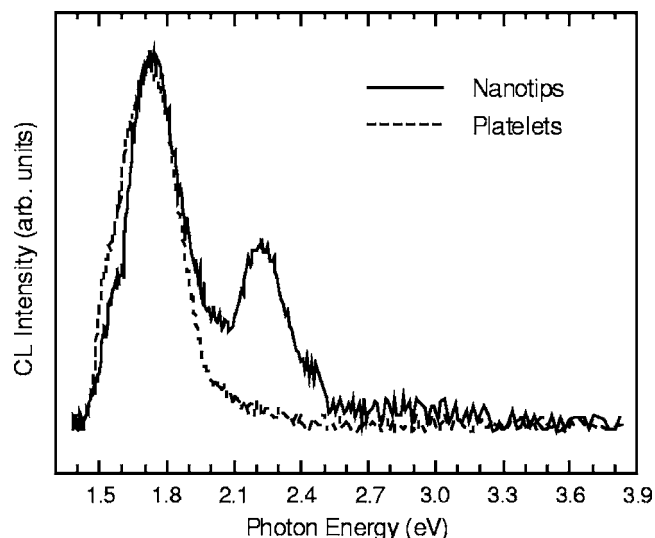
FIG. 5. Representative CL spectra (85 K, 12 kV, 0.5 nA) from V_2O_5 nanotips (solid line) and platelets (dashed line) grown at 700 °C for 15 h on Si substrates.

grown when solution methods are used. It was reported recently[3] that V_2O_5 nanotubes with 100-nm tip radius exhibit excellent field emission properties. This suggests that V_2O_5 nanotips, such as those grown in this work (Fig. 4), have potential applications as field emitters. Though the exact growth mechanism is still not known, the strong dependence of the morphology of the obtained nanostructures on the substrate material suggests that the growth is likely governed by a solid-solid mechanism, such as that proposed by Dai *et al.*[12]

The CL spectrum of the V_2O_5 nanotips is different from that measured on the platelets where they stem from (Fig. 5). In fact, the spectral distribution of the emission from the platelets is rather similar to that measured in the starting V_2O_5 powder, showing the dominant emission peaked near 1.70 eV and a weak shoulder at about 2.20 eV. However, CL spectra of the nanotips show the 1.70-eV band as well as a clearly resolved intense emission, centered near 2.25 eV, related to the optical band gap of vanadium pentoxide. Compositional and structural measurements did not reveal the existence of impurities or other oxides different from V_2O_5, which suggests that the band centered at about 1.70 eV is probably a V_2O_5 defect-related emission. Oxygen vacancies are the most commonly found defects in vanadium pentoxide.[22,24] The structure of V_2O_5 consists of alternating layers of V+O atoms and O alone, which can be seen by the translation along the c axis. Oxygen vacancies can be easily formed in the O layer between two V-O layers in (001) type planes. Empty $3d$ orbitals of vanadium atoms adjacent to a vacancy are able to localize excess electrons. This leads to the formation of localized states in the band gap,[24] which may be involved in the emission observed peaked at 1.70 eV. Actually, enhanced absorption above 2.4 eV has been reported in vacuum annealed V_2O_5 films and attributed to a decreased oxygen content.[25,26]

IV. CONCLUSIONS

In summary, vanadium pentoxide nanostructures have been grown on 4H-SiC and Si substrates by a thermal deposition method without a catalyst using V_2O_5 powder as the starting material. High aspect ratio nanowires with rectangular cross sections were grown on 4H-SiC. HRTEM observations reveal that these elongated nanostructures are single-crystalline and grow along the [010] direction. CL spectra from the nanowires show a single band centered at about 2.0 eV corresponding to the vanadium pentoxide optical band gap, which supports the crystal quality of the grown nanowires. Thermal deposition on Si substrates leads to the growth of V_2O_5 platelets or rod-shaped crystals ending in arrays of parallel sharp nanotips. CL spectra from both structures show an emission band, peaked at about 1.70 eV, tentatively attributed to defect centers involving oxygen vacancies.

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