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Influence of growth ambient on the surface and structural properties of vanadium oxide nanorods

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ABSTRACT

The influence of growth ambient on the surface and structural properties of vanadium oxide nanorods have been studied by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS). The vanadium oxide nanorods, which were synthesized through an ambient controlled vapor transport process, exhibit different surface electronic properties depending upon the growth ambient. The Raman data indicates that the as-grown samples are orthorhombic V_2O_5 phase with a small variation of stoichiometry. Under highly oxidative conditions, nearly stoichiometry sample can be grown. If the samples were grown under less oxidizing conditions, an increase of structural disorder was observed. The observed V 2p core level spectra of both samples showed a single peak with chemical shifts corresponding to the V^{5+} and V^{4+}. XPS results suggested that the highly oxidized vanadium ions (V^{5+}) are gradually reduced to lower oxidation state (V^{4+}) with the decreases of ambient oxygen levels during growth. The results clearly show that surface non-stoichiometry may be correlated with structural disorder of V_2O_5 nanorods. The growth ambient and post-annealing may influence the vanadium oxidation state and subsequent surface reactivity significantly.

1. Introduction

Vanadium oxides have been studied for decades due to their unique electronic, optical, and chemical properties [1,2]. Because of the many possible valence states of vanadium, a large numbers of compounds can be synthesized in the vanadium–oxygen system. The single-valence oxides including V_2O_5, VO_2, V_2O_3, and VO, where the vanadium presents in oxidation states of V^{5+}, V^{4+}, V^{3+}, and V^{2+}, respectively. Also mixed-valence vanadium oxides known as the Wadsley phase ($V_{2n}O_{5n-2}$) and the Magneli phase (V_nO_{2n-1}), have also been reported in the literature [3,4]. Furthermore, vanadium oxides and vanadium-based compounds are widely used as catalysts for oxidation reactions [5–7].

Many of the interesting properties in vanadium oxides are characteristically related to the broad range of valence states achievable for different vanadium chemical bonding. Among various phases of vanadium oxides, the formation of vanadium pentoxides (V_2O_5) as nanowires carries potential advantages. Promising device constructs have been realized for various V_2O_5 nanowires systems [8–11]. One-dimensional V_2O_5 nanowires are particularly attractive for gas sensing and energy storage, promising to deliver enhanced performance as compared to bulk or thin film materials due to their large surface area. Given the diversity of phases available in the vanadium oxide system, the specific crystalline phase achieved is highly dependent on the technique employed and process parameters selected. The catalytic properties of metal oxide catalysts are strongly dependent on the surface valence states, and the reducibility is an important factor allowing it to function as a catalyst with enhanced catalytic activity and selectivity [12,13]. It is generally agreed that even small variation of surface states in oxide nanostructures may give rise to large effects on their catalytic performance. Owing to their high surface area, it would be of significance to study the effect of ambient on the surface valence states of vanadium oxide nanorods.

In this paper, we utilize Raman spectroscopy (RS) and X-ray photoelectron spectroscopy (XPS) to elucidate the influence of growth ambient on the variation of local structural property and surface valence state of V_2O_5 nanorods. Distinct valence states for V_2O_5 nanorods synthesized under different ambient oxygen are uncovered and the samples synthesized under reducing ambient are more susceptible to oxidation. Of particular interest is the apparent formation of partially reduced surface of V_2O_5 nanorods under less oxidative and reducing ambient. The results revealed that controlling the ambient oxygen during the growth could be an effective way to control the V^{5+}/V^{4+} ratio of V_2O_5 nanorods. This study may establish a more direct route to fabricate one-dimensional V_2O_5 nanostructures with desired catalytic properties.

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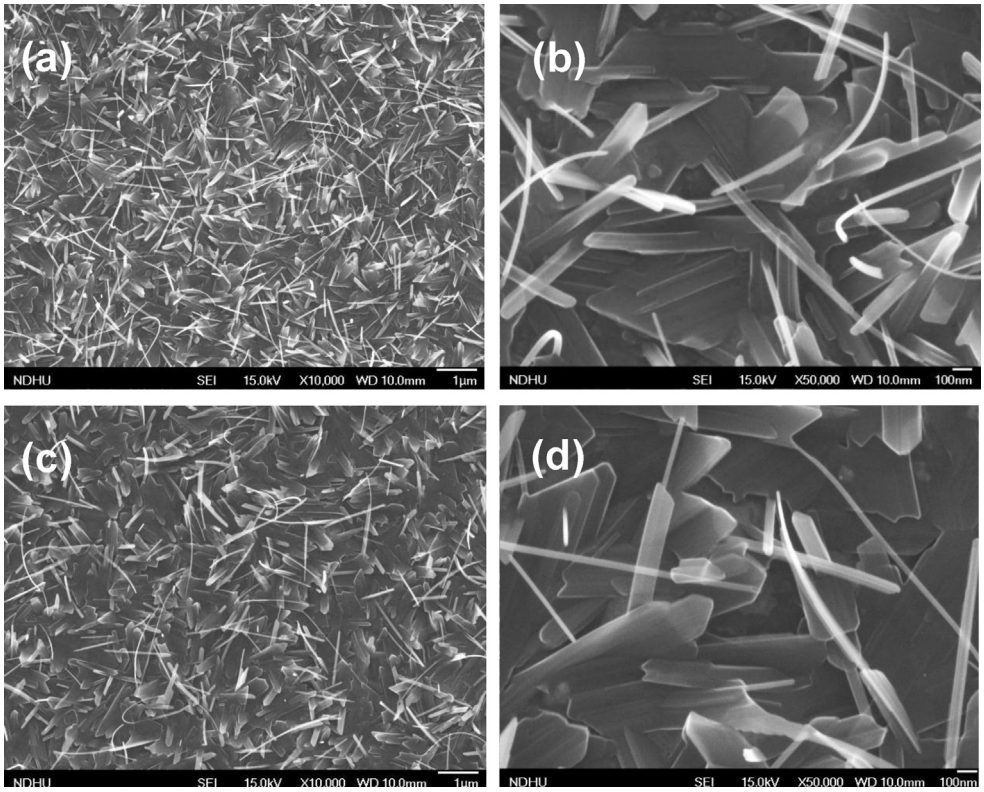

Fig. 1. Scanning electron microscopy images of V_2O_5 nanorods deposited on the Si(001) substrate at 450 °C under (a)–(b) 1% ambient oxygen, and (c)–(d) 10% ambient oxygen.

2. Materials and methods

2.1. Sample preparation

The V_2O_5 nanorods were synthesized by a catalyst-free vapor transport process. A horizontal tube furnace (Lindberg Blue) with three independent heating zones was used for the V_2O_5 nanorods growth. The V_2O_5 powder (0.5 g, 99.9999%, Alfa Aesar) was used as source material, put in a boat and placed at the center of the quartz tube. The Si(0 0 1) substrates were put in another boat and placed at downstream. The quartz tube was evacuated by a mechanical pump and purged several times with flowing argon. The furnace was then heated to 750 °C at a rate of 10 °C/min. Once furnace reaches growth temperature, the carrier gas (O_2/Ar, 1/99 and 10/90 SCCM) was fed into quartz tube. The background pressure was maintained at 0.3 Torr. After 1 h growth, the samples were cooled under the same ambient gas as was used during growth.

2.2. Characterization and surface analysis

The as-grown samples were characterized by a scanning electron microscope (FE-SEM; JEOL-7000F). Raman spectra were collected on a Horiba Jobin-Yvon T64000 micro-Raman scattering system with the excitation line at 532 nm and a power of 21 mW. All Raman measurements were performed at room temperature. The XPS experiments were carried out in an X-ray photoelectron spectrometer system (K-Alpha, Thermo Scientific) with a base pressure better than 3×10^{-9} mbar. XPS measurements were performed using an Al K_α ($h\nu$ = 1486.6 eV) source equipped with micro-focused monochromator. XPS spectra were collected from sample at two different angles: normal emission (0°) and grazing emission (60°). The spectra are given in binding energy (BE) referred to the binding energy of carbon 1s (284.85 eV). Spectra deconvolution for both V 2p and O 1s core level spectra was performed using a combination of Gaussian and Lorentzian profiles.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows top-view FE-SEM images of products deposited under (a)–(b): 1% and (c)–(d): 10% ambient oxygen on Si substrate. As shown in Fig. 1(a), the low-magnification FE-SEM image indicates that the as-synthesized products consist of nanostructures covered the whole substrate. The nanorods randomly nucleate on the surface and continue to grow for the duration of the deposition. The results clearly revealed that it was composed of nanorods with sizes approximately 30–100 nm in diameters and 1–2 μm in length. The obtained nanorods are with moderate aspect ratios (10–60) and good yield covering the whole substrate. For materials nucleated under the high ambient oxygen (10%), similar microstructure was observed but with slightly larger nanorod diameters. Since no metal catalysts employed during growth, we suggest that the nanorods growth follows a vapor-solid (V-S) mechanism, has been demonstrated previously [14].

The orthorhombic α-V_2O_5 consists of infinite chains made of VO_5 square pyramids sharing edges and corners along the *b*-axis. (Fig. 2(a)) The structure is composed of distorted trigonal bipyramidal coordination polyhedra of O atoms around V atoms. The polyhedra share edges to form $(V_2O_4)_n$ zigzag double chains along the (0 0 1) direction and are cross linked along (1 0 0) through shared corners. The structure in the *c*-axis consists of weak electrostatic interactions, which facilitate the ion insertion between the adjacent layers. Raman spectroscopy is sensitive to ordering arrangements of crystal structures, which is known to be more sensitive to short range order than XRD. Fig. 2 (b) shows the room