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Enhanced mechanical properties of yttrium doped ZnO nanoparticles as determined by instrumented indentation technique

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ABSTRACT

Yttrium doped (1, 3 and 5 wt%) zinc oxide nanoparticles were synthesized via sol-gel process. The phase, structural and mechanical properties were investigated using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and micro hardness based on indentation technique. The lattice parameters and grain sizes of the samples were calculated from the XRD data. As the lattice parameters increased, the grain sizes decreased dramatically, resulting in more grain boundaries and strong grain connectivity in the ZnO microstructure. Load-depth curves were obtained by applying indentation loads in the range from 400 to 2000 mN at room temperature. As the Y concentration increased, a significant increase was observed in the hardness values computed from loading-unloading curves using the Oliver and Pharr method. The indentation modulus of the samples reached a saturation value for 3% Y and then decreased as the doping rate increased. Moreover, the crack formation around the indent on the sample surface was examined by electron microscopy and was identified as radial/median type. The fracture toughness of the samples was calculated using the Vickers indentation fracture method. Increased fracture toughness values confirm that ZnO nanoparticles are mechanically strengthened by Y doping.

1. Introduction

In recent years, much attention has been dedicated to the use of semiconductors in integrated circuit applications in various areas. Among various metal oxide semiconductors, considerable research has been focused on ZnO because of its unique physical, chemical, magnetic, electrical, optical, piezoelectric, and mechanical properties. Many devices such as solar cells, power generators, laser diodes, light emitting diodes, transducers, actuators, and sensors have been developed using these properties [1–9]. In addition, with the discovery of biocompatibility in this semiconductor material, ZnO-based biosensor devices gained intense attention in both scientific and biomedical research due to their potential applications [10]. ZnO nanostructures are produced in different forms such as nanoparticle, nanorod, nanowires, nanofiber, nanobelt, and nanocomb for use in various applications. Many methods exist to obtain these structures including sol-gel [11], hydrothermal synthesis [12], RF sputtering [13], chemical vapor deposition [14], pulsed laser deposition [15], and electrodeposition [16]. All of these methods have both advantages and disadvantages depending on the experimental process. Among these methods, sol-gel is one of the most suitable methods for producing nanoparticles distributed uniformly in powder form. In addition to synthesis methods, mechanical properties also play an important role in the integration of nanostructured ZnO with the applications mentioned above. ZnO has high electromechanical coupling, resulting in strong piezoelectric and pyroelectric properties, which make this material ideal for mechanical applications [17]. It is well known that the mechanical properties can be improved by introducing impurities into the lattice and by a sintering process, which affects the microstructure of the materials. To our best knowledge, although there are several studies on the structural, optical, electrical and magnetic properties of Y doped ZnO, no report has been published on the mechanical properties of this material. In the present paper, changes in the mechanical properties of ZnO with Y doping have been investigated in detail by indentation technique. Instrumented indentation is widely used in determining mechanical properties and is also considered to provide more accurate and precise results compared to static indentation technique. By analyzing the load-depth curves obtained from an indentation test, it is possible to evaluate mechanical properties including hardness and indentation modulus. Furthermore, the indentation fracture (IF) method, which is extensively

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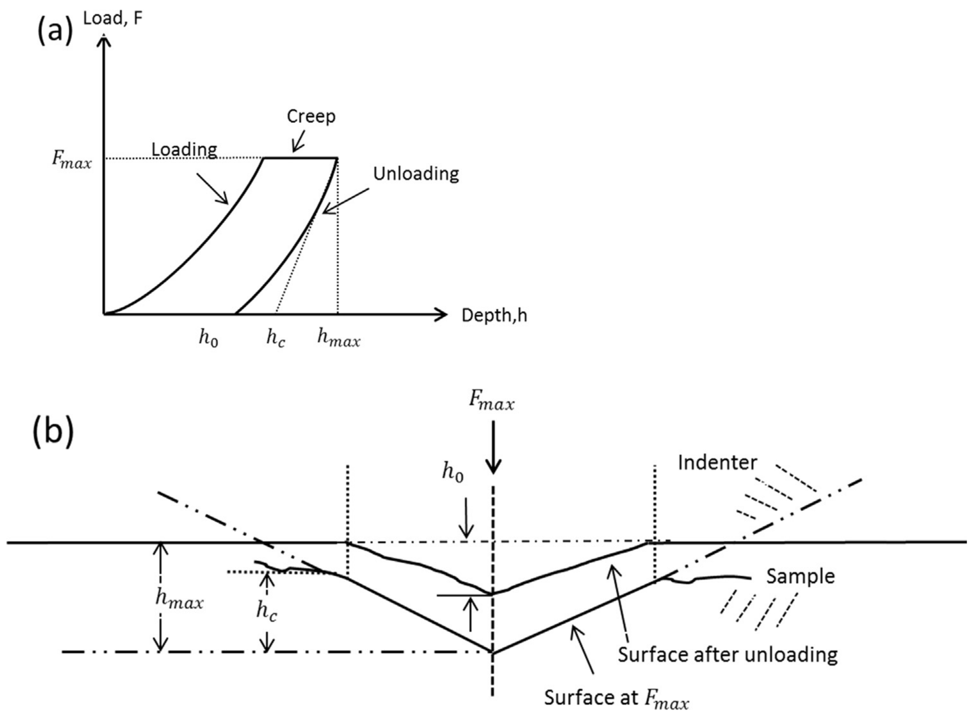

Fig. 1. (a) Schematic representation of indentation load- contact depth curve (b) A cross-sectional view of an indentation.

reported in the literature, was used for assessing fracture toughness as well as examining crack initiation and propagation on the sample surface [18].

2. Background

In conventional indentation techniques, a test load is applied to the sample surface and measurements are taken after the indenter is removed from the surface. However, the effects of elastic deformation are not observed correctly. In the instrumented indentation technique, which we have used in this study, mechanical parameters can be calculated by considering both the load and depth during plastic and elastic deformation, and there is no need to measure the diagonal of the indentation imprint with an optical system [19]. In 1992, Oliver and Pharr developed a method for measuring the hardness and elastic modulus of materials from a loading-unloading curve [20]. By using this method, the hardness and elastic modulus can be determined more accurately and precisely compared to static indentation techniques. A typical load-depth curve and a cross-sectional view of an indentation are shown in Fig. 1.

According to Fig. 1(a), the loading part can be expressed as

$$F = Ch^m \tag{1}$$

where F is the applied load, h is the contact depth, and C and m are constants related to the geometry of the indenter tip (Fig. 1(b)). The value of the exponent m for cones is 2 [20]. The fitted unloading curve is given by

$$F = a(h - h_0)^m \tag{2}$$

where h_0 is the final contact depth, and a and m are fitting parameters related to the geometry of the indenter tip. The contact stiffness is obtained from the derivative of the fitted unloading curve as expressed below [21]

$$S = \left|\frac{dF}{dh}\right|_{F_{max}} = ma(h - h_0)^{m-1} \tag{3}$$

and the contact depth can be written as

$$h_c = h_{max}\mathscr{E}\frac{F_{max}}{S} = h_{max}\mathscr{E}\frac{F_{max}}{dF/dh} \tag{4}$$

where F_{max} is the maximum load and $\mathscr{E}$ is the contact model parameter, which is 0.75 for the Vickers indenter [22]. In the case of hard material indentation, the indenter deformation can be taken into account by considering the reduced modulus determined from the slope of the unloading curve at maximum load as given below

$$E_r = \frac{\sqrt{\pi}}{2\beta\sqrt{A_c}} \tag{5}$$

where A_c is the area of the indent imprint and β is a contact model parameter [23]. From equation (5), the indentation modulus can be expressed as

$$\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-v_i^2}{E_i} \tag{6}$$

where E and v are Young's Modulus and Poisson's ratio for the sample, while E_i and v_i are the same parameters for the indenter; hence, the hardness is

$$H = \frac{F_{max}}{A_c} \tag{7}$$

where F_{max} is the maximum applied load and A_c is the area of the indent imprint.

3. Experimental method

Y doped ZnO nanoparticles were synthesized by a sol-gel route. Zinc acetate dihydrate (Zn $(CH_3COO)_2{\cdot}2H_2O$, Merck), and yttrium acetate tetrahydrate ($Y(CH_3CO_2)_3{\cdot}4H_2O$, Alfa Aesar) were used as precursor materials. Precursors were of analytical grade and were used without further purification. HPLC grade methanol (Merck) was used as solvent, and monoethanolamine (Merck) was used as sol stabilizer. In a typical synthesis, 0.25 M methanolic precursor solution was prepared, stirred, and aged for 24 h. Aging solutions were then dried in ambient atmosphere to form the gel. Once all the solvent was evaporated, gels were heat treated at 400 °C for 10 min to burn the organic material and at