SYNTHESIS OF P-TYPE ZnO FROM THE HIGH TEMPERATURE THERMAL TREATMENT OF BULK ZINC PHOSPHATE

K. MAHMOODa, M. I. ARSHADb, A. ALIb, M. A. NABIa, N. AMINA
M. ANWARc, M. ASGHARB
aDepartment of Physics, Government College University Faisalabad, Pakistan
bDepartment of Physics, The Islamia University of Bahawalpur, Pakistan

This paper demonstrated the synthesis of p-type ZnO by high temperature annealing of zinc phosphate powder. Zinc phosphate pellets were annealed in programmable furnace with 140 sccm oxygen flow rate at various temperatures (500 to 1000 °C) for one hour. XRD data confirmed that Zinc Phosphate orthorhombic phase completely converted into Zinc Oxide hexagonal phase at annealing temperature 800°C. It is argued that P-Zn bond was broken due to high temperature thermal annealing and oxygen atom gained enough thermal energy to replace the P atom in the lattice. Arrhenius plot (1000/T verses log resistivity) was drawn to calculate the dissociation energy of P-Zn bond which was found to greater than energy required to break P-Zn bond. PL data consists of neutral-acceptor emission of ZnO at 3.35 eV when annealed over 600°C but un-annealed sample has not showed any PL peak. Hall measurements were demonstrated the hole carriers in the samples annealed at 800, 900 and 1000°C. A representative Raman data measured at 800°C also verified the E2 (high) mode of ZnO along with p-related LVM at 342 cm⁻¹.

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1. Introduction

ZnO has very much potential to use in various electronic devices due to its superior properties of wide band gap and exciton binding energy when compared with its counterparts like GaN [1, 2]. These properties make ZnO an ideal candidate for the fabrication of UV light emitting diode, laser diode and sensors [3-5]. To realize such devices, n and p conductivity is essential, but literature suggested that stable p-type ZnO is very difficult to grow [6, 7]. There are different reasons published in the literature for this p-type doping difficulty for example formation of donor intrinsic defects such as oxygen vacancies and zinc interstitials in ZnO during growth, poor solubility of acceptors dopants and formation of deep acceptor levels in the band gap of ZnO [8-10]. Different techniques are being employed by the researchers to overcome this problem; for example Benoit et al grow N doped p-type ZnO which possessed p-type conductivity up to two years [11], Gao et al developed a new method for the growth of p-type ZnO nanowires by the decomposition of ZnP but failed to got stable p-type ZnO [12], Kao et al has also attempted to grow Sb doped p-type ZnO on Si (100) substrate by chemical vapor deposition [13]. Despite all these reports, still stable p-type ZnO is lacking which is core hurdle in the commercialization of ZnO based devices. Therefore much work still needed to produce stable p-type ZnO.

In this manuscript, we have used a different approach to synthesize the p-type ZnO. Zinc phosphate pellets were annealed at different temperatures from 500 to 1000°C in oxygen environment for one hour. At annealing temperature 800°C, oxygen atoms gained thermal energy to knock out the P atoms in the lattice and occupied their places and consequently form ZnO lattice. XRD, PL and Raman spectroscopy measurements confirmed the formation of ZnO hexagonal structure at annealing temperature 800°C. Hall measurements showed the p-type conductivity of transformed samples.

*Corresponding author: khalid_mahmood856@yahoo.com
2. Experimental Summary

Zinc Phosphate (99.99%) from Sigma Aldrich was used as starting material for the growth of p-type ZnO. Zinc Phosphate powder was pressed into pellets having 1mm thickness and about 8mm length using a hydraulic press using a high pressure of 13 ton. The pellets were then subjected to heat treatment using a programmable furnace. The pellets were annealed at various temperatures range from 500 to 1000 °C in oxygen environment with flow rate of 140 sccm for one hour. It is pertinent to mention here that flow rate, rate of heating and rate of cooling for samples was kept constant. The structural characterization of annealed samples was performed by X-Ray Diffraction by Rigaku having X-Ray source 1.54 Å. The room temperature PL measurements were performed by mini PL/Raman of Photon system USA having laser wavelength 248 nm. Hall data was collected using Hall Effect Ecopia 3000 which have 1.5 T magnetic field.

3. Results and discussion

3.1 XRD

The fig. 1 represents the XRD pattern of zinc phosphate pellets annealed at 500-1000°C in oxygen environment with step of 100°C in programmable furnace for one hour. The un-annealed sample (inset of fig. 1) consists of six peaks at angles 11.6, 18.9, 23, 37.8, 46.8 and 62° and related to (020), (220), (201), (102), (281) and (660) planes of orthorhombic crystal structure of Zn3(PO4)2.4H2O confirmed by comparing with JCPDS file no 74-2275. But after annealing all these peaks almost disappeared and a new strong peak appeared at 2theta angle 34.7° which is the characteristic peak of ZnO hexagonal (002) plane [14, 15]. It is also evident from the graph that peak intensity of (002) plane increases with annealing temperature up to 800 °C. The emergence of (002) ZnO confirmed our argument that ZnP phase transformed into hexagonal ZnO phase. We can explained the transformation mechanism as two step process; i. ZnP lattice gained enough thermal energy during annealing process therefore Zn-P bond dissociate ii. The oxygen replaced phosphorus atom in the lattice and P atom may diffused out of the sample and/or moved to inactive sites. We have calculated the dissociation energy of Zn-P bond by the slope of In (Resistivity) verses 1000/T plot [16] and demonstrated in figure 2. The measured value of dissociation energy was found to be 4.15 eV much higher than reported value of dissociation energy (1.41 eV) for Zn-P bond[17].

![Image of XRD pattern](image-url)

*Fig. 1 XRD pattern of annealed Zinc Phosphate pellets at different annealing temperatures from 500°C to 1000°C using a step of 100°C in oxygen environment for one hour. The inset shows the XRD spectrum of un-annealed Zinc Phosphate sample.*
3.2 PL

Fig. 2 shows the PL spectrum of zinc phosphate samples annealed at different temperatures in oxygen environment. The figure is evident that there is no PL peak for un-annealed and samples annealed at 600 and 700°C. But as the annealing temperature further increases; we observed a peak 3.35 eV which is related to neutral-acceptor-bound peaks and always found in P-doped ZnO [18, 19]. It is also evident from PL graph that 800°C annealed sample has maximum intensity of neutral-acceptor peak demonstrated that sample has high density of acceptor defects as compared to other samples. It is important to mention here that we observed this neutral-acceptor PL at room temperature confirming the presence of acceptor level even at room temperature. Generally this peak appeared at low temperature (10K) and disappeared at room temperature because all acceptor levels thermally ionized at room temperature and sample not more shows p-type conductivity [20].

![Image of Arrhenius plot](image1)

Fig. 2 Arrhenius plot of annealed samples. The slope of graph gives dissociation energy of Zn-P bond.

3.3 Hall Measurements

Hall measurements were performed to study the conductivity type of annealed and un-annealed samples. The data demonstrated that un-annealed samples annealed at 600 and 700°C exhibit n-type conductivity whereas other samples demonstrated p-type conductivity. It is evident from table 1 that zinc phosphate sample transformed into p-type ZnO at annealing temperature 800°C and this p-type conductivity is due to presence of P atoms on oxygen site because all of the P sites were not completely occupied by the oxygen atoms at 800°C. Therefore further increase of annealing temperature above 800°C would results in the decrease of hole concentration because more and more oxygen atoms occupied the lattice site of P atoms. The high resistivity of annealed samples may be due to the imperfection of lattice. Similar types of high resistive results have been already published in reference [12]. To check the stability of p-type conductivity in transformed samples, we have performed Seebeck measurements after two months. The Seebeck data shows that sample annealed at 800°C has positive Seebeck coefficient which confirmed that conductivity is due to holes.

![Image of Hall measurement graph](image2)

Fig. 3 PL spectrum of un-annealed and annealed zinc phosphate samples.
Table 1: Effect of annealing temperature on conductivity type, carrier concentration, mobility and resistivity of Zinc Phosphate pellets.

<table>
<thead>
<tr>
<th>Sr#</th>
<th>Annealing temperature (°C)</th>
<th>Conductivity type</th>
<th>Carrier Concentration (cm⁻³)</th>
<th>Resistivity (Ohm-cm)</th>
<th>Mobility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Un-annealed</td>
<td>N</td>
<td>6.85x10⁹</td>
<td>1.6x10⁹</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>N</td>
<td>1.18x10⁹</td>
<td>5.4x10⁷</td>
<td>90.78</td>
</tr>
<tr>
<td>3</td>
<td>700</td>
<td>N</td>
<td>1.08x10⁹</td>
<td>9.0x10⁷</td>
<td>60.03</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>P</td>
<td>1.71x10⁹</td>
<td>3.04x10⁸</td>
<td>10.19</td>
</tr>
<tr>
<td>6</td>
<td>900</td>
<td>P</td>
<td>1.57x10⁹</td>
<td>1.51x10⁷</td>
<td>200.60</td>
</tr>
<tr>
<td>7</td>
<td>1000</td>
<td>P</td>
<td>1.16x10¹⁰</td>
<td>2.47x10⁷</td>
<td>20.16</td>
</tr>
</tbody>
</table>

3.4 Raman Spectroscopy

Fig. 4 is the Raman spectroscopy measurements of a representative sample annealed at 800°C. According to the selection rules, the pure ZnO sample shows only Raman peaks A₁(TO), E₂(high) and E₁(LO) as demonstrated in the literature [21, 22] but P doped ZnO should have some additional peaks related to P dopant. Assuming that phosphorus either occupies a zinc or oxygen site in the ZnO lattice, than we can obtain P-related local vibrational modes (LVMs) at 482 and 342 cm⁻¹, respectively discussed in reference [23]. The presence of 342 cm⁻¹ LVM suggested that P atoms are not completely replaced by the O atoms and there are few Zn-P bond in the structure.

![Raman spectroscopy measurements](image)

Fig. 4 Raman spectroscopy measurements of a representative sample annealed at 800°C.

4. Conclusion

In this study, we have synthesized stable p-type ZnO by the high temperature thermal treatment at various temperatures (500-1000°C) of Zinc Phosphate powder in oxygen environment using a programmable furnace. The XRD measurements confirmed that Zinc phosphate phase completely converted into hexagonal ZnO phase at annealing temperature 800°C. The dissociation energy of Zn-P bond was calculated from Hall data and found to be 4.15eV, high enough to break the Zn-P bond and formed Zn-O bond. The Hall data also confirmed the p-type conductivity of sample annealed at 800°C.

References