Structural Evolution and Room Temperature Stabilization of Bi_2O_3 Polymorphs

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Abstract

We report the structural evolution sequence from β-Bi_2O_3 → γ-Bi_2O_3 → α-Bi_2O_3 at the expense of metallic Bi nanoparticles (NPs) simply by annealing in the air. The room temperature (RT) stabilization of metastable β- and γ-Bi_2O_3 NPs is confirmed using synchrotron radiation powder X-ray diffraction and Raman spectroscopy. All the annealed samples with different crystalline phases exhibited strong red-band emission peaking around 700 nm and covering around 60-85 % integrated intensity of photoluminescence spectra. Our findings suggest that the RT stabilization of β- and γ-Bi_2O_3 is mediated by reduced surface energy and oxygen ion vacancies.

Keywords - β-Bi_2O_3, γ-Bi_2O_3, α-Bi_2O_3, XRD, Raman scattering, PL, XPS, oxygen vacancies, carbon species.

Introduction

Recently Bi_2O_3 semiconductor has attracted enhanced research interest from both fundamental and research points of view due to its wide optical bandgap energy (Eg) (1.4 eV to 3.99 eV) [1]. However, the wide range of Eg is severally affected by nine different crystalline phases of Bi_2O_3 (α, β, γ, δ, ω, ε, η, ζ and R) [2-10]. The five (β, γ, ε, ω, η) out of nine polymorphs are metastable phases which invite the main challenge in the syntheses and characterization of pure targeted phase. In this study, we shed light on the air annealing induced oxidation of Bi nanoparticles (NPs) to different polymorphs of Bi_2O_3 and investigate their structural and optical properties. The various Bi_2O_3 annealed samples were thoroughly characterized using sensitive probes, such as synchrotron radiation powder X-ray diffraction (PXRD), Raman scattering, UV-Vis, photoluminescence (PL), and x-ray photoelectron spectroscopies (XPS).

Experiments

To investigate the evolution in the structural and optical properties of Bi_2O_3 with T_A, the air annealing of Bi nanoparticles (prepared by physical vapor deposition PVD) was carried out at various temperatures starting from 50 °C to 800 °C at a step of 50 °C (total 16 samples) for a duration of 2 h.

Results

Fig. 1 depicts stacked PXRD spectra over a narrow scattering range 2θ (from 13° to 16°) with the increase of annealing temperature T_A from 0 °C to 800 °C (bottom to top), where 0 °C corresponds to Bi NPs. From 0 °C to 100 °C, a diffraction peak (10-2) indexed based on R-3m reveals the existence of pure Bi and at 150 °C, Bi becomes thermally unstable due to which additional diffraction peak (201) indexed based on P-42_1c of the β-Bi_2O_3 appeared. At 250 °C, a pure β-Bi_2O_3 formed (green spectra). Annealing from 300 °C to 450 °C leads to the appearance of additional weak diffraction peaks (310) and (120) indexed based on I23 and P12_1/c1 of the γ- and α-Bi_2O_3, respectively. The intensity of γ-Bi_2O_3 increases with T_A and at 550 °C, a pure γ-Bi_2O_3 formed (blue spectra). At 700 °C, a strong α-Bi_2O_3, weak γ-Bi_2O_3, and an unknown Bi_2O_3 phase appeared which we coined as x-Bi_2O_3. Further annealing up to 800 °C leads to suppression of α-Bi_2O_3 and the enhancement in x-Bi_2O_3. Furthermore, the increase of T_A broadening of diffraction peak decreases suggesting annealing induced grain growth possibly due to melting and nucleation. The Rietveld refinement of the above spectra shows the presence of oxygen vacancies in all the samples.

Discussion

The formation of RT stable β- and γ-Bi_2O_3 at 250 °C and 550 °C is significantly lower than the previously reported temperatures. However, so far why the air annealing of Bi NPs results in the formation of β- and γ-Bi_2O_3 over RT stable α-Bi_2O_3? and the reason behind their RT stabilization is remaining unanswered. From the PXRD, we may depict a phase transformation sequence Bi → β-Bi_2O_3 → γ-Bi_2O_3 → α-/x-Bi_2O_3. In our fining the RT stabilization of oxygen-deficient β-Bi_2O_3 is attributed to a finite size effect induced reduced surface energy. The surface energy can reduce further by the absorbed carbon species as evident from surface-sensitive XPS measurements. Annealing at higher temperatures leads to the vaporization of carbon-containing species. Hence apart from the size-effect induced reduces surface energy the oxygen vacancies may have played a significant role in the RT stabilization of γ-Bi_2O_3. Further annealing leads to the formation of micro-sized crystalline oxygen-deficient α/x-Bi_2O_3. The obtained phase transformation from PXRD is consistent with the Raman scattering. From the literature and our experimental findings using PXRD, Raman scattering, and observed strong red-band emission in PL it appears that along with the finite-size effect oxygen vacancies play an important role in both structural stabilization and phase transformation within various Bi_2O_3 polymorphs which will be discussed further at the time of presentation.

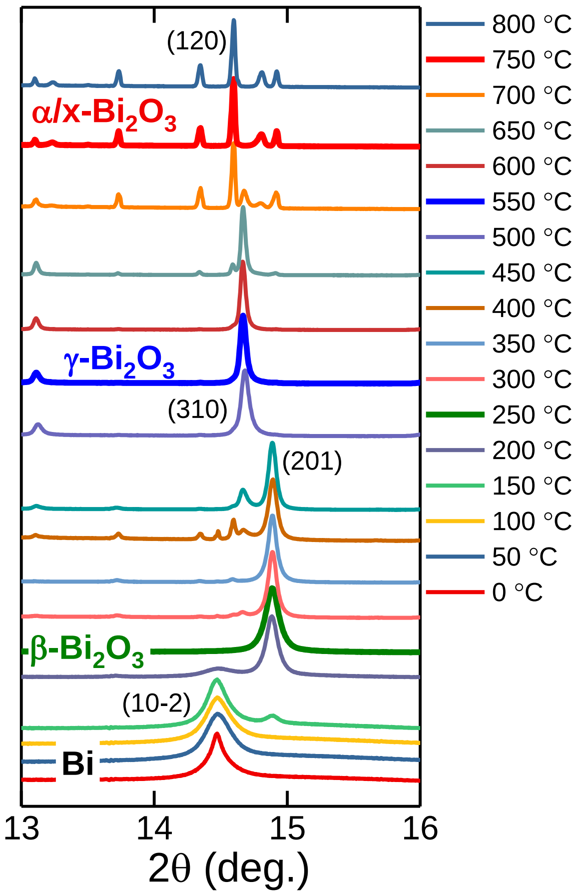

Fig. 1 Stacked PXRD plot with the increase of TA from 0 °C to 800 °C (bottom to top). 0 °C corresponds to Bi NPs.

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