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Synthesis of ZnO nanoparticles using Ball milling method

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ABSTRACT

Zinc oxide nanoparticles are fabricated using Ball milling method. For the synthesis of these nanoparticles, 99.9% pure zinc oxide powder is milled for 40 hours. Transmission electron microscopy is employed to study the microstructure of these nanoclusters. It is seen from the transmission electron microscope (TEM) images that the nanoparticles of ZnO are aggregated and form nanoclusters. The diameter of these nanopaticles varies from 5-10 nm, whereas the diameter of these nanoclusters is of the order of several tens of nanometers. The X-ray diffraction technique is used to verify the structure of these synthesized zinc oxide nanoparticles. From the XRD pattern, it is suggested that these nanoparticles are crystalline in nature. The UV visible spectrum shows a broad peak at 380 nm, which is a characteristic of ZnO.

Key words: Synthesis of ZnO nanoparticles, Ball milling method.

INTRODUCTION

Zinc oxide (ZnO) is a direct wide bandgap (3.37 eV) semiconductor with a large excitation binding energy (60 meV). ZnO-based nanoscale materials have received increasing attention over the past few years due to their potential applications in optoelectronic switches, high-efficiency photonic devices, near-UV lasers, and assembling complex three-dimensional nanoscale systems[1-6]. ZnO nanostructures are fabricated by various methods, e.g. Arc discharge, Laser ablation, Pyrolysis, Electrodeposition, and chemical or physical Vapor deposition[7]. However, the most popular method to produce ZnO nanostructures involves a Vapor transport process which is based on a so-called vapor–liquid–solid (VLS) mechanism of anisotropic crystal growth. Many studies have been made on the synthesis of 1D ZnO nanostructures by direct decomposition of ZnO powder at a high temperature of 1400°C[8,9] or carbon thermal reduction of ZnO powder at temperatures in the range 880-1100°C[10-12]. Although the ZnO nanostructures fabricated using the above methods have a high-purity and high-crystalline structure, but the growth temperature is too high to make them compatible with low-temperature endurance substrates such as glass. Therefore, we need a low-temperature, large-scale, and simple synthetic process for the synthesis of ZnO nanostructures, which can be used for nanoscale devices. Recently, the synthesis of ZnO nanostructures in low-temperature range (lower than 600^{o}C) has received much attention as it is more compatible with microelectronics processing. Various methods have been developed to produce ZnO nanorods[13-14]. The ball milling method is one of the well known methods for producing the nanostructures of inorganic materials such as boron nitride (BN) nanotubes[15]. It has become a successful method for the large scale production of nanostructures for commercial use. Both nanostructures size and structures can be controlled. The ball milling method has been adopted by many research groups in synthesis of different nanostructures since it was first reported in 1999[15,16].

Recently, the researchers are using a new ball milling technique i.e. high-energy ball milling (HEBM), which is quite different from the traditional ball-milling technique. There are some major differences between conventional ball milling and the high-energy ball milling. The impact energy of HEBM is typically 1000 times higher than the conventional ball milling energy. The main jobs of the conventional ball milling is the particle fracturing and size reductions, which correspond only to the first stage of the HEBM. In high energy ball milling, a longer milling time is generally required to activate and complete the structural changes and chemical reactions and to control the milling atmosphere and temperature which are crucial to produce the desired structural changes or chemical reactions. HEBM can perform most of the work normally performed by conventional ball milling. Therefore, conventional ball milling system cannot be used directly to conduct any HEBM work and specially designed ball mills with a higher milling energy are preferred for HEBM.

Using new HEBM technique, many new meta-stable materials have been successfully produced. These new meta-stable materials cannot be synthesized using thermal equilibrium processes in past several decades[17,18], for example, amorphization of ZrNi alloys under a dynamic equilibrium between mechanical driven disordering or amorphization process and thermal reordering process[19], mechanical alloying of nanocrystalline compounds, nanoparticle-reinforced metal nanocomposite[20-22], and nanoporous materials[23]. Using controlled reactive ball milling, the researchers have produced nanosized particles of metal oxides[24], nitrides[25], hydrides[26] and carbides[27] at room temperature. Therefore, keeping in view of importance of this high energy ball milling method, we have also used this method to synthesize the ZnO nanoparticles in the present work.

EXPERIMENTAL

ZnO nanoparticles are synthesized using high energy ball milling method. Here, ZnO powder (99.999 % pure) is milled for 40 hours in 250 ml stainless steel jar using 10 balls. Powder X-ray diffraction (XRD) is performed by a Regaku X-ray diffractometer Ultima IV with Cu K-b radiation. The microstructure of these nanoparticles are studied using a transmission electron microscope (TEM) performed at 100 kV. UV–Vis absorption spectrum is recorded using a V-570 Shimadzu UV–Vis double-beam spectrophotometer. The scanning wavelength range is 200-800 nm. In this experiment, we have successfully grown the ZnO nanoparticles using ball milling method.

RESULTS AND DISCUSSION

It is observed from the TEM image (Fig. 1) that the nanoparticles of ZnO are aggregated and form nanoclusters. The typical diameter of these nanoparticles is in the range of 5 to 10 nm, whereas the diameter of the nanoclusters is of order of several tens of nanometers. The typical X-ray diffraction (XRD) pattern of these nanoparticles is presented in Fig. 2. The X-ray diffraction pattern suggests that as-deposited ZnO nanoparticles are crystalline in nature. From the XRD data, the lattice constants of the ZnO nanoparticles are calculated as a = 0.32501 nm and c = 0.52107 Å, which are very close to the reported values (a = 0.32539 nm and c = 0.52098 nm) in JCPDS card No. 80-0075. All of the diffraction peaks can be perfectly indexed to typical hexagonal structure of ZnO, not only in the peak position but also in relative intensity. The strong intensity and

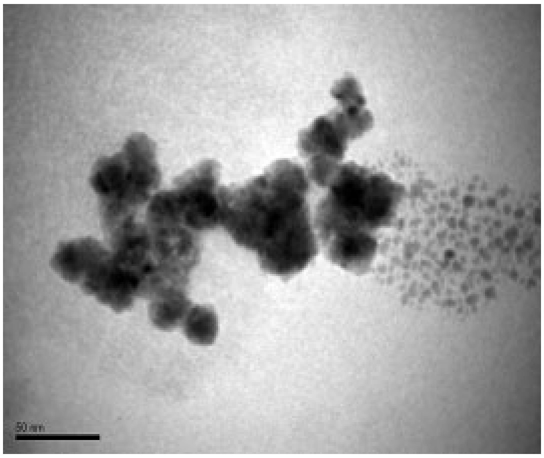

Fig. 1: TEM images of as grown ZnO nanoclusters

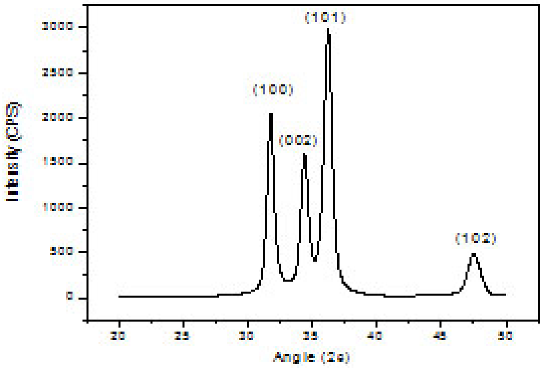

Fig. 2: XRD spectra of as grown ZnO nanoclusters

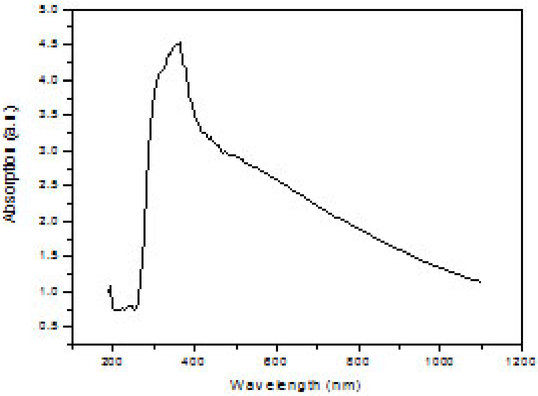

Fig. 3: UV visible spectra of as grown ZnO nanoclusters

narrow width of ZnO diffraction peaks indicate that the as-prepared nanoparticles are of high crystalline quality. No diffraction peaks of Zn or other impurities were found in the synthesized products.

The above experimental results show that high energy ball milling plays an important role in the formation of these crystalline ZnO nanoparticles. Therefore, the understanding of the role of ball milling is necessary for the formation mechanisms and controlled production of ZnO nanoparticles. In the process, material particles are repeatedly flattened, fractured and welded during the high energy ball milling. Every time two steel balls collide or one ball hits the chamber wall, they trap some particles between their surfaces. The high-energy impacts rigorously deform the particles and create atomically fresh, new surfaces, as well as a high density of dislocations and other structural defects[28]. Such a high defect density can accelerate the diffusion process[29]. Furthermore, the deformation and fracturing of particles cause continuous size reduction and lead to reduction in diffusion distances. This can at least reduce the reaction temperatures significantly, even if the reactions do not occur at room temperature[30-32].

Fig. 3 shows the room temperature absorption spectra of ZnO nanoparticles. The absorption spectra have a very narrow peak near the band edge in the exciton absorption region (at about 380 nm). This may be due to near-band-edge emission (NBE), which is originated from the recombination of free-exciton through an exciton–exciton collision process. Whereas the green emission, also known as deep-level emission appears due to the radial recombination of a photo-generated hole with a singly ionized charge state of the specific defect (oxygen vacancies)[33-34]. It is generally understood that the green emission is responsible for structural defects, oxygen vacancies, interstitials of zinc, impurities, etc.[35-36]. In the present work, the appearance of a sharp and strong intensity NBE emission with out green emission shows that these nanorods are highly crystalline with superior optical properties. These as-grown ZnO nanoparticles produced by high energy ball milling methode are quite interesting for nano-optoelectronic devices in near future due to the excellent optical properties.

CONCLUSION

From the above studies it is concluded that the highly crystalline nanoparticles of ZnO are successfully produced using high energy ball milling method. These nanoparticles are aggregated and form nanoclusters with the diameter of the order of several tens of nanometers. The X-ray diffraction pattern suggests that as-deposited ZnO nanoparticles are crystalline in nature. The diffraction patterns are indexed to a typical hexagonal structure with unit cell constants of a = 0.32501 nm and c = 0.5207 nm, which are very close to the reported values (a = 0.32539 nm and c = 0.52098 nm) in JCPDS card No. 80-0075. From the absorption spectra, a band peak at 380 nm is accountable for near-band-edge emission (NBE), which is originated from the recombination of free-exciton through an exciton–exciton collision process.

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