Impact of sintering temperature on structural, optical and ferroelectric properties of V-doped ZnO

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Keywords: zinc oxide, crystal structure, Raman spectroscopy, ferroelectricity

Abstract

This paper reports the effect of sintering temperature on the structural, optical and ferroelectric properties of vanadium (V) doped zinc oxide (ZnO) samples. X-ray diffraction (XRD) study confirms the formation of a hexagonal wurtzite phase. It has been found that the increase in sintering temperature leads to very small enhancement in lattice parameters as well as in grain sizes. The presence of E₂ (high) modes in Raman spectra of V-doped ZnO indicate the stability of the wurtzite structure of ZnO, consistent with the XRD results. The optical band gap estimated from UV–Vis spectroscopy reveals the reduction in band gap of ZnO. Furthermore, changes in ferroelectric polarizations are also observed with an increase in the sintering temperature. The above results are understood based on the increased crystallinity and the presence of mixed phases of the samples with sintering temperature.

1. Introduction

As an important wide band gap semiconductor, wurtzite-structured ZnO with band gap 3.37 eV and large exciton binding energy 60 meV has been extensively investigated and has intrigued the scientific community due to its concomitant optical, electrical and magnetic properties [1–3]. Doping with transition metal ions in the host ZnO matrix has attracted a great deal of attention for more than two decades due to its versatile applications. Vanadium-(V-) doped ZnO is superior among all the dopants, contributing to improved electrical, optical and magnetic properties [4, 5]. Sato et al [6] theoretically predicted the existence of room temperature ferromagnetism in V-doped ZnO. Doping of V in the host lattice enhances the carrier concentration, giving rise to an increase in electrical conductivity and introduces ferroelectric behaviour, which adds an additional dimension towards its multifunctionality [7]. Earlier, perovskite structure–based materials were utilized for achieving ferroelectric memory devices. However, it is very difficult to synthesize and to realize these materials for industrial applications. Ferroelectric behaviour has also been observed in doped ZnO systems in addition to perovskite structure–based materials [8]. The persistence of ferroelectric behaviour, at and above room temperature in V-doped ZnO, opens up new possibilities for high temperature nano–piezotronics applications and ferroelectric memory devices [9]. It is well known that material properties are very much dependent on growth techniques and sintering temperature [10]. Sintering is an effective method and a widely used technique for the improvement of structural, optical and ferroelectric properties. It has been observed that the grain growth occurs and the crystallinity of the samples increases with sintering temperature [11, 12]. The sintering temperature plays an important role in controlling the intrinsic defects of ZnO, which in turn are responsible for the modifications in various physical properties [13, 14]. In view of the above, the present work aims to study the effect of heat treatment on the microstructural, optical and ferroelectric properties of V-doped ZnO sample.
2. Experimental

A 5% V-doped ZnO sample was synthesized by solid state reaction method using ZnO and vanadium pentaoxide (V₂O₅) as initial precursors. Both the precursors are mixed together in the respective ratio and grounded for more than 1 h for uniform mixing. The powder was then calcined at 700 °C for 8 h, and again ground and pelletized. The resultant solid was subsequently sintered at 800, 850 and 900 °C respectively for 14 h. The synthesized samples were then characterized by various techniques for their structural, optical and ferroelectric properties. A Bruker D8 x-ray Diffractometer was used for structural investigations and surface morphology was investigated using a scanning electron microscope (SEM; MIRA II LMH, TESCAN). Raman spectroscopy was performed on the samples with InVia Raman microscope (Renishaw) with Ar⁺ ion laser beam having wavelength of 514.5 nm and 50 mw power. Furthermore, the ferroelectric hysteresis loops were measured using a ferroelectric loop tracer.

3. Results and discussion

3.1. Crystal structure and surface morphologies

Figure 1 show the SEM micrographs of 5% V-doped ZnO samples sintered at various temperatures. It is apparent from the figure that the surface morphology of the samples including grain sizes are strongly dependent on the sintering temperature. Comparing the particle sizes of 5% V-doped ZnO (1.8 μm) and the pure ZnO (0.48 μm), there is a drastic change in the particle sizes. Such change is attributed to the difference in ionic radii of V ions as compared to that of the Zn²⁺ ions. The ionic radii of V²⁺ (0.93 Å) is much larger that Zn²⁺ (0.60 Å) [9]. It has been observed that the presence of relatively larger heteroatoms generate some defects in the host matrix and these defects can act as a nucleation centre that may accelerate the formation of grain boundaries resulting in an increase in the average particle size of the sample. The average particle size for 5% V-doped ZnO sample is found to be ~1.8 μm for 800 °C, ~3.46 μm for 850 °C and ~4.6 μm for 900 °C. The increase in sintering temperature results in the change of well-defined particles at 800 °C into the platelet-like structure (900 °C) having larger grain size.

Figure 2 depicts the XRD pattern of 5% V-doped ZnO samples at different sintering temperatures. All the diffraction peaks observed could be indexed to hexagonal wurtzite structure of ZnO (JCPDS database of card number 36–1451). However, an impure phase corresponding to ZnV₂O₆ was also found, which is marked as * in the XRD patterns. As is evident from the figure, the increases in sintering temperature leads to the reduction in peak intensity of impure phase. However, the intensity of peaks corresponding to the wurtzite structure of ZnO increases with the sintering temperature, indicating the improvement in crystal structure with temperature. Further increase in the sintering temperature may result in melting because of the lower melting point of V₂O₅.

A visual inspection over the diffraction pattern shows that the increase in sintering temperature results in the shifting of diffraction peaks towards lower 2θ. This shift in the diffraction pattern would lead to the change in lattice constants. It is observed from table 1 that there is almost no variation in the a-axis lattice parameter whereas a small increase in the c-axis lattice parameter is observed with the sintering temperature (800, 850 and 900 °C). This indicates that more Zn²⁺ ions are substituted by V ions, implying an increase in solubility with the sintering temperature. Further, the average crystallite size of the samples was determined from the broadening of XRD peaks using the Scherrer’s equation $D = \frac{0.89\lambda}{β\cosθ}$ [15], where D is crystallite size, β is FWHM and λ is 1.54 nm.
the wavelength of x-rays used. It has been observed that the crystallite size increases with an increase in sintering temperature.

### 3.2. Optical properties

Figure 3 shows the influence of sintering temperature on the absorbance spectra of 5% V-doped ZnO. The optical band gap of the samples was estimated by employing Tauc’s relation \[ (\alpha h\nu) = (h\nu - E_g)^{1/2} \]. Here, \( \alpha \) is the absorption coefficient, \( h\nu \) is the energy of the radiation (photon energy) and \( E_g \) is the optical band gap of the materials. Therefore, the absorption coefficient \( \alpha \) is given by \( \alpha = 2.303 \log_{10}(A)/t \). Where \( A \) is the absorbance and \( t \) is the thickness of pellets. The band gap of the samples was calculated from the extrapolation of the straight line along the x-axis. The band gap for 5% V-doped ZnO sample at 800 °C is \( \sim 3.25 \) eV. The band gap of the V-doped ZnO sample is found to be lower as compared to pure ZnO (3.35 eV) as can be seen from our earlier report \[11\]. The change in the band gap is attributed to V-doping. The reported band gap of V_2O_5 is 2.3 eV whereas it is 3.37 eV for pure ZnO. In the process of mixing of V_2O_5 in ZnO, V ions occupy some interstitial positions in the host lattice instead of substituting Zn ions, giving rise to an impure phase of ZnV_2O_6 (marked as

| Temperature °C | \( a \)-axis lattice parameter (Å) | \( c \)-axis lattice parameter (Å) | Cell Volume (Å³) | Crystallite Size (nm) |
|----------------|-----------------------------------|-----------------------------------|------------------|----------------------|
| 800            | 3.251                             | 5.206                             | 47.66            | 42.87                |
| 850            | 3.252                             | 5.208                             | 47.69            | 44.18                |
| 900            | 3.252                             | 5.21                              | 47.71            | 49.08                |

Figure 3. UV-Vis spectra of Zn_{1-x}V_xO (x = 0.05) sintered at various temperatures.
* in the XRD pattern) which in turn is responsible for the reduced band gap of ZnO after V$_2$O$_5$ doping. It can be clearly seen from the figure that the UV absorption edge is red-shifted with the increase in sintering temperature, indicating the narrowing of the optical band gap. It may be suggested that the decrease in band gap with sintering temperature is attributed to the increased crystallinity [17] and mixing of the impure phase (i.e. decrement in the peak intensity of the impure phase) of the samples.

In order to corroborate the results and to get the detailed crystal structure information, Raman spectroscopy measurements were performed on these samples. It is well known that ZnO exhibits hexagonal wurtzite structure having a P63mc space group. According to group theory, Raman active optical phonon modes are represented by $A_1 + 2B_1 + E_1 + 2E_2$. From all the modes present in the system, $A_1$ and $E_1$ are the polar phonon modes, $E_2$ is a nonpolar phonon mode and the $B_1$ modes are silent modes which are Raman and infrared inactive [18]. The nonpolar $E_2$ mode consists of two wave numbers, $E_2$ (high) and $E_2$ (low), where $E_2$ (high) mode is related with the oxygen atoms and $E_2$ (low) mode is related with the Zn atoms [19, 20]. Figure 4 represents the Raman spectra for 5% V-doped ZnO samples at different sintering temperatures in wave number range of 100–1200 cm$^{-1}$. A visual inspection of the spectra shows the existence of many peaks corresponding to different modes of ZnO and impurities. The peak present at 439 cm$^{-1}$ is associated with the $E_2$ (high) phonon mode and representative of the band characteristic of wurtzite phase. For stress-free bulk ZnO, the $E_2$ (high) mode exists at 437 cm$^{-1}$. The shift in the peak position of 5% V-doped ZnO is attributed to the difference in ionic radii. Apart from the main peak corresponding to the ZnO hexagonal wurtzite crystal structure, there are some additional peaks in the region 300–670 cm$^{-1}$ corresponding to the ZnO phase and in the range of 130–340 cm$^{-1}$ and 750–1000 cm$^{-1}$ corresponding to the vanadium oxide. The peaks corresponding to the ZnO phase in the Raman spectra are present at 332, 379, 583 cm$^{-1}$ and 656 cm$^{-1}$ respectively. The peaks at 332 cm$^{-1}$ and 583 cm$^{-1}$ correspond to the transverse optical (TO) phonons and longitudinal optical (LO) phonons of the $A_1$ mode. Usually the origin of the $A_1$ modes is supposed to be due to the presence of defects such as oxygen vacancies, Zn interstitials and also their complexes. The phonons corresponding to the transverse optical mode of $E_1$ was also observed at 379 cm$^{-1}$. Further, the band observed at 656 cm$^{-1}$ appears due to the second-order Raman processes (multiple-phonon processes). As mentioned, there are several modes corresponding to different phases of the vanadium oxides in the low wave number region 100–300 cm$^{-1}$ as well as in high wave number region 700–1000 cm$^{-1}$. Karamat et al [21] discussed that the origin of the peak in the lower wave number side at 136.8 and 189.4 cm$^{-1}$ is related with the stretching mode of (V$_2$O$_2$)$_n$ resulting in the chain translation. The peak at 264.6 cm$^{-1}$ represents V–O–V bending mode and the peak at 313.6 cm$^{-1}$ is supposed to be originating from the tripoly coordinated oxygen (V$_3$–O) bonds [22]. Further the presence of peaks in the higher wave number side (900–1000 cm$^{-1}$) may correspond to the terminal oxygen (V–O) stretching mode arising due to unshared oxygen [23]. The careful inspection of the Raman data in the higher wave number region shows that the peak intensities corresponding to the impure phase of vanadium oxide is reducing with the increase in sintering. The decrease in peak intensity of the impure phase indicates the increase in the crystalline nature of the sample is consistent with the XRD and SEM results.

Figure 4. Raman spectra of Zn$_{1-x}$V$_x$O ($x = 0.05$) sintered at various temperatures.

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3.3. Ferroelectric hysteresis (P–E loop)

Figure 5 represents the polarization hysteresis curves for 5% V-doped ZnO samples at different sintering temperatures. The hysteresis curves for all the samples exhibit unsaturated ferroelectric behaviour. High voltage is not applied to avoid the samples from damage which in turn is responsible for the unsaturated ferroelectric hysteresis loops [24]. Usually, ferroelectric behaviour is related to dipole orientation. In the absence of any external electric field, the dipoles are randomly oriented and hence there is no ferroelectric behaviour. With the application of an electric field, dipoles align themselves in the field direction and contribute to the ferroelectric nature. In the case of V-doped ZnO, there are two possible origins of the ferroelectric behaviour. First is the difference in the ionic radii of the dopant and host atom. Due to the difference in ionic radii, ions occupy the off-centred positions, contributing to the ferroelectric behaviour. The ionic radii of Zn$^{2+}$ and the dopant ion V$^{2+}$ ions are found to be 0.60 Å and 0.93 Å respectively. Therefore V$^{2+}$ ions occupy the off-centred positions and give rise to permanent local electric dipoles (ferroelectric behaviour) when the electric field is applied. Secondly, the substitution of V on the Zn site gives rise to the formation of V–O bonds and results in the breakage of Zn–O bonds. The newly formed V–O bonds exhibit a strong polar nature and are non-linear. It can be clearly seen from figure 5 that ferroelectric behaviour is improving with an increase in sintering temperature. However, there is a decrement in the ferroelectric behaviour for the sample sintered at 900 °C. As mentioned above, the ferroelectricity may originate either due to the difference in ionic radii of V and Zn ions and or due to the dipole formation of Zn–O and V–O bonds. Both of these factors contribute towards ferroelectric behaviour in the present system. At high sintering temperature, there is significant reduction in the peak intensity of XRD corresponding to the ZnV$_2$O$_6$ phase. Therefore, V–O bonds may contribute in weakening the ferroelectric behaviour for the 900 °C sintered sample. Apart from this, due to very high sintering temperatures the dipoles may also break, and disturb and hence reduce the ferroelectric nature. Chand et al [25] also observed a similar kind of variation, i.e. the reduction in ferroelectric behaviour for ZnO samples after a particular sintering temperature.

4. Conclusion

Sintering temperature plays an important role in modifying the various physical properties of V-doped ZnO samples. XRD analyses show that the increase in sintering temperatures leads to an improvement in crystalline structure and a reduction in the peak intensity of XRD corresponding to the ZnV$_2$O$_6$ phase. Therefore, V–O bonds may contribute in weakening the ferroelectric behaviour for the 900 °C sintered sample. Apart from this, due to very high sintering temperatures the dipoles may also break, and disturb and hence reduce the ferroelectric nature. Chand et al [25] also observed a similar kind of variation, i.e. the reduction in ferroelectric behaviour for ZnO samples after a particular sintering temperature.

Acknowledgments

Authors (PK & RJ) would like to acknowledge Inter University Accelerator Centre, New Delhi for providing the experimental facility.
References

[1] Ozgur U, Alivov Y I, Liu C, Teke A, Reshchikov M A, Dogan S, Avrutin V, Cho S and Jand Morkoc H 2005 J. Appl. Phys. 98 041301
[2] Kumar P, Malik H K, Ghosh A, Thangavel R and Asokan K 2013 Appl. Phys. Lett. 102 221903
[3] Kumar V, Singh N, Mehra R M, Kapoor A, Purohit L P and Swart H C 2013 Thin Solid Films 539 161
[4] Schlenker E et al 2007 Superlatt. Microstruct. 42 236
[5] Naydenova T et al 2010 Thin Solid Films 518 5505
[6] Sato K and Karayama-Yoshida H 2002 Semicond. Sci. Technol. 17 367
[7] Jin Z, Murakami M, Fukumura T, Matsumoto Y, Ohtomo A, Kawasaki M and Koinuma H 2000 J. Cryst. Growth 55 214
[8] Kumar P, Singh J P, Malik H K, Gautam S, Chae K H and Asokan K 2013 Superlatt. Microstruct. 78 183
[9] Joshi R, Kumar P, Gaur A and Asokan K 2014 Appl. Nanosci. 4 531
[10] Kumar P, Kumar Y, Malik H K, Annapoorni S, Gautam S, Chae K H and Asokan K 2013 Appl. Phys. A 114 453
[11] Singh R G, Singh F, Kumar V and Mehra R M 2011 Curr. Appl. Phys. 11 624
[12] Kumar V, Singh R G, Purohit L P and Mehra R M 2011 Inver. J. Sci. Techno. 4 127
[13] Sendi R K and Mahmud S 2012 Appl. Surf. Sci. 261 128
[14] Kumar L, Medwal R, Sen P and Annapoorni S 2014 Mater. Res. Exp. 1 015045
[15] Rana G and Johri U C 2013 J. Alloys Compounds 577 376
[16] Kumar P, Malik H K and Asokan K 2013 AIP Conf. Proc. 1536 497
[17] Lovchinov K, Nichev H, Angelov O, Sendova-Vassileva M, Mikli V and Dimova-Malinovska D 2010 J. Phys.: Conf. Ser. 253 012030
[18] Kumar P, Singh J P, Kumar Y, Gaur A, Malik H K and Asokan K 2012 Curr. Appl. Phys. 12 1166
[19] Ashkenov N, Mbekum B N, Bundesmann C, Riede V, Lorenz M, Sperrmann D, Kaidashev M E, Kasic A, Schubert M and Grundmann M 2003 J. Appl. Phys. 93 126
[20] Damen T C, Porto S P S and Tell B 1966 Phys. Rev. 142 570
[21] Karamat S, Rawat R S, Lee P, Tan T L, Ramanujan R V and Zhou W 2010 Appl. Surf. Sci. 256 2309
[22] Chen W, Mai L, Peng J, Xu Q and Zhu Q 2004 J. Solid State Chem. 177 377
[23] Wang X J, Li H D, Fei Y J, Weng X, Xiong Y Y, Nie Y X and Feng K A 2001 Appl. Surf. Sci. 177 8
[24] Yang Y C, Song C, Zeng F, Pan F, Xie Y N and Liu T 2007 Appl. Phys. Lett. 90 242903
[25] Chand P, Gaur A and Kumar A 2013 Adv. Mater. Lett. 4 220