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Effect of Vanadium Substitution on Structural and Electrical Properties of Sol–Gel Grown Nanostructured Zinc Oxide

Hetal Boricha[1], Bhargav Rajyaguru[1], Keval Gadani[1], K.N. Rathod[1], V.G. Shrimali[1,2], Bhagyashree Udeshi[1], M.J. Keshvani[1], A.D. Joshi[3], D.D. Pandya[4], P.S. Solanki[1], N.A. Shah[1,a)]

[1]*Department of Physics, Saurashtra University, Rajkot – 360 005, India*
[2]*Government Polytechnic, Gujarat Technological University, Rajkot – 360 003, India*
[3]*Department of Nanoscience and Advanced Materials, Saurashtra University, Rajkot – 360 005, India*
[4]*Human Resource Development Centre, Saurashtra University, Rajkot – 360 005, India*

[a)]Corresponding author: snikesh@yahoo.com

Abstract In the present communication, we report the results on the structural and electrical studies on nanostructured pure (ZnO) and Vanadium (V) doped $Zn_{0.95}V_{0.05}O$ samples synthesized using low cost Sol-Gel technique. To understand the structural properties and their dependence on V substitution, X–Ray diffraction (XRD) measurement was carried out for both the samples understudy. XRD results reveal the single phasic wurtzite nature of both the samples showing hexagonal unit cell structure. A minor phase of ZnV_2O_6 is observed in V doped ZnO sample. Improved dielectric permittivity, enhanced ac conductivity (σ_{ac}) and suppression in impedance have been discussed on the basis of structural modifications by the substitution of V in ZnO, enhanced charge carrier concentration, charge carrier polarization and correlated barrier hopping due to the localized state.

INTRODUCTION

Oxide based diluted magnetic semiconductors (DMS), such as zinc oxide (ZnO), V_2O_5, CeO_2, TiO_2, etc, have been extensively studied for their advanced spintronic applications and multifunctional properties. ZnO has wide band gap (~ 3.3eV) and large exciton binding energy (~ 60meV) at room temperature. Substitution in these metal oxides modifies the electrical, magnetic, optical and other physical and chemical properties. In the past decade, ZnO has attracted a lot of research and development attention due to its technical applications such as in ultraviolet (UV) detectors, field effect devices, gas sensors, short wavelength optoelectronic devices, etc [1–4]. It is reported that substitution of V at Zn site in ZnO enhances the charge carrier (electron) concentration and gives rise to an increase in conductivity [5]. Apart from these properties, V doped ZnO exhibits good ferroelectric nature at and above room temperature [6], therefore, it will be interesting to study the dielectric properties of V doped ZnO and compare the results with pure ZnO. Since, very few reports exist on the studies on impedance spectroscopy for V doped ZnO nanoparticles, in this communication, we have synthesized pure and V doped ZnO ($Zn_{0.95}V_{0.05}O$) nanoparticles using cost effective acetate precursor based modified Sol–Gel technique. We report the structural characterizations, dielectric, ac conductivity and impedance for pure and doped ZnO nanoparticles.

EXPERIMENTAL DETAILS

$Zn_{1-x}V_xO$ (x=0.00 and 0.05) nanoparticles were grown using cost effective acetate precursor based modified sol–gel technique. Zinc acetate and V chloride were taken as starting materials which were dissolved in double distilled

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water. All the chemicals, used in this work, were high purity reagents without any impurity. In sol–gel synthesis process, molar ratio of $ZnCH_3COO_2 \times H_2O$ and VCl_3 were completely dissolved. The aqueous solution was then stirred on hot plate for about 3h at 100°C, in order to mix them uniformly and evaporates excess water content under constant stirring. When the water was completely evaporated, the solution then converted in gel form. Gel–like material undergoes a strong self propagating combustion reaction to give a fine powder. Samples were calcined and sintered at 250˚C and 500˚C, respectively. XRD patterns were collected at room temperature for both the samples to understand their structural properties. In order to understand the electrical properties of the samples, frequency dependent dielectric, ac conductivity and impedance measurements were carried out at room temperature in the frequency range of 100Hz–2MHz.

RESULTS AND DISCUSSION

Fig.1(left) shows XRD patterns of sol-gel grown pure ZnO and V doped ZnO samples. All the diffraction peaks can be analyzed with pure wurtzite phase of ZnO with hexagonal structure. By the doping of V in ZnO, same crystal structure is obtained with slight impure phase of ZnV_2O_6, found in XRD pattern [indicated by * in Fig.1(left)]. It can be seen from Fig.1(left) that with the doping of V, intensity of peak increases, which can be understand by the improvement in crystallinity [7]. Average crystallite size (D) was calculated by employing Scherer's formula: $D = 0.9\,\lambda / \beta \cos\theta$, where D is crystallite size, β is FWHM and λ is the wavelength of X–ray source used. The crystallite size for pure ZnO is found to be ~ 19.44nm and for V doped ZnO is ~ 22.69nm. Increase in crystallite size upon substitution of V at Zn site in ZnO supports our earlier observation of improved crystallinity in V:ZnO sample.

Fig.1(right) shows the variation in room temperature real (ε′) and imaginary (ε′) [in the inset of Fig.1(right)] parts of dielectric constant for pure and doped ZnO nanoparticles. Both the samples have large values of dielectric at lower frequencies which decrease with increase in frequency due to higher relaxation time at lower frequencies [8]. At low frequencies, all the polarizations such as dipolar, electronic, ionic and interfacial polarizations respond easily to the time varying electric field but as the frequency of the electric field increases, different polarization contributions decreases, thereby, net polarization of the material decreases which leads to the decrease in the value of dielectric constant [9]. Also, for both the samples, imaginary part of dielectric constant is comparatively smaller than real part which suggests the high electrical quality of the samples understudy. In addition, upon substitution of V in ZnO, dielectric constant gets enhanced throughout the frequency range studied. This can be understood as: (i) V^{2+} (0.79Å) is larger ion substituted at comparatively smaller ionic site of Zn^{2+} (0.74Å) resulting in the occupation of V^{2+} at off–centered position in the hexagonal structure. This gives rise to permanent local electric dipoles upon the application of external electric fields. (ii) Substitution of V at Zn site breaks some Zn–O bonds and forms new V–O bonds in the structure. Newly formed V–O bonds are non–collinear and can easily rotate upon the application of electric field (frequency), thereby, exhibiting large dielectric. (iii) Newly formed V–O bonds have stronger polar nature as compared to Zn–O matrix bonds which results into the strong dielectric behavior in the sample doped with V.

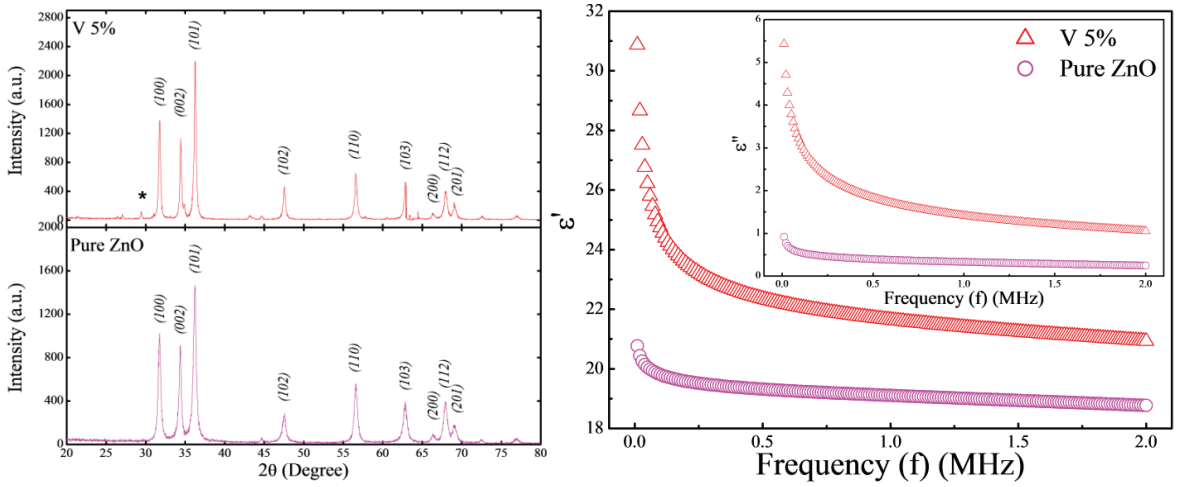

FIGURE 1. (left) XRD patterns, (right) variation in real part with frequency and (inset in right) variation in imaginary part with frequency for pure and V doped ZnO synthesized by Sol–Gel method.

The ac conductivity response was studied for both, pure and doped, ZnO samples and obtained results are shown in Fig.2(left). Frequency dependence of ac conductivity curve was understood throughout the frequency range by "Jonscher's Universal Power Law" given by the relation [10] $\sigma_{ac} = \sigma_{dc} + A\omega^n$, where σ_{ac} is ac conductivity, σ_{dc} is dc conductivity, A is temperature dependent constant and n is power law exponent. The power law exponent n in Jonscher's Universal Power Law shows the degree of interaction between mobile ions and lattice sites around them. Here, n = 1 suggests that non–interacting Debye system exists while n < 1 indicates improved interaction. The ac conductivity curve was fitted throughout the studied frequency range [Fig.2(left)] for both the samples and values of power law exponent are found to be ~ 0.714 and ~ 0.627 for pure and doped ZnO samples, respectively. Exponent value is smaller for doped sample compared to pure which is adequate to ions and lattice interaction increased in the case of doped sample. In addition, V doped ZnO nanoparticles possess higher conductivity as compared to pure sample due to: substitution of larger ion at smaller ionic site creates distortion in the structure thereby supports the formation of large oxygen vacancies in the lattice. This in turn enhances the charge carrier concentration and hence conductivity of the doped ZnO nanoparticles. One can observe that dielectric (polarizability of the metal – oxygen bands) and ac conductivity (charge carrier concentration) are higher for V doped ZnO nanoparticles which can be ascribed to the correlated barrier hopping mechanism [11]. Also, the crystallite size increases upon the substitution of V at zinc site resulting in the reduction in crystal boundary density thereby decrease in scattering sites in the lattice. This indicates an enhancement in conductivity in V doped ZnO nanoparticles.

Electrical behavior of the samples has also been studied over a wide frequency range by utilizing complex impedance spectroscopy technique which enables to differentiate between the real and imaginary part of the complex impedance and other related parameters which in turns gives the information about structure property relationship in the presently studied nanoparticles. Fig.2(right) shows frequency dependent real impedance (Z') and inset shows the imaginary impedance (Z") of both the samples. Real impedance (Z') decreases with increase in frequency for both, pure and doped, ZnO samples which can be due to the enhancement in the mobility of the trapped charges at higher frequencies. The Z' decreases upon the addition of V in ZnO which can be attributed to increased charge carrier concentration and crystallite size upon addition of V in ZnO nanoparticles. In opposite to real impedance, imaginary impedance, Z", is larger for doped ZnO as compared to pure one. This can be understood as: in actual sense, Z" represents the loss in impedance, i.e. gain in conduction by charge carriers. Upon the substitution of V in ZnO matrix, as discussed above, charge carrier concentration gets enhanced which results in the improved conduction [Fig.2(right)] and hence improved impedance loss in V doped ZnO sample. It is worth to note that Z" is much larger than Z' which strongly suggests that the crystal boundaries are highly insulating as compared to crystal cores. Furthermore, large values of imaginary impedance for both the nanoparticles indicate the good electrical quality of the samples and samples are highly stoichiometry with minimum possible oxygen vacancies and other defects.

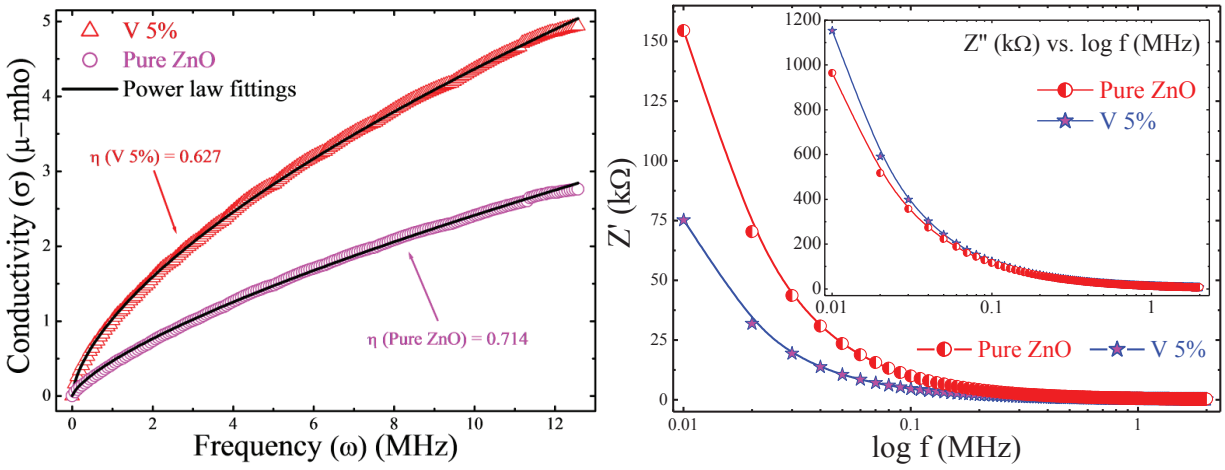

FIGURE 2. (left) Variation in conductivity with frequency plots fitted theoretically using power law, (right) variation in real part of impedance with frequency and (inset in right) variation in imaginary part of impedance with frequency for pure and V doped ZnO synthesized by Sol–Gel method.

CONCLUSION

In summary, we have studied the structural and electrical properties of pure and V doped ZnO nanoparticles synthesized by employing acetate precursor based modified sol–gel method. XRD patterns reveal that, both, pure and doped ZnO samples exhibit wurtzite nanophasic hexagonal structure with improved crystallite size and crystallinity upon substitution of V at Zn site in ZnO matrix. Larger dielectric constant is obtained for V doped samples mainly due to off–centered position of V in the lattice, flexibility of V–O bonds and large polarizability of V–O bonds as compared to Zn–O bonds. Frequency dependent ac conductivity measurements showed higher conduction in doped samples due to enhancement in charge carrier concentration in V doped ZnO nanoparticles. Power fits to conductivity shows the adequate interaction between the ions and lattice which is increased in the case of doped sample as compared to pure ZnO nanoparticles. Impedance spectroscopic measurements suggest that crystallite boundaries are more resistive than crystal cores and hence samples are highly stoichiometric with minimum possible oxygen vacancies and other defects.

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