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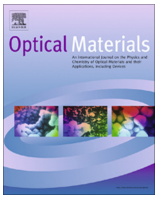

Role of annealing temperatures on structure polymorphism, linear and nonlinear optical properties of nanostructure lead dioxide thin films

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ABSTRACT

The powder of as synthesized lead dioxide (PbO_2) has polycrystalline structure β-PbO_2 phase of tetragonal crystal system. It becomes nanocrystallites α-PbO_2 phase with orthorhombic crystal system upon thermal deposition to form thin films. Annealing temperatures increase nanocrystallites size from 28 to 46 nm. The optical properties of α-PbO_2 phase were calculated from absolute values of transmittance and reflectance at nearly normal incidence of light by spectrophotometer measurements. The refractive and extinction indices were determined and showed a response to annealing temperatures. The absorption coefficient of α-PbO_2 films is $>10^6$ cm^{-1} in UV region of spectra. Analysis of the absorption coefficient spectra near optical edge showed indirect allowed transition. Annealing temperature decreases the value of indirect energy gap for α-PbO_2 films. The dispersion parameters such as single oscillator energy, dispersion energy, dielectric constant at high frequency and lattice dielectric constant were calculated and its variations with annealing temperatures are reported. The nonlinear refractive index (n_2), third-order nonlinear susceptibility ($\chi^{(3)}$) and nonlinear absorption coefficient (β_c) were determined. It was found that $\chi^{(3)}$, n_2 and β increase with increasing photon energy and decrease with increasing annealing temperature. The pristine film of α-PbO_2 has higher values of nonlinear optical constants than for annealed films; therefore it is suitable for applications in manufacturing nonlinear optical devices.

1. Introduction

Lead dioxide is the highest known oxide of lead, which is one of metal oxides that has important applications in various industries because of its distinguished properties such as good conductivity, cheap, high stability and relatively long cycle life. Since Planté [1] invented the rechargeable lead-acid batteries in 1860, the lead dioxide, PbO_2, has been widely used as active material on positive electrode of lead-acid batteries due to its utility in many electrochemical processes.

Applications of PbO_2 are expanded to include different fields in modern technology such as optoelectronic devices [2], solar cells [3], gas sensors [4], optical energy storage devices [5] and batteries [6]. Recently, it is used in the new generation of nanostructured devices such as dye-sensitized solar cells [7], quantum-dot sensitized solar cells [7] and perovskite solar cells [8]. The first polycrystalline thin film lead oxide applied in a rectifying Schottky barrier junction photovoltaic device was demonstrated by Darbe et al. [9].

The PbO_2 is found in three polymorphs; the maroon-colored β-PbO_2 has a tetragonal crystal system called rutile structure [10,11], the darkish brown-colored α-PbO_2 with an orthorhombic crystal system called columbite structure [10,11] and a third polymorph of PbO_2 exists only at high pressures [12] and has a cubic crystal system.

Fig. 1(a) and (b) illustrates the unit cells of the α and β phases of PbO_2. In both polymorphs, the tetravalent lead ion is in the center of a distorted octahedron surrounded by six oxygen ions. The polymorph structure is based on the same oxygen octahedral but the main difference is in the arrangement of the octahedral hole in the crystal structure; specifically, in the way of how the octahedral hole is packed. In α-PbO_2 polymorph neighboring octahedral holes share non-opposing edges as zig-zag chains (Fig. 1(c)). In β-PbO_2 the neighboring octahedral holes share opposite edges, which results in the formation of linear chains of octahedral holes (Fig. 1(d)). The resulting chains are connected with each other by sharing corners for both α- and β-PbO_2 polymorphs [11,13].

α-PbO_2 can transform into β-PbO_2 under normal conditions (room temperature and ambient humidity) [14]. This has been

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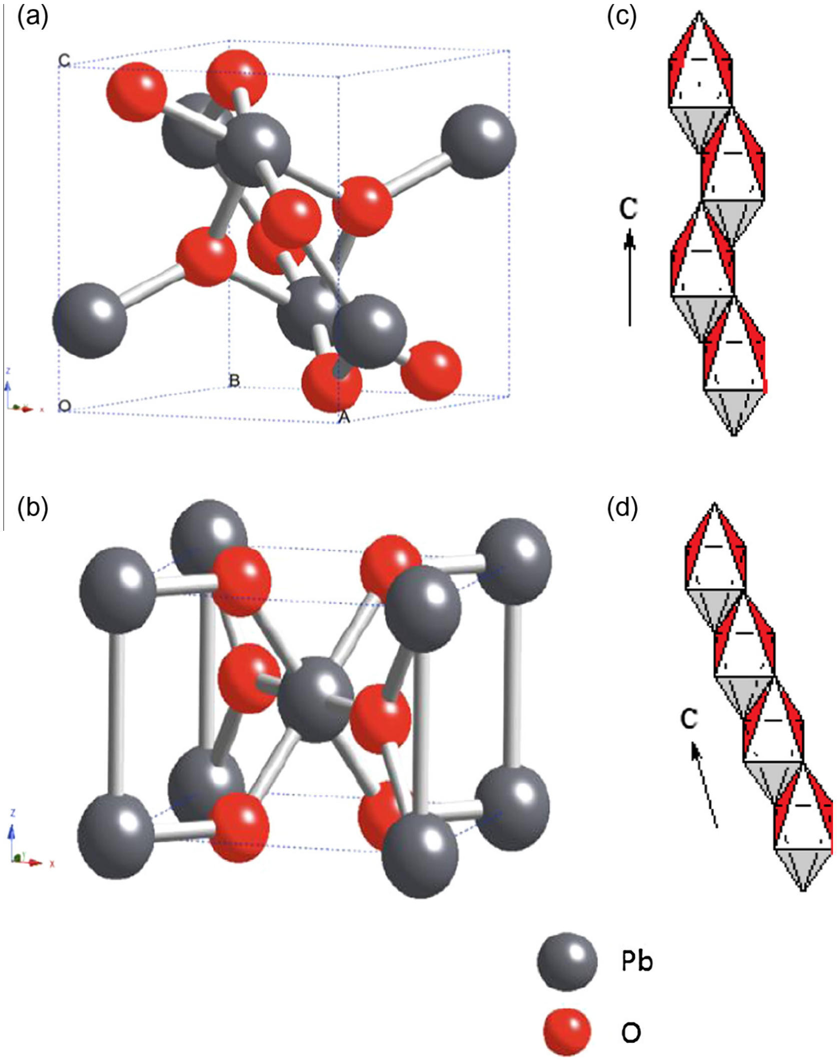

Fig. 1. The crystal structure of polymorphs of PbO_2: (a) orthorhombic α-PbO_2, (b) tetragonal β-PbO_2, (c) α-PbO_2 packed as octahedral zig-zag chain and (d) β-PbO_2 packed as octahedral linear chain.

explained in terms of the stable β-PbO_2 recrystallizing on the superficial layers of the metastable α-PbO_2 crystals [15]. White et al. [14] reported that β-PbO_2 could undergo an irreversible phase transition to form α-PbO_2 under high pressures. The mechanisms of formation of α-PbO_2 and β-PbO_2 in aqueous phase have been studied in the field of electrochemistry [13,16]. Bagshaw et al. [16] suggested that the nucleation energy barrier determines the pathway for forming the specific PbO_2 phase from oxidation of Pb(II) in solution. It is well known that the crystal structure of PbO_2 deposits on substrates depends on the pH of electroplating solution [15] or temperature [17]. α-PbO_2 is obtained from bases while β-PbO_2 is obtained from acids [1,13]. α-PbO_2 undergoes a phase transition to β-PbO_2 at 489 °C and the pure α-PbO_2 phase can be obtained only at temperatures range 240–290 °C [17].

Perry and Wilkinson [18] have reported a new method to synthesize α-PbO_2 using quartz glassware. Torabi and Razavi [19] have synthesized β-PbO_2 by hydrothermal method. The synthesized α-PbO_2 has a more compact structure than β-PbO_2 resulting in better contact between the particles but that compact structure of α-PbO_2 makes it more difficult than β-PbO_2 used in lead-acid batteries [20]. However, Rüetschi [21] showed that α-PbO_2 has a higher catalytic activity than β-PbO_2. Zhao et al. [22] studied the behavior of PbO_2 thin films prepared by metalorganic chemical vapor deposition. Eftekhari [23] reported the fabrication of a pH sensor based on lead oxide thin films prepared by chemical deposition. The electro-crystallization of lead oxide thin film was reported by Saez et al. [24] and Shen and Wei [25] studied the morphological behavior of electrochemically grown PbO_2 thin films.

Thin film deposition technology using thermal evaporation deposition technique is relatively simple and suitable for industrial scale deposition and this technique allows an automatic controlling and monitoring of the deposition rate and film thickness. A number of parameters exist that influence the properties of the films such as the deposition rate, temperature of the vapor atoms, angle of incidence of vapor atoms, substrate and source material distance, substrate temperature and the composition of the ambient atmosphere [26].

Even though several studies report on the characterization of lead oxide films produced by different techniques including pulsed laser-assisted deposition [27], electro-deposition [28] and reactive RF magnetron sputtering [29]. However, most of these studies have concerned with β-polymorph for PbO_2. In the present study, characterization of α-PbO_2 polymorph films produced by thermal evaporation technique is presented as well as a systematic investigation on the impact of annealing temperatures on the structure, morphology, linear and nonlinear optical properties of α-PbO_2 thin films is reported.