



The variation of E_g -shape dependence of NiO nanoparticles by the variation of annealing temperature



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ABSTRACT

Nickel oxide (NiO) nanostructures were synthesized by thermal decomposition of pre-synthesized $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanowires at three annealing temperatures (T_a): 400, 600, and 800 K. Since bandgap energies depend on the structures' size and shape, resulting from the synthesis method, the effect of magnetic exchange energy on the optocrystalline structure of NiO was investigated. X-ray diffractometry, field-emission scanning electron microscopy, Fourier transform infrared spectroscopy, ultraviolet-visible spectrophotometry, and vibrating sample magnetometer were employed to study the influence of calcination temperature on morphological and optical properties of the obtained NiO nanostructures. The bandgap energies of the NiO nanocrystals were calculated ~ 3.35 , 3, 1.55 eV for the annealing temperatures of 400, 600, and 800 K, respectively, suggesting the significant decrease in the bandgap of the sample calcined at 800 K. Next, an attempt was made to resolve the controversy related to the decrease of lattice constant, strain and bandgap of NiO and the increase of crystallite size when the annealing temperature increases. The mechanism behind the effect of annealing temperature on the geometrical shape and optical character of the obtained NiO was supposed to be a consequence of magnetic exchange energy. The mechanism was considered concerning the antiferromagnetic phase transition below and above the Neel temperature of NiO that is $T_N = 525$ K. Below T_N (i.e., $T_a = 400$ K), NiO nanowires (with a flaky shape) are formed, resulting in a strong UV absorption and a longer range of hysteresis loop. A little above T_N (i.e., $T_a = 600$ K), the magnetic energy is released, resulting in the decomposition of nanowires to irregular shapes and a lower UV absorption with a broader peak and a shorter range of hysteresis loop. High above T_N (i.e., $T_a = 800$ K), NiO nanoparticles are formed in aggregation, and there occurs no significant change in the magnetization as compared to the sample annealed at 600 K.

1. Introduction

One of the most important parameters in semiconductor physics is the bandgap energy [1]. Producing semiconductor materials with small dimensions and narrow bandgap energies is very important in developing research on photovoltaic, photocatalytic, and dye-sensitized solar cell technologies. Narrowing bandgap energies allows low-energy absorptions and excitations for the effective operation of wide-gap semiconductors under UV and solar light irradiation [2]. Several factors contribute to the bandgap narrowing, such as temperature [3], doping and alloying [4], pressure, lattice volume [2], defects [5], etc. On the other hand, studies of materials in nanoscale require the characterization of microstructure with an emphasis on the particle's size and microstrain. Because, lattice strain plays a crucial role in properties of nanoparticles and can effectively tune their optical, electrical and mechanical properties [6].

NiO is a charge-transfer insulator [7] that has a cubic (NaCl type)

structure [8]. The performance of NiO in applications depends on its crystalline phase state, dimension, and morphology [9–12]. Therefore, it is very important to control the powder property during the preparation process. The preparation method, especially the temperature, has an extreme influence on the properties of NiO [13]. NiO is an attractive material due to its applications in various fields such as catalysis [14], electrochromic films [15], electrodes of electrochemical capacitors [16], electrodes of Li-ion batteries [17], and p-type transparent conducting films [18], etc. Bulk NiO usually presents a non-stoichiometric, Ni-defect structure and shows a wide-bandgap p-type semiconducting behavior (3.6–4 eV) [15,19]. Although the exact origin, nature, and size of the fundamental gap of the nickel monoxide (NiO) has been subjected to debate for many years among both experimentalists [20,21] and theorists [22–24], the insulating properties of NiO, both below and above its Neel temperature ($T_N = 525$ K), have not been well-understood yet. Achieving a narrower bandgap for NiO could be useful for various applications. For example, a reduced

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bandgap can provide a higher photocatalytic activity under solar light for NiO structures, and the highly stable material could play a more significant role both for photocatalytic degradation of organic molecules and photocatalytic evolution of hydrogen. Moreover, it can affect the mechanism behind the action of NiO in catalysts, batteries, and supercapacitor through influencing on its highest occupied molecular orbital and lowest unoccupied molecular orbital. It could also play a significant role in the field of electrochromic material, that is reversible modulation of optical properties under applied electrical fields.

So far, various values for the bandgap energies of NiO have been reported depending on their preparation method, size, shape, etc. Bandgap energies reported experimentally for NiO were in the range of 2.8–4.2 eV [25–28]. Due to the well-known fact that semiconductors with nanoscale size show a blue shift in their absorption spectra due to the quantum confinement effects [29], the energies less than those of bulk NiO have been reported for NiO nanostructures. However, in many papers, the bandgap narrowing and its reasons have not been well-discussed [30–33], and several reasons have been reported such as the increase of crystallinity [34], chemical defects or vacancies present in the intergranular region [35], impurity levels introduced during deposition [36], transformation from amorphous to crystalline phases, and doping other elements [37]. Values less than 2.8 eV have never been experimentally reported for pure NiO bandgap energies; however, Alidoust et al. [38] have theoretically shown that the bandgap dramatically decreases to ~ 2.0 eV (the optimal bandgap for PC applications) when NiO is alloyed with Li_2O .

Although the value of E_g effectively depends on the size, shape and synthesis method, it seems that magnetic exchange energy also plays an important role. Here it is a question whether direct exchange J_{ij} or super exchange J_{i-O-j} dominates. Since, anti-ferromagnetism is a consequence of two main theoretical descriptions: (i) the first one arises from the strong-exchange between localized unpaired - atomic electrons attributed to " J_{ij} " of exchange interaction on nearby ion resulted in strength of internal magnetic field H_{im}^{ex} , and (ii) the second description developed by the Fermi-liquid state results from the strength of hybridization ended to the mixing of s-d orbital states in a direction to decrease T_N by emerging of spin density wave.

Here, $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanowires were prepared by a hydrothermal reaction, and the nanowires were calcined at three temperatures of 400, 600, and 800 K to obtain NiO nanostructures, and to study the effect of calcination temperatures. Next, we conducted a study on morphological, optical, and magnetic properties of the NiO structures. We calculated mean crystallite sizes of the obtained NiO nanostructures from their X-ray diffraction patterns by using the Williamson-Hall method and by considering the effect of microstrain. The fracturing of NiO nanowires (into flaky shapes) and their growth along the diameter occurs as calcination temperature increases. The calcination

temperature strictly affects the bandgap energy. Although the bandgap energy is expected to increase as the annealing temperature increases, here it is surprisingly decreased. The main goal of the article is to discuss the observation based on the range of magnetic exchange interaction, which results in the Weiss molecular field.

2. Materials and methods

All the chemicals used in our experiments were of reagent grade and used without further purification. The synthesis method was inspired by other work [34,39]. First, 0.715 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98.0%, Sigma-Aldrich) was dissolved in 23 mL deionized water in a beaker, stirred with a magnetic stirrer at room temperature until a transparent solution was obtained. Next, 0.189 g of $\text{Na}_2\text{C}_2\text{O}_4$ (99.0%, Samchun Chemicals) was added gradually to the solution while stirring. Then, 1.5 g polyethylene glycol ($M = 20000$, Merck) and 40 mL ethylene glycol ($\geq 99\%$, Merck) were added to the mixture, respectively. The mixture was then stirred at room temperature for 30 min. The mixed solution was then transferred into a 75 mL Teflon-lined stainless steel autoclave, sealed and maintained at an oven for heating at 180°C for 12 h and then it was allowed to be cool to room temperature naturally. The resulting blue-green precipitate was separated by centrifugation (8000 rpm) and washed with deionized water and ethanol five times. After that, it dried at 60°C in a vacuum oven for 10 h. Finally, the sample was divided into three parts for calcination at different temperatures of 400 K, 600 K, and 800 K for 2 h and they were named as samples (a), (b), and (c), respectively. The calcined products had different colors of dark gray, light gray, and green for samples (a), (b), and (c) respectively, and they were then collected for analysis.

The size and phase purity of the products were characterized using an X-ray diffractometer (XRD, Philips, X'Pert MPD) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The chemical structure information of the products (as KBr pellets) was collected by a Fourier transform infrared spectrometer (FTIR, Nicolet 680). Morphologies of the products were studied using a field-emission scanning electron microscope (FESEM, Hitachi S-4160). Ultraviolet-visible (UV-Vis) absorption spectra were obtained by a Unico 4802 UV-vis spectrophotometer in the range 200–1000 nm. Vibrating sample magnetometer (VSM, MDK-Magnetics) was employed to measure magnetic hysteresis loops of the samples.

3. Results and discussion

The XRD pattern of the $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanowires as NiO precursor is shown in Fig. 1A. Moreover, Fig. 1B (a, b, and c) show the NiO structures synthesized by thermal decomposition of nickel oxalate nanowires in the ambient air at three annealing temperatures ($T_a = 400, 600, \text{ and } 800 \text{ K}$), and all of them were attributed to the cubic crystalline structure of NiO.

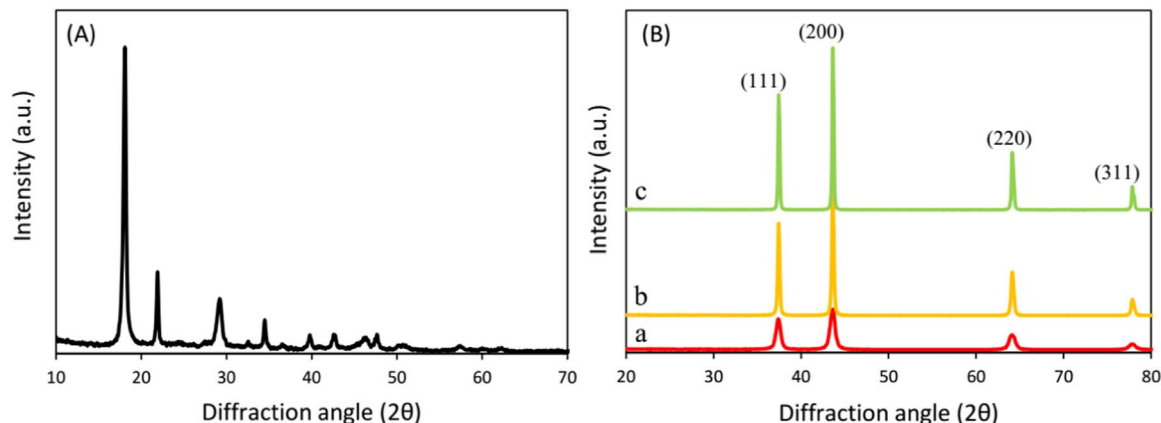


Fig. 1. (A) XRD pattern of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanowires as NiO precursor. (B) XRD patterns of NiO nanostructures obtained by annealing the precursor at (a) 400 K, (b) 600 K, and (c) 800 K.

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