Research Article

Study of Structural and Optoelectronic Properties of ZnO Codoped with Ca and Mg

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ZnO codoped with Ca and Mg in various proportions was prepared by a chemical method and annealed at 600 C. The structural and optical properties of these oxide samples were systematically studied by XRD, SEM, EDS, and PL spectrometer. XRD pattern shows a hexagonal wurtzite structure. The size of particle as shown by XRD machine and calculated by Scherer's formula is found in the nano range. The formation of particles showed that they were polycrystalline. Due to larger ionic and covalent radii of Ca than those of Zinc, a lattice deformation occurs with the development of strain field. New phases were observed in XRD pattern of few samples ZnO-2.2 and ZnO-2.4. SEM micrograph shows the formation of nanoparticles. EDS study confirms the codoping of ZnO with Ca and Mg. Optical properties like photoluminescence emission showed a blue shift in peak wavelength. General conductivity and photoconductivity were found high in samples containing certain proportion of Ca and Mg in comparison with pure ZnO.

1. Introduction

Zinc Oxide has attracted a lot of research interest due to its enormous potential for application in a variety of optoelectronic and electronic devices. The main advantages of ZnO for optoelectronic applications are its large exciton binding energy [60 meV], wide band gap energy of 3.2 eV at room temperature, and the existence of well developed bulk and epitaxial growth processes. ZnO can be prepared by an easy and cheap chemical method. It is nonpoisonous; so it can be used widely. ZnO thin films are used as transparent electrodes in photovoltaic cell in place of expensive Indium Tin Oxide [1]. ZnO nanowires have also been investigated as gas sensors [2, 3]. ZnO is suitable for UV detection by using its photoconduction properties [3]. ZnO normally forms in the hexagonal (wurtzite) crystal structure with $a = 3.25$ Å and $c = 5.12$ Å. The Zn atoms are tetrahedrally coordinated

with four O atoms where the d-electrons of Zn hybridize with the p-electrons of O. Layers occupied by Zinc atoms alternate with layers occupied by Oxygen atoms. Presence of free electrons in undoped ZnO has been attributed to Zn interstitials and Oxygen vacancies [4]. The intrinsic defect levels that lead to n-type doping lie approximately 0.01 to 0.05 eV below the conduction band. The photoluminescence study of ZnO reflects the intrinsic direct band gap, a strongly bound exciton state, and the gap states due to point defects [4]. Visible emissions in violet blue, green, and red orange range in case of ZnO are due to transitions between self-activated centers formed by doubly ionized Zinc Vacancy and an ionized interstitial Zn⁺, Oxygen vacancies, and donor acceptor pair recombination involving an impurity acceptor [4].

For the fabrication of optoelectronic devices, knowledge about the properties of impurities like donors and acceptors is

FIGURE 1: Circuit for photoconductivity measurement.

of essential interest. The binding mechanism can be described as a consequence of the lattice deformation due to atomic size difference between impurity and host atom. The replacement of host atom on cation site has been reported in many journals. Preparation and characterization of alloys like (Zn-Ca-Mg) O are important for band gap engineering, as p-n junction applications and creating a new combinations to form a substance of modified optical properties. Covalent radii of Zn, Ca, and Mg are 122, 176, and 141 pm, respectively. Similarly, ionic radii of Zn, Ca, and Mg are 88, 114 and 86 pm, respectively [4]. Ca having larger radii, can set in place of Zn in ZnO lattice structure with less deformation. Few work have been done on doping ZnO with other elements, but work on codoping ZnO with Ca and Mg has not been done. Our effort is to find certain proportion of dopant like Ca and Mg in ZnO which will increase the conductive behavior. We have prepared the samples by a simple and economical chemical method. Samples were characterized by XRD and PL spectrometer. General and photoconductivity studies were done on Ca-Mg codoped ZnO nanocrystals.

2. Experimental

The chemical route is simple and economical for preparing high quality nanomaterial like Zinc Oxide. Zinc Oxide nanoparticle can be prepared by treating Zinc Sulphate or Zinc Nitrate with Sodium Hydroxide in aqueous solution and then heating the white precipitate (Zinc Hydroxide) at a temperature greater than 100°C. All chemicals used were of high purity taken from Merc India Ltd. To prepare pure Zinc Oxide, nanomaterial Zinc Nitrate and Sodium Hydroxide were taken in stoichiometric ratio in aqueous solution and stirred for 12 hours. The white precipitate was washed with deionized water 8 times so that only Zinc Hydroxide precipitate remained. It was then dried at 100°C for 2 hours. Dried samples were annealed at 600°C for half an hour. Next for doping with Ca and Mg, their nitrates were mixed with Zinc Nitrate in the ratio such that the number of atoms of Zn and those of (Ca and Mg) were in the ratio of 90:10. The amount of Ca and Mg were varied to obtain samples containing the number of atoms of Ca and Mg in (0, 10), (2, 8), (4, 6), (6, 4), (8, 2), and (10, 0) percent ratios. The percentage of Ca and Mg can be expressed by equation as $\text{Zn}_{0.9}\text{Ca}_x\text{Mg}_{0.1-x}\text{O}$, where $x = 0, 0.02, 0.04, 0.06, 0.08,$

and 0.1. Each sample was dried and then annealed at 600°C. The XRD patterns of these samples were obtained by Rigaku Miniflex 2 X-ray Diffractometer with Cu $K\alpha$ X-radiation of wavelength 1.5406 Å. Photoluminescence spectra of all samples were studied with excitation wavelengths of 254 nm by the help of Fluorescence spectrometer (Perkin Elmer LS 55). The photoconduction studies were done by pressing ZnO nanopowders on self-designed interdigital electrode and covering it with glass cavity and illuminating it with visible light from general 100 W bulb kept at two heights such that the illuminance at the sample is 40 Lx, 332 Lx, and 1640 Lx, respectively (Figure 1). The effective area of cross-section (A) and effective length between two electrodes (L) for the calculation of resistivity were taken as $(2.4 \times 0.15 \times 7 + 3.6 \times 0.5 = 4.32 \text{ cm}^2)$ and 0.15 cm, respectively, by measuring the dimension of electrode.

3. Results and Discussions

The ZnO samples containing different proportions of Ca and Mg are coded as given below.

$\text{Zn}_{0.9}\text{Ca}_0\text{Mg}_{0.1}\text{O}$:- ZnO-2.1, $\text{Zn}_{0.9}\text{Ca}_{0.02}\text{Mg}_{0.08}\text{O}$:- ZnO-2.2, $\text{Zn}_{0.9}\text{Ca}_{0.04}\text{Mg}_{0.06}\text{O}$:- ZnO-2.3, $\text{Zn}_{0.9}\text{Ca}_{0.06}\text{Mg}_{0.04}\text{O}$:- ZnO-2.4, $\text{Zn}_{0.9}\text{Ca}_{0.08}\text{Mg}_{0.02}\text{O}$:- ZnO-2.5, $\text{Zn}_{0.9}\text{Ca}_{0.1}\text{Mg}_0\text{O}$:- ZnO-2.6.

XRD patterns of Pure Zinc Oxide showed that the formation was polycrystalline. The doping of ZnO with Ca and Mg such that the number of doped atoms is up to 10% of the number of Zn atoms form the new substance. They have the same phases as that of ZnO except the formation of few new phases in samples number ZnO-2.2 and ZnO-2.4. The size of nanoparticle was in the range of 20 nm to 50 nm. The peaks were found in basically 8 directions (100, 002, 101, 102, 110, 103, 112, and 201) among which prominent peak was in the third, that is, (101), direction. The distance between two planes of crystal and the size of nanoparticles was calculated by Rigaku software and by Scherrer equation, $\{D = 0.9\lambda/\beta \cos \theta\}$ where D is the size of crystal, λ is the wavelength of X-ray 1.5406 Å, β is the full width at half of maximum (FWHM), and θ is the angle of diffraction. The XRD pattern of all samples ZnO pure, ZnO-2.1, ZnO-2.2, ZnO-2.3, ZnO-2.4, ZnO-2.5 and ZnO-2.6 as found is shown in order in Figure 2.

FIGURE 2

(a)

(b)

FIGURE 3: SEM micrograph of $\text{Zn}_{0.9}\text{Ca}_0\text{Mg}_{0.1}\text{O}$ (ZnO-2.1).

TABLE 1

$\text{Zn}_{0.9}\text{Ca}_0\text{Mg}_{0.1}\text{O}$	O	Zn	Mg
Atomic percentage	59.49%	36.42%	4.09%

SEM micrograph shows that ZnO powder was with small grain of size in nanorange. The SEM study of samples was done one year after its preparation so the size of grain was increased comparing to that found by XRD machine which was smaller than 50 nm at the time of preparation. The structure of grain was like long stones. The picture is given in Figure 3.

The atomic percentage of all elements as studied by the help of EDS of $\text{Zn}_{0.9}\text{Ca}_0\text{Mg}_{0.1}\text{O}$ [ZnO-2.1] is as shown in Table 1.

EDS study confirm the presence of Mg in ZnO. The amount of Ca is zero matching with the intended doping amount. The amount of doped elements Ca and Mg is found to be less than the actual amount intended to dope in ZnO. This may be due to inhomogeneity of sample.

The spectrum obtained by EDS study of $\text{Zn}_{0.9}\text{Ca}_0\text{Mg}_{0.1}\text{O}$ [ZnO-2.1] is given in Figure 4.

PL measurement of doped Zinc Oxide was done at excitation wavelength 254 nm. Figure 5 represents the PL spectra of doped Zinc Oxide at excitation wavelength of 254 nm at room temperature. There are five sharp peaks in case of pure ZnO and three peaks in case of doped samples at room temperature. The exciton emission (in UV range)

Full scale 2610 cts cursor: 0.000

FIGURE 4: EDS study of ZnCaMgO (ZnO-2.1).

FIGURE 5: Photoluminescence spectra of ZnCaMgO (ZnO-2 series).

is found in case of pure and doped ZnO but peaks are not found. The first peak in case of Pure ZnO is at 414 nm while in case of doped are from 410–417 nm (violet range). The second peak in case of pure ZnO is at 429 nm while in doped ZnO is absent. Third peaks are in 482–483 nm (blue range) while for pure ZnO is 491.5 nm, fourth peaks are in 525–527 nm (green range) while for pure ZnO is 534.5 nm. Third and fourth peaks are little blue shifted due to more electrons contributed by the dopant. Fifth peak is only in case of pure ZnO at 616–620 nm (red range). The radiation in visible range is due to recombination between point defects and oxygen vacancies. The intensities of peak are not in certain order because the number of defects depend on the amount of oxygen present in the atmosphere during annealing of samples.

The study of photoconduction reveal that pure and doped ZnO are photosensitive. The amount of current increases as the light intensity falling on the sample surface is increased. The sample illuminated with light intensities 40 Lx, 332 Lx, and 1640 Lx are coded as A, B, and C, respectively. The amount of current is very low in case of pure ZnO, that is, less than $0.6 \mu\text{A}$. The amount of current is enormously high

FIGURE 6

in case of the sample ZnO-2.5 in which amount of Ca and Mg is in ratio (80 : 20). The observed resistance and resistivity of all samples are given in Table 2. The least resistivity of doped ZnO [i.e., $\text{Zn}_{0.9}\text{Ca}_{0.08}\text{Mg}_{0.02}\text{O}$] was found to be $1.81131840 \Omega\text{-Cm}$ which is very small in comparison with that of undoped ZnO [i.e., $976.27118 \Omega\text{-Cm}$]. The least resistivity is still higher than that of doped ZnO found by other researchers. This is due to the less compactness of powder in comparison to that of film. The current (in μA) versus potential difference (in V) graph at different light intensities are shown in Figure 6.

The data of particle size, interplanar distance, average resistance, resistivity, and initial rate of decay of current can be tabulated as shown in Table 2.

4. Conclusion

ZnO was doped successfully by a very simple chemical method. XRD pattern shows its high crystallinity. New phases were found in few samples, ZnO-2.2 and ZnO-2.4. The SEM

TABLE 2

Sample name	Particle size in [101] direction in (nm)	Interplanar distance [d] in Ångstrom	Average resistance ($\Delta V/\Delta I$) in M Ω	Resistivity ($\rho = RA/L$) in Ω -Cm	Initial rate of decay of current in $\mu A/S$
Pure ZnO	26	2.4590	33.333333	976.27118	0
ZnO-2.1	37.7	2.4650	0.1438848	4.14388224	0
ZnO-2.2	35	2.4544	0.1724137	4.96551456	0
ZnO-2.3	33.8	2.4746	0.2020202	5.81818176	0
ZnO-2.4	44.9	2.4543	3.5087719	101.052631	0
ZnO-2.5	37.6	2.4654	0.0628930	1.81131840	0
ZnO-2.6	40.3	2.4279	0.2631578	7.57894464	0

micrograph shows the formation of nanoparticles of ZnO. EDS study shows the success of doping ZnO with Mg. The presence of Ca was not seen due to the test of first sample [ZnO-2.1] in which amount of Ca was intentionally doped zero percent. PL study shows a little blue shift in the blue and green range emission due to doping with Ca and Mg. Photoconductive study reveal that when the amount of Ca increases and that of Mg decreases, the resistance increase, that is, conductance decrease up to certain proportion of Ca and Mg [Ca-6%, Mg-4%] in ZnO for which it is highly conductive in comparison with pure ZnO. It shows that the presence of both elements Ca and Mg in ZnO increases its conductivity.

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