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Morphological, microstructural, and photoluminescence characterization of heterogeneous/homogeneous TeO_2 nanostructures based on effect of different N_2 gas flow rates

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ABSTRACT

TeO_2 nanowires with diameters ranging from a few tens to hundreds of nanometers and lengths of a few tens of micrometers were prepared by thermal evaporation of Te powder with a Co catalyst. Initially, bead-like γ-TeO_2 nanoparticles on the surface of pre-formed thick TeO_2 nanowires were heterogeneously formed. Subsequently, uniform thin TeO_2 nanowires without the γ-TeO_2 phase were homogeneously synthesized by changing only the inlet N_2 gas flow rates and keeping other process parameters constant. The morphological and microstructural evolution of the two different nanomaterials was examined by X-ray diffraction, energy-dispersive X-ray spectrometry, and scanning and transmission electron microscopy. The optical properties of the nanomaterials were also investigated using photoluminescence spectroscopy. The emission peaks in the PL measurement without the supply of N_2 gas showed a synergetic effect between (1) bead-like orthorhombic γ-TeO_2 nanoparticles that show two specific emission bands at 388 nm and 590 nm; and (2) uniform tetragonal TeO_2 nanowires that show a characteristic emission band at 440 nm. In contrast, the pure tetragonal TeO_2 nanostructures synthesized under a N_2 gas flow rate of 2 standard liters per minute flow rate revealed a red-shifted emission band at 450 nm compared to heterogeneous structures of the same composition. The origins of the growth and emission mechanisms in the different TeO_2 structures are also discussed.

1. Introduction

γ-TeO_2, a metastable crystal, has an orthorhombic unit cell belonging to the space group $P2_12_12_1$ [1]. There are two different kinds of bonding between Te and O in γ-TeO_2, symmetric and asymmetric bridge structures, implying that disphenoids could be firmly deformed. Hence, γ-TeO_2 is a very promising candidate for non-linear optical applications [2–4]. In particular, γ-TeO_2 is formed as an independent phase in the first stage [3] before the crystallization of TeO_2, which is obtained from many synthetic routes, such as spray pyrolysis [5], rf reactive sputtering [6–8], sol-gel [9–11], and solution-based chemical techniques [12–16].

On the other hand, TeO_2 as a stable crystal has a tetragonal unit cell with space group $P4_12_12$ [17]. TeO_2 is a versatile semiconducting oxide because of its excellent optical properties for tunable filters [18], laser devices [9], modulators [19], optical storage [20], and deflectors [21]. Jiang et al. [22] fabricated tellurium dioxide nanorods having uniform size distribution in a hot air atmosphere via laser ablation. Lecomte et al. [11] proposed that TeO_2 thin layers based on sol-gel processes can be developed via dip-coating and heat treatment, by controlling the reactivity of tellurium alkoxide.

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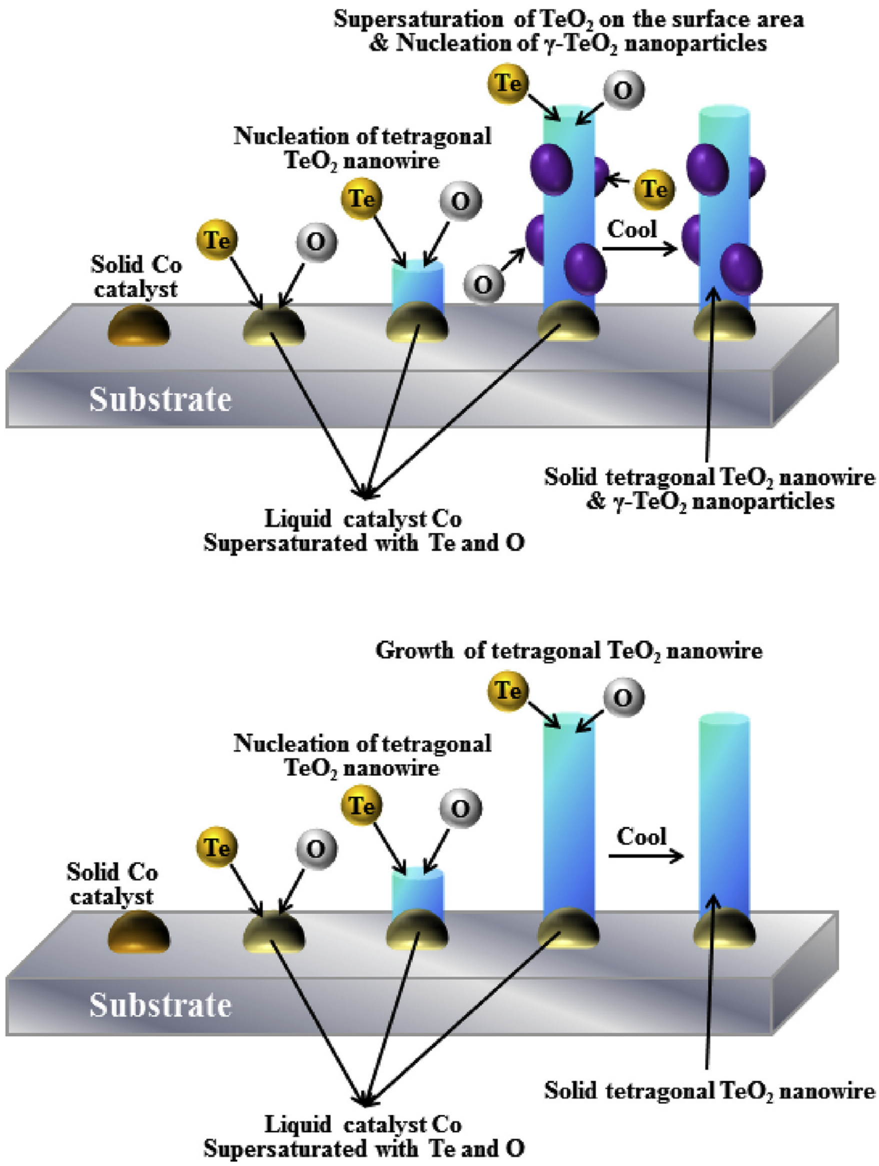

Fig. 1. Schematic diagram of the evolution of mixed γ-TeO_2 with TeO_2 (upper image) and only TeO_2 (lower image) nanostructures during the thermal evaporation process.

Vinogradov et al. [23] suggested that single crystal TeO_2 with a large diameter of up to 60 mm can be grown via the Czochralski technique in specially designed setups. Huriet et al. [24] reported that titanium additives enhanced the aspect ratio and crystallization of TeO_2 crystals at low temperature.

Usually, TeO_2 is one of the wide band-gap semiconducting oxides (i.e., ~4.05 eV) [25] including both orthorhombic and tetragonal structures as described above. However, so far hybrid nanostructures of two different kinds of TeO_2 has not been synthesized because most of TeO_2 microstructures have a tendency to transform into stable tetragonal-structured TeO_2. Nevertheless, it is very important to form the hybrid nanostructures for synergetic interaction and extraordinary interface reaction of two different components. To the best of our knowledge, there are no reports on the morphology, microstructures of the different phases of TeO_2-based nanostructures that coexist, and their optical properties. This study reports the synthetic conditions and dimensional properties of γ-TeO_2 and TeO_2 nanostructures using different N_2 flow rates, from 0 to 2 standard liters per minute (slm), along with their photoluminescence (PL) characteristics.

2. Experimental

Two different types of TeO_2 nanostructures based on the vapor-liquid-solid (VLS) mechanism were synthesized in a vertical tube furnace. For the thermal evaporation process of source materials, incident Te powders (300 mg, 99.99%, Sigma-Aldrich) were positioned on the lower holder. A piece of Si substrate (3 cm × 3 cm, p-type Si (100)) with a 3 nm-thick cobalt (Co) film, pre-deposited by ion sputtering, was placed on the upper holder. The distance of the two points from the N_2 gas entrance to the upper holder is approximately 50 cm. The process temperature was increased to 450 °C at a heating rate of 10 °C/min and maintained there for 1 h. The internal flow rate was gradually controlled by flowing high-purity N_2 gas at 0, 0.5, 1, and 2 slm, without any extra reaction gas, to obtain an influx effect from only the carrier gas. After completing the product synthesis, the supply of N_2 gas was stopped and the temperature of the furnace was decreased to room temperature. Finally, light-white colored TeO_2 samples were collected.

X-ray diffraction (XRD, glancing angle, 0.5°) was performed using a Philips X'pert MRD diffractometer (Cu K_α radiation) for