Bandgap Engineering of ZnO Nanostructures through Hydrothermal Growth

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Abstract: ***The optical, electronic and magnetic properties changes with the reduction of particle sizes, this is because the nano sized structures exhibits certain unique properties different from their bulk counterpart. Bandgap engineering for nano structures is one of the prominent area of research now. All though the bandgap increases with the reduction in the particle size, however there are several other ways by which the band gap can be changed. Fast crystallization method has been reported here and is compared with the conventional method. Absorption spectra are obtained using UV-vis optical spectrometer and from the absorption spectra tauc plot is drawn to find out the band gap theoretically. The band gap of nano particles and nano rods grown with the same nano particles as seeds are found to be different. The work shows a comparative study on the resultant bandgap for ZnO nano particles and ZnO nano rods grown with hydrothermal method. It is observed that the fast crystallization method results in decreases of band gap by around .8 eV compared to conventional method.***

Keywords:ZnO, nano particle, nano rod, bandgap

1. Introduction

Light is being considered as an attractive option for data transmission for advantages such as low loss, high bandwidth etc. To build up an effective communication system using light as an information carrier, the development of highly sensitive photo detectors has become essential. Development of photo detectors sensitive to narrow bandwidth can facilitate data transfer over narrow channels that can lead to high throughput. Enhancement of photodetector efficiency parameters are now in the fore front of research. Nanostructures are attractive as detecting elements owing to their large surface area to volume ratios allowing higher absorption of impinging photons. The bandgap of wide band gap semiconductors can be effectively tailored to allow high absorption at a particular bandwidth. Typical materials that have been widely studied as photodetectors, are zinc oxide[1], tin dioxide , Titanium dioxide [2] etc. The bandgap can be controlled through techniques like doping, where some foreign atoms are included into the crystal lattice of the parent semiconductors or by incorporating intentional defects into the crystal of the detecting element through rapid crystallization [1,3]. Phodetection characteristics of metal oxide nano rods, nano belts etc. have been reported by several researchers [1,4] and came up with interesting results which shows superior sensitivity to light. Similarly, the other morphologies such as nano needles, nano flowers etc. can also be considered for comparative study. There are several synthesis method for metal oxide nanostructures like chemical precipitation, sol-gel synthesis, gas phase synthesis, hydrothermal synthesis, etc.[5]. However the hydrothermal synthesis will be promising alternative [6] as it has several advantage over other processes such as use of less expensive equipments, environmental friendly, less hazardous and low temperature operation, easy control of morphology, etc.

Photodetectors are used to covert light energy to electrical energy [7]. When photon energy falls on the sensing materials which are mainly semiconductors, electron hole pairs are generated. These charge carriers can be pulled through circuit under voltage bias to constitute current. When no light falls than the current in the circuit is minimum which is called dark current. Photodetectors are mainly photodiodes and phototransistors[8]. Figure 1. shows a schematic diagram of a photodetector circuit and its respective V-I characteristic with and without illumination. Upon illumination the photocurrent increases exponentially with the applied voltage following the relation,

$$I = I_0 e^{\alpha t} \qquad (1)$$

where, α is the absorption coefficient of the sensing material.

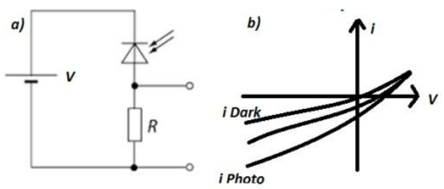

Figure 1: a) Schematic circuit diagram of a photodetector.
b) Current versus voltage response in dark and photon

As mentioned earlier, apart from size controlled bandgap tailoring there are other methods for bandgap engineering such as doping, fast crystallization etc. With these methods the effects states are created which subsequently changes the bandgap.

As shown in figure 2, by doping the ZnO nanoparticle with the transition metals such as, manganese (Mn^{2+}) and copper (Cu^{2+}), the band gap of 3.37eV of ZnO can be reduced to 3 eV and 2.5 eV respectively [9,10].

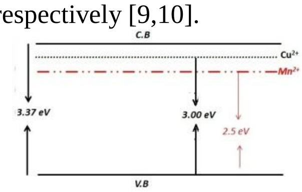

Figure 2: Band structure after doping ZnO with manganese and cooper

Fast crystallization is another popular method used to create defect states in crystals [**Error! Bookmark not defined.**]. In conventional hydrothermal method the nano particles are prepared through convectional currents developed resulting from heating on a hotplate, where the reaction rate is slow. However instead of hot plates microwaves (~2.5 GHz) can also be used for creating local hotspots through high frequency oscillations of the water dipole. This results in very fast crystal growth which increases the possibility of creating defect states within the bandgap.

The fundamental absorption which corresponds to electron excitation from the valance band to conduction band can be used to determine the value of the optical band gap. The relation between absorption coefficient (α) and the incident photon energy ($h\upsilon$), described by Tauc, is used for the calculation and it is given as

$$(\alpha h\mu)^{\frac{1}{n}} = k(h\upsilon - E_g) \qquad (2)$$

and α can be calculated from the following relation,

$$\alpha = \frac{2.303\ A}{t} \qquad (3)$$

Where, α is the absorption coefficient in cm^{-1}, h is Planck's constant, υ is the frequency of incident light, k is constant, E_g is the band gap of the material, A is the absorbance, t is the sample thickness or the length of light path through the sample (cuvette) and the value of n depends on the transition. It has a value of ½ for direct allowed transition, 2 for indirect allowed transition, 3/2 for direct forbidden transition and 3 for indirect forbidden transition. The value of optical band gap of the material is obtained by extrapolating the straight line portion of $(\alpha h\upsilon)^2$ versus (hυ) plot to the (hυ) axis. The intercept in the (hυ) axis, for α=0, gives the value of band gap.

2. Experimental

2.1 Synthesis of ZnO nanoparticles

For ZnO nano particles 20 ml of 4mM zinc acetate with ethanol as solvent is rigorously stirred at 60^0 C for an hour on a hot plate. The solution is then diluted with another 20 ml of fresh ethanol. Under mild continuous stirring at room temperature 20 ml of 4mM sodium hydroxide is added drop wise and stirred for 30 minutes. The mixture is then kept in water bath for 3 hours at 60^0C. After that the mixture is cooled to room temperature.

2.2 Fast Crystallization of ZnO nanoparticles

The same chemicals and procedure is used for fast crystallization as described in sec. II. A. However here instead of a hot plate, a microwave oven is used for heating and stirring purpose. The oven was used in defrost mode and heating was carried out for 15 minutes.

2.3 Synthesis of ZnO nanorods

Nano rods are grown in sealed chemical bath containing equimolar solution of zinc nitrate hexahydrate and hexamethylenetetramine. Before growing the nano rods the nano particles obtained using conventional method were seeded in a glass substrate. For seeding purpose the glass substrate is dipped in the solution for 15 minutes and then heated at 150^0C for another 15 minutes. This process is repeated for 3 times. Before each dipping in the solution the loosely attached nano particles are washed away from the substrate using deionized water.

The seeded substrate is arranged in such a way that the seeded side is placed upside down inside a petri dish. Than 30 ml of each of 10 mM zinc nitrate hexahydrate and 10 mM hexamethylenetetramine solution is poured in the petri dish. The arrangement is kept in hot air oven at 90^0C. The solutions are changed after 5 hours and kept in the oven for another 5 hours. After that the substrate is heated at 250^0C for annealing to remove organic deposits.

3. Characterization

For characterization UV-VIS spectrometer (ELICO SL - 159) is used and absorption spectra is obtained. The band gap was measured using Tauc's plot. Plotting software Origin was used to plot the Tauc's plot.

4. Result & Discussion

A thin white colored solution is obtained for ZnO nanoparticles grown with conventional method. The absorption spectra of the nano particles is obtained using UV-VIS optical spectrometer. The spectra is shown in figure 3. a. Figure 3. b. shows the tauc plot that provides the band gap of the nano particles.

It is seen from the figures that the absorption peak is found to at 259 nm and the band gap obtained from the tauc plot is around 4.76 eV.

The resultant solution for fast crystallization was more transparent compared to the conventional method.

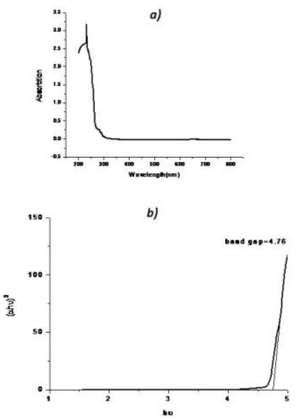

Figure 3: a) Absorption spectra b) tauc plot of ZnO nano particle using conventional method.

The absorption spectra is found using UV-VIS spectrometer and from the spectra the tauc plot is drawn as shown in figure 4. a) and b). As seen from the spectra and the tauc plot the absorption peak is around 300 nm and the band gap is 3.92 eV. As fast crystallization creates defects in the atomic structure of the nano particles, the band gap reduced compared to the conventional method.

For characterizing ZnO nano rods the substrate has been cut as the size of the cuvette and is observed with UV-VIS spectrometer by taking reference as another clean glass substrate. However the results were not satisfactory as space between the cubate wall and the substrate were also absorbing some light. So the rods were scraped away from the substrate and the spectra is obtained using the UV-VIS spectrometer. The absorption spectra and the tauk plot is shown in figure 5. a) and b). It is found that compared to conventionally grown nano particles the band gap of the nano rods prepared from the same nano particle increased by around 1 eV. It can be understood that, since the rods were annealed at high temperature for around one and half hours, the defect states came out of the structures for which higher bandwidth has been obtained.

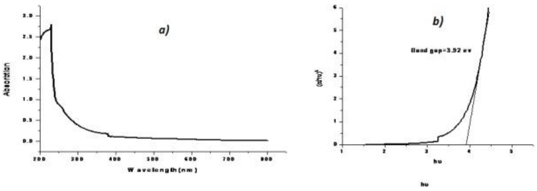

Figure 4:a) Absorption spectra b) tauc plot of ZnO nano particle using fast crystallization method.

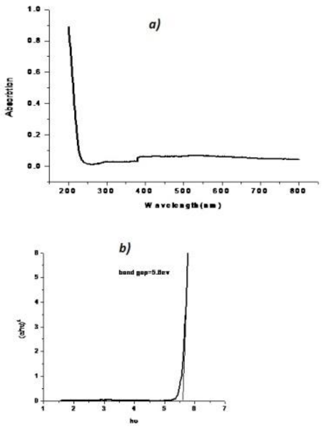

Figure 5:a) Absorption spectra and b) tauc plot of ZnO nano rod.

5. Conclusion

Band gap of nano structures can be tuned by several ways so that they can be used to detect specific wavelengths. The work here shows that fast crystallization of the ZnO nano particles creates defects in the crystal structure and as a result reduces the band gap by around .8eV compared to conventional crystallization. Further, the annealing of ZnO nano rods under high temperature reduces defects and the band gap increased up to 5.8 eV. Thus, in a hydrothermal growth process, the bandgap can be controlled through variations in growth conditions.

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