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Acetone sensing property of ZnO quantum dots embedded on PVP

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ABSTRACT

We report synthesis of ZnO quantum dot embedded in polyvinylpyrrolidone (PVP) matrix and its functioning as acetone sensor. The specimen is prepared via quenching technique where bulk ZnO powder is calcined at very high temperature of 1200 °C and then quenched into ice cold polyvinylpyrrolidone solution. The samples have been characterized by using UV/vis spectroscopy, X-ray diffraction study, high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). These studies infer the sizes of quantum dots to be within 10 nm. The prepared quantum dot samples have been tested for sensing acetone vapour by exploring the variation of their resistance with time at different operating temperatures. It has been revealed that ZnO quantum dots can sense acetone at low operating (230 °C) temperature with less response time.

1. Introduction

Preparation of semiconductor quantum dots and their applications as electronic switch, optical detector, various kinds of sensors, etc. are the frontier research areas at present [1–6]. Recently, different techniques [1–4] like molecular beam epitaxy (MBE), radio frequency sputtering (RF), liquid phase epitaxy (LPE), quenching, etc. are adopted to synthesize semiconductor quantum dots. But due to manifold advantages [3,6] viz. like simplicity, low cost, etc. quenching method draws the interest of recent researchers. In this article, we discuss preparation of ZnO quantum dots on polyvinylpyrrolidone (PVP) matrix (which embeds the quantum dots) by quenching method and study of their acetone vapour (gas) sensing behaviour which is a new and original work. The advantage of PVP over other polymer matrices viz. PVA (polyvinyl alcohol) is that circular and uniformed quantum dots can be fabricated on PVP. The prepared samples have been analysed by different characterizing methods to reveal their nano-natures [2]. These studies infer the formation of quantum dots within the dimension of 10 nm. Next, acetone sensing property of ZnO sample (i.e. ZnO quantum dots embedded in PVP) has been examined by exploring the variation of sample resistance with time in the presence of acetone vapour [7]. Gas/vapour sensing property of semiconductor is purely a surface phenomenon [7–19]. That is why, low dimensional specimen possessing large surface area is suitable for this purpose. Earlier, acetone sensing of ZnO microstructure has been reported where the sensing starts at 300 °C [13]. In another work, it has been revealed that acetone sensitivity in semiconductor microstructures increases with higher doping concentration of impurity like cobalt [17,19]. Further, Sahay reported acetone sensing by ZnO thin film but it is of long response and recovery time [18]. In the present work, it has been experimentally observed that undoped ZnO quantum dots embedded in PVP matrix can act as gas sensor with lower operating temperature (230 °C), with less response and recovery time. Thus, testing of ZnO quantum dots for acetone sensing, which has not been focused in any report earlier, is interesting, and technically very important.

2. Materials and methods

To synthesize [3] ZnO quantum dots by quenching method, 3 g of ZnO powder (99.99% pure, E Merck) is calcined at ∼1200 °C for 10 h and then quenched into 4 wt% aqueous solution of polyvinylpyrrolidone (PVP) matrix (99.9% pure, E Merck) kept at ice cold temperature followed by its moderate stirring (∼175 rpm). This solution contains ZnO quantum dots embedded in polyvinylpyrrolidone (chemical structure is shown in Fig. 1). The film is developed on the laboratory glass slides by placing a few drops of ZnO quantum dot solution (embedded in PVP) on a clean slide and stretching over it by another clean slide.

3. Results and discussion

ZnO specimen has been characterized by UV/vis optical absorption spectroscopy (Perkin Elmer Lamda 35 1.24), X-ray diffraction study (Bruker AXS, X-ray source: Cu K_a, where a is alpha in Greek

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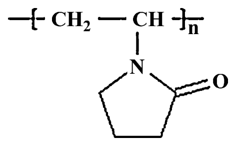

Fig. 1. Chemical structure of PVP.

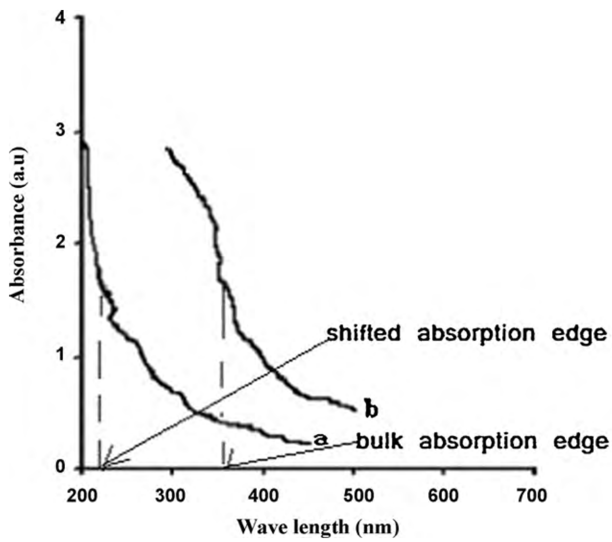

Fig. 2. UV/vis absorption spectra of ZnO specimen: (a) quantum dots and (b) bulk.

character) and high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) (JEM 1000 C XII).

Optical absorption spectroscopy [6] shows sharp blue shifted absorption edge of the prepared samples with respect to that of bulk (Fig. 2). Blue shift is a distinct signature of quantum dot formation [1,3,4] (Fig. 2a). By considering shifted absorption edge (at 210 nm) of ZnO sample, average crystallite (particle) size has been estimated and found to be 10 nm by using the following hyperbolic band model [5].

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m*(E_{gn}^2 - E_{gb}^2)}} \quad (1)$$

where R is the quantum dot radius (2R is the diameter and hence the particle size), E_{gb} is the bulk band gap, E_{gn} is the quantum dot band gap (calculated from the sharp absorption edge which is 210 nm as shown in Fig. 2a), h is the Planck's constant, m^* is the effective mass (29.15×10^{-31} kg for ZnO).

Similarly, from X-ray diffraction study (Fig. 3) average particle size (crystallite size) is calculated by using Debye–Scherrer formula [2] $D = 0.9\lambda/W\cos\theta$, '$\lambda$' is the wave length of X-ray (0.1541 nm), 'W' is FWHM (full width at half maxima), 'θ' (theta) is the glancing angle and 'D' is particle diameter (crystallite size). Considering all the peaks [3] (2θ in degree) in the X-ray diffractogram, the average crystallite (quantum dot) size has been assessed and found to be 9 nm. Further, by analyzing the X-ray diffractogram with the help of ICDD (International Center Diffraction Data) it has been revealed that ZnO quantum dots are "wurtzite" in structure. HRTEM images of PVP film, ZnO quantum dots and SEM image of ZnO quantum dots are shown in Fig. 4(i-a), (i-b) and (ii), respectively. It is evident in the HRTEM image of Fig. 4(i-b) that ZnO crystallites (quantum dots) are circular in shape with sizes within 10 nm.

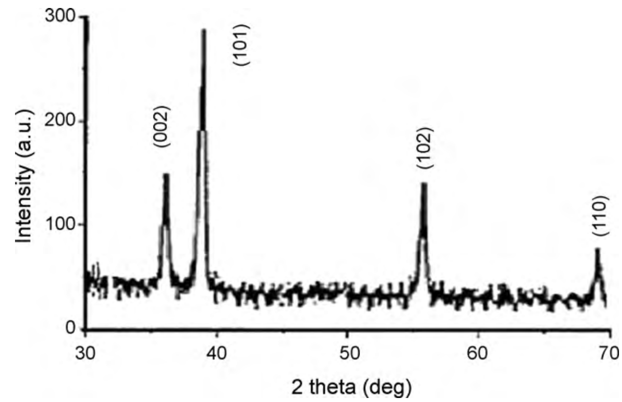

Fig. 3. XRD spectra of ZnO quantum dots.

ZnO sample sizes assessed from these three studies are well matching, which is a distinct advantage over earlier reports [2,3]. This matching occurs due to the formation of well uniformed and circular shaped quantum dots by using PVP matrix instead of PVA (polyvinyl alcohol) matrix [3]. All these characterizations infer that ZnO quantum dot sizes (diameter) are within 10 nm.

4. Acetone sensing

To test acetone sensing, ZnO sample is mounted on a two-probe assembly placed in sample holder into a silica tube which is inserted coaxially inside a tubular furnace. The furnace temperature is controlled within ±1 °C and the temperature variation over the length of the sample is found to be within ∼±1 °C. A known volume (parts per million, in short "ppm") of acetone is put with the help of a micro-syringe into the closed silica tube. The electrical resistance of the sample is measured before and after exposure to acetone using a Keithley System Electrometer (Model: 6514). The sensing response of ZnO quantum dots is determined at different operating temperatures in the range 200–360 °C to various concentrations of acetone in air [9,10].

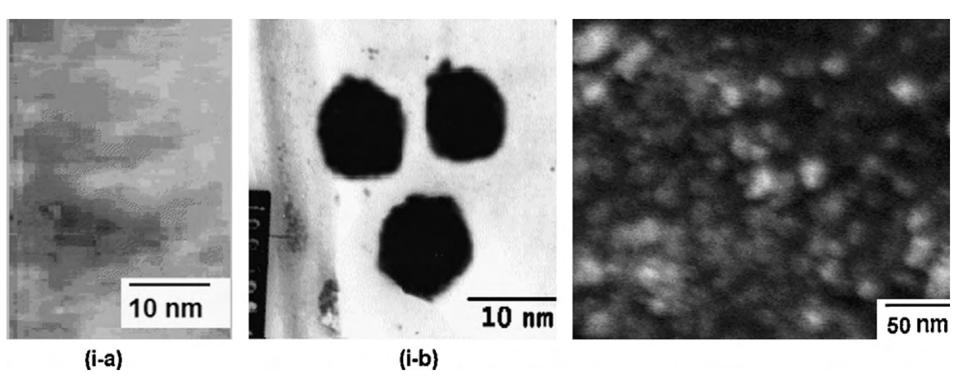

Fig. 4. (i-a) HRTEM images of PVP matrix. (i-b) ZnO quantum dots embedded in PVP. (ii) SEM image ZnO quantum dot surface.