Synthesis and Characterization of microstructures of Sb_2O_3

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Abstract

In this work, we synthesized microstructures of antimony oxide by carbothermal reduction process associated with the vapor-solid (VS) mechanism. The samples were characterized by Field Effect Gun Scanning Electron Microscopy (FEG-SEM), X-ray Diffraction (XRD) and Raman Spectroscopy. FEG-SEM images show that the structures collected in the hottest zone of growth (760-630°C) are mainly composed by belts with branched morphology while in the cooler zone of growth (510-440°C) crystals with dendritic structure and Diffraction data showed that these samples were grown in the cubic phase and orthorhombic phase of Sb_2O_3 , respectively. The diffractogram presented evidence that the microstructures of Sb_2O_3 are single crystals with crystalline quality and with preferential growth orientation. Raman spectroscopy confirmed the crystalline quality of the samples and also that samples grow in different phases of antimony trioxide, cubic and orthorhombic. Raman measurements showed a break in the selection rules for the orthorhombic phase of Sb_2O_3 (branched belts). This effect is probably associated with intrinsic defects in the structure of the belts such as oxygen vacancies.

Introduction

Transparent conductive oxides (TCOs) are an important class of materials because it presents simultaneously good conductivity and high optical transparency [1-3]. Due to these characteristics, it can be said that these materials are of great interest for applications in optoelectronic devices [4-6].

Bulk antimony trioxide can be founded in the cubic phase (senarmontite) and orthorhombic (valentinite) phase, the latter being the most stable phase at 570°C [7] and has been widely used in the industry as flame retardants [8], as sensors [9] and catalytic agent [10-11].

Both cubic and orthorhombic phases have been successfully synthesized by using several methods [12-14]. Structures of orthorhombic Sb_2O_3 phase have been synthesized with different morphologies: micro- and nanorods [15,16], nanobelts [17,18], nanowires [12,19], nanoribbons [20], nanotubes [21], hierarchical structures [22]. Recently, a special attention has been given to the optical properties of these structures. An optical band gap of 3.3 eV (375 nm) for nanowires and nanobelts was identified from the 325 nm light-excited photoluminescence spectrum [21]. According to Deng et al [19] oxygen-related defects results in a PL band centered at 425 nm (2.92 eV). Fan et al [22] showed that the last

band in luminescence spectra of hierarchical microstructures should be related to oxygen vacancies or other possible structural defects such interstices and antisite defects.

Cebriano et al to investigated the mechanical properties of micro- and nanostructured Sb_2O_3 . The authors performed PL measurements and showed that micro- and nanotriangles used as building blocks of microstructures of the cubic Sb_2O_3 phase can be used as optical cavities [23]. Subsequently they to detected mechanical resonances induced by electric field in nanorods of the orthorhombic Sb_2O_3 phase and calculated the Young's modulus for these structures [24].

In this work, we investigated the structural properties of the cubic and orthorhombic phases of Sb_2O_3 synthesized by the VS mechanism associated to carbothermal reduction. For this purpose experiments of FEG-SEM, XRD and Raman spectroscopy are carried out and data about crystalline quality, phase, morphology and presence of structural defects was obtained.

Methods and Results

For this work, it was synthesized microstructures of antimony trioxide (crystals and belts) by using

carbothermal reduction method combined with the vapor-solid (VS) mechanism. In this method a carbon source is mixed with the precursor aiming reduce MO_x phases so that the synthesis can be carried out at lower temperatures. The carbothermal reduction is a process essentially dependent on temperature, pressure and synthesis time. So these parameters were carefully controlled during the growth as described as follow.

The source powder for the growth of the microstructures was obtained by mixing Sb_2O_3 powder (Sigma Aldrich, < 250nm particle size, > 99.9% purity) to the graphite (Sigma Aldrich, < 500nm particle size, > 99.9% purity) in a proportion of 95:5 in weight. In order to reduce the particle size and obtain a homogeneous mixture, these powders have undergone a grinding process for 60 h in a balls mill. The mixture was placed inside an alumina crucible and inserted into the center of an alumina tube reactor positioned inside a horizontal tubular furnace (Lindberg/Blue M). The alumina was sealed and the chamber was purged with nitrogen gas (flux). After purging the growth chamber the N_2 flux was adjusted to 50 sccm which was maintained for the entire synthesis. The furnace was heated to 950°C (heating rate of 8°C/min) and this temperature was maintained for 10 minutes and then it was cooled down to room temperature.

Morphological characterization of the samples were performed by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) TESCAN, model MIRA 3.

Raman Spectroscopy e X-Ray Diffraction (XRD) were also performed for structural characterization of the as-synthesized samples.

The Raman measurements were taken by using a Horiba LabRAM HR Evolution spectrometer in backscattering geometry configuration and the samples were excited by a 514.5 nm line of an Ar⁺ laser at room temperature. The experimental settings were adjusted to present a spectral resolution of 2 cm^{-1} . Raman spectroscopy measurements were performed in the samples by using two different configurations: with parallel and crossed polarization in the Micro-Raman mode of analysis.

XRD measurements were performed by using Panalytical X'pert Pro diffractometer with Cu $\text{K}\alpha$ radiation at wavelength of 1.5418 Å.

FEG-SEM micrographs of the as-grown samples are depicted in Figure 1.

Figure 1. FEG-SEM images of Sb_2O_3 microstructures of (a) region 1 and (b) region 2 of furnace.

As we collected samples in different parts of the growth chamber we characterized then by X-Ray diffraction (Figure 2) and data on crystalline quality and the phase of the samples were obtained.

Figure 2. X-Ray diffraction pattern (a) microcrystals and (b) microbelts of Sb_2O_3 .

As it is a non-destructive powerful tool to characterize materials Raman spectroscopy was used for structural characterization of samples. The spectra obtained for the synthesized structures can be viewed in Figure 3.

Figure 3. Raman spectra taken at 300K for a single (a) cubic microcrystal and (b) a single orthorhombic microbelt of Sb_2O_3 showing the main features expected these structures.

The spectrum of each phase unambiguously shows the expected phonon modes for the cubic and orthorhombic phase of Sb_2O_3 (panels 3a and 3b, respectively).

Discussion

Figure 1 shows the micrograph of the as-grown Sb_2O_3 samples which were collected from different regions of the growth chamber: a transparent material was collected in region 1 ($510^\circ\text{C} < T < 440^\circ\text{C}$) and a yellow wooly-like material was collected in region 2 ($760^\circ\text{C} < T < 630^\circ\text{C}$). Figure 1a shows the morphology and sizes of samples collected in region 1. It can be seen that samples lengths ranges from 400 to 950 micrometers. Samples have very well-defined faces which can be an evidence of good crystalline quality. The morphology of these samples seems to be like that reported by Cebriano et al [25]: structures with dendritic growth in which triangular and pyramidal crystallites acts as building blocks.

The structures showed in Figure 1b were grown in the hotter region of furnace (region 2). The

micrographs presented in Figure 1b shows that the samples produced are branched microbelts: the main trunk consisting of a thick belt of rectangular section with short branches arising from its surface. The branches have varying thickness; some of them are as thick as the trunk and give rise to new branches while others are much thinner than the main structure. This indicates that the formed branches evolve continuously along with the primary structure in a very similar way of that structures reported previously by Fan et al [22]. The length of the trunk and the thicker branches ranges from 3.4 to 25 microns while the thinner branches have length ranging from 0.5 to 2.4 microns. It is possible to observe small spheres on all the belts and branches. The origin of these spheres has not been yet fully understood, but they do not play an active role in the nucleation of new branches.

The X-Ray pattern showed in the Figure 2a for the microcrystals collected in region 1 of growth was indexed as the cubic phase of Sb_2O_3 (PDF 01-072-1334; space group: Fd-3m). The narrow and sharp peaks are an evidence of the growth of single crystalline structures with high crystalline quality. In addition, it is possible to verify that the peak corresponding to the plane (222) is of the highest intensity, indicating that growth occurs along a preferential direction.

Figure 2b shows the diffractogram of the branched microbelts grown in region 2 of the furnace and these samples were indexed as the orthorhombic Sb_2O_3 (PDF 01-071-0383; space group: Pccn). The observation of narrow and well defined peaks observed in the diffractogram indicates the samples have high crystalline quality. Non-assigned peaks in the pattern are associated to be the phase of antimony trioxide which we believe to be related to the microspheres grown on the surface as reported in previous works [25]. It is further noted that the peak related to plane (200) is the most intense in the pattern indicating that the microbelts grow along a preferential direction.

Raman spectroscopy measurements were performed in the as-grown samples at 300 K (Figure 3).

The spectrum for a single microcrystal grown in region 1 presents narrow and sharp peaks for both polarization configurations and unambiguously indicates samples are high quality single crystals. The peaks observed in 88, 123, 194, 259, 360, 377, 455 and 716 cm^{-1} are a fingerprint of the cubic (Fd-3m) Sb_2O_3 structures with symmetry T_1 , E , T_2 , A_1 , E , T_2 , A_1 and T_2 , respectively, as reported previously [26-28]. No significant change is observed in the spectrum of Sb_2O_3 cubic samples when the polarization is changed. This is an indicative of the absence of structural defects in the sample. Raman scattering is strongly dependent on electron-phonon interactions so that the presence of structural

defects affects the properties of the material resulting in changes in Raman spectra peaks [29].

Therefore, we believe this is a sample with low amount of defects and high crystalline quality.

Raman spectrum of a single branched microbelt is depicted in Figure 3b. The spectra obtained in both polarization configurations correspond to the orthorhombic phase of antimony trioxide [7, 30]. Raman selection rules were tested in samples grown in orthorhombic phase and this analysis showed that spectra change, including the disappearance of a peak at 487.8 cm^{-1} and the appearance of a peak at 441.2 cm^{-1} , when the orientation changes from crossed to parallel polarization configuration. This is a true evidence of the break of Raman selection rules.

It is known that Raman selection rules are strongly affected by the presence of structural defects in the crystal structure [31]. Such defects affects Raman spectroscopy in three different ways: I) breaking the selection rules of the wave vectors that define the momentum values allowed for the phonons in the whole the Brillouin zone; II) reduction in local symmetry so that Raman selection rules are no longer strictly prohibited by reducing the distinction between active and inactive Raman modes; III) local modes of vibration can be introduced into the lattice and become Raman active.

On the other hand, we know that oxygen vacancies are the main defects type observed in TCOs [32,33]. This defects type could be identified in Sb_2O_3 photoluminescence spectra: the vacancies can recombine with electrons and give rise to an emission band in 2.92 eV [19]. In fact, defect levels associated with oxygen vacancies in orthorhombic Sb_2O_3 phase were identified from this technique [35, 36].

Thus, we believe that the change in the spectra of the orthorhombic phase of antimony trioxide is due to defects in its structure such as oxygen vacancies. This result indicates that these structures can present interesting new electronic features which are desirable for applications in electronic devices and certainly deserve attention in the future.

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