Structural and optoelectronic properties of glucose capped Al and Cu doped ZnO nanostructures

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Al and Cu doped ZnO nanoparticles are considered as appropriate for modulation of structural and optoelectronic properties. Al atoms are found to substitute the host Zn whereas Cu dopants mainly segregate in grain boundaries and thereby determine the optical properties. The undoped as well as Al and Cu doped ZnO exhibit spherical well defined particles. The spherical nanoparticles change to rod type structures on co-doping. The average particle size decreases on doping what consequently results in an increment in band gap. Blue shift in UV absorption is governed by the functional group of glucose; further blue shift occurring on metal doping may be attributed to Burstein-Moss effect. PL spectra of doped and undoped ZnO show a dominant near band gap UV emission along with visible emission owing to the defects. The PL peak intensity increases on doping with Cu and Al. The linear I-V characteristics indicate the ohmic behavior of ZnO nanostructures.

Keywords: d-value; doping; defects; band gap; Burstein-Moss effect; conductivity

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1. Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor material ($E_g \sim 3.37$ eV at 300 K) whose properties in a nanoform differ exceptionally to that of the bulk because of quantum confinement effects. It has got large exciton binding energy $(\sim 60 \text{ meV})$ which results in an intense near-bandedge excitonic emission. Doping of different metals into the nanosized ZnO is very effective, especially in enhancing its multifunctional properties, including the electrical, optical, magnetic, piezoelectric, etc. These composite nanomaterials have a great potential in the fabrication of optoelectronic devices, such as photoconductors, phototransistor, field effect transistors, LEDs and solar cells. The piezoelectric properties of ZnO have been utilized in the fabrication of micro-electromechanical devices and in making chemical and gas sensors [1]. Glucose is an organic sugar molecule useful for biomedical applications. It can be used as a good capping agent to passivate the surface

of particles with excellent stability and reproducibility [2]. Faleni and Moloto [3] reported the formation of ZnO nanorods and nanospheres using glucose as a capping agent. They explained the shape oriented ZnO nanostructures as a result of variation in percentage of glucose in the matrix solution. Aluminium doped ZnO (AZO) has received wider recognition for its high transparency, gassensing property, stability, good conductivity and optical properties. Mondal et al. [4], Tarasov and Raccurt [5], Alkahlout et al. [6], and many other scientists reported blue shift in AZO nanomaterials, identified to be the Burstein-Moss effect. Doping of ZnO with Al was also attempted by other researchers to realize transparent ohmic contact for applications such as n-type layers in photovoltaic devices, especially in solar cells, FET and lightemitting devices [7]. Doping with Al can produce highly conducting n-type ZnO films having carrier concentration in excess of 10^{20} cm⁻³ [8]. Cu doped ZnO films possess high electrical resistivity. The electron trap level of Cu doped ZnO was studied by Furukawa et al. [11]. Also the other research groups found that the resistivity of the ZnO films increased with an increase in Cu concentration [9-11].

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The (I-V) current-voltage characteristics of ZnO may be either linear or non-linear depending on the electrode-film contact as well as inherent defects controlled electron transport properties. Normally, the electrical properties of undoped ZnO films have been found to be of n-type owing to the formation of native defects. Intrinsic defects, such as the zinc interstitial (Zn_i) and oxygen vacancy (V_0) act as a source of donors in ZnO. The background carrier concentration in ZnO is of the order of 10^{16} to 10^{17} cm⁻³ [7, 12]. Different theoretical models exist to explain the mechanism of conduction through nanostructures. Space charge limited current (SCLC) conduction mechanism often affects the carrier concentration and the distribution of electric field and as a result exhibits a variety of non-linear behaviors [13].

Keeping the above aspects in mind, it is felt that more experimental work is desirable for studying the doping mechanism. Our present work is focused on studying the effect of aluminium and copper doping as well as co-doping on glucose capped ZnO nanostructures. The structural, optical and electrical characterizations have been reported in this paper and it is seen that single copper doping is more favorable to tune the device oriented optoelectronic properties.

2. Experimental

2.1. Synthesis

Doped and undoped ZnO nanostructures were synthesized using chemical bath deposition (CBD) method. Into a 3 % aqueous solution of glucose amounting 200 mL, zinc chloride (ZnCl₂) of 0.1 M weighing 2.7256 g was added. Temperature of the mixture solution, which was constantly stirred using a magnetic stirrer, was raised to 355 K. At the same time another 200 mL solution of 0.1 M of NaOH weighing 0.8 g was added drop by drop to the said mixed solution at 355 K. The stirring of the solution was carried out for 3 hours. This led to the synthesis of undoped ZnO nanostructure. The 10 % aluminium doped solution of 0.1 M was prepared by adding 2.7256 g of ZnCl₂ and 10 % AlCl₃, i.e. 0.27256 g into 3 % glucose solution. Into this mixed solution, NaOH solution (200 mL) was added drop by drop under continuous stirring with a magnetic stirrer at 355 K. Another 10 % copper doped solution of 0.1 M was prepared by adding 2.7256 g of ZnCl₂ and 10 % copper sulphate, i.e. 0.27256 g into 3 % glucose solution and adding NaOH solution (200 mL) drop by drop under stirring with a magnetic stirrer at 355 K. The codoped solution of 0.1 M of aluminium and copper in ZnO was obtained by similar procedure but this time 0.13628 g of each copper sulphate and aluminium chloride was added to the mixed solution at 355 K and the corresponding solution was stirred magnetically.

2.2. Characterization

X-ray diffraction (Seifert 3003 T/T) method was employed to obtain fingerprint characterization and crystal structure of the as-prepared samples. The necessary scanning of 2θ was done in the range of 3 to 40° using MoK α radiation $(\lambda = 0.0709 \text{ nm})$ operating at 40 kV/30 mA. The shape and size of the doped and undoped ZnO nanostructures were characterized by HRTEM (JEM 2100, 200 kV, Jeol). The UV-Vis absorption spectra of the as-prepared samples were obtained with the help of automated spectrophotometer (Shimadzu, UV-3101P) in the wavelength range of 200 to 800 nm. For the investigation of photoluminescence (PL) spectra of the prepared samples, we used Xenon flash lamp as a source of excitation (Thermospectronics, Model:AB2, Aminco Bowman Series 2). The excitation wavelength used for this purpose was 325 nm. The distribution of PL peaks was done by deconvolution technique using Origin Pro 7.0. Lorenzian function was used for multi-peak fitting of PL curves. The electrical conductivity measurement was done using a digital picoammeter (DPM-111; SES Instruments).

3. Results and discussion

3.1. XRD study

By XRD study we attempted to perform fingerprint characterization of the crystalline samples. MoK α radiation ($\lambda = 0.0709$ nm) was employed in order to study the structure and morphology of the crystals of doped, co-doped and undoped nano-ZnO. XRD spectra of the doped and undoped samples in glucose matrix are shown in Fig. 1 and Fig. 2. The diffraction peaks agree with the standard data and the samples thereby exhibit a good crystallinity. They exhibit a clear polycrystalline nature with a preferred orientation along [0 0 2] direction. The peaks are fairly broadened what indicates the quantum confinement in ZnO nanoparticles by the attachment of OH groups of glucose. The intensity data that we have obtained varied from 5 to 40° in the 20 range. The intensity of the peaks was found to be maximum in case of ZnO:Al and it decreased consecutively in ZnO, ZnO:Cu, achieving the lowest value in ZnO:(Al,Cu). Thus, a decrease in crystallinity was observed from ZnO:Al to ZnO:Cu and finally to codoping. It was also observed that there was a slight shift in 2θ values for the doped samples with respect to that of pristine ZnO. In Al doped ZnO, the most preferred growth direction was [0 0 2] along with $(1 \ 0 \ 1)$ shift towards the right whereas the shift towards the left was observed for Cu doped ZnO as well as co-doped ZnO. Bragg's law:

$$n\lambda = 2d\sin\theta \tag{1}$$

was used to calculate the lattice spacing corresponding to the (h k l) planes, which is shown in Table 1 and compared with the standard data (PC PDF# 790207 for ZnO.

The ionic radius of Zn^{2+} (0.072 nm) is greater than that of Cu^{2+} (0.057 nm) and Al^{2+} (0.053 nm). This implies the reduction of lattice constant after Al doping which can be attributed to the substitution of lattice site of host Zn by Al ions. However, an increase in lattice constant on Cu doping and that of co-doping is unclear. Doping is quite a complex problem. The actual doping percentage was always less than that of the percentage of doping during laboratory preparation of the doped samples. It is possible that the dopant atoms either moved to interstitial positions or formed other products reacting with those anions in the matrix solution. In the present case the increase of lattice constant may be attributed to the non-uniform substitution



Fig. 1. XRD spectra of undoped and doped ZnO.



Fig. 2. XRD spectra of doped and co-doped ZnO.

Standard d	Observed d	Observed d	Observed d	Observed d	
value [nm]	value of ZnO	value of ZnO:Al	value of ZnO:Cu	value of ZnO(Al,Cu)	(h k l)
0.28204	0.28047	0.28760	0.273697	0.270137	100
0.26062	0.26073	0.25919	0.265534	0.265534	002
0.24806	0.24116	0.23220	0.253398	0.251864	101
0.19141	0.19838	0.19745	0.183749	0.188419	102
0.16284	0.16554	0.16620	0.155873	0.162570	110
0.14793	0.14919	0.14316	0.144454	0.152229	103
0.13810	0.13471	0.13234	0.137529	0.134283	112

Table 1. Change of d values corresponding to lattice planes.

of dopants. The copper atoms may have replaced zinc in the hexagonal lattice and/or copper could segregate to the non-crystalline regions in the grain boundaries. Earlier reports also revealed that there may be either left or right slight shift of two theta diffraction peaks on Al or Cu doping with respect to the host undoped ZnO that signifies either expansion or shrinkage of lattice constants [14, 15]. The observed deviation in lattice spacing induces lattice stress and strain in ZnO. In a pristine sample the stress and strain are less. Aluminium introduces compressive stress and strain whereas Cu develops longitudinal stress and strain on doping and co-doping a sample of ZnO. In case of co-doping, mutual interaction between Cu and Al atoms and their segregation in grain boundaries contribute to longitudinal stress and strain [16, 17].

The crystallite size of undoped and doped ZnO are obtained using Scherrer equation:

$$D = 0.89\lambda/\beta\cos\theta \tag{2}$$

Here, D is the crystallite size (nm), λ is the wavelength of the incident X-ray (nm), β is the full width at half maximum (FWHM) and θ is the diffraction angle [18]. Origin software was used to obtain the value of β and hence, the crystallite sizes of ZnO, ZnO:Al, ZnO:Cu and ZnO:Al,Cu were calculated to be 6.25 nm, 5.67 nm, 9.39 nm and 7.46 nm, respectively. This is consistent with the change in lattice parameters. Aluminium in the lattice sites forms smaller crystal units of ZnO.

3.2. HRTEM study

To investigate the structure of the samples into finer details, a high resolution transmission electron microscope (HRTEM) was used. The HRTEM images show the shape morphologies of pristine, doped and co-doped (Al,Cu) ZnO nanoparticles. They show almost spherically shaped nanoparticles with an average size of 5.3 nm for undoped ZnO (Fig. 3a). On Al and Cu doping into ZnO, the particle size seems to undergo a small change up to 4 nm (Fig. 3b and Fig. 3d). HRTEM images show an uniform distribution of particles embedded in glucose. Glucose is expected to effectively control the growth rate during nucleation and thereby stabilizes the particles shape and size against aggregation. The selected area electron diffraction (SAED) pattern usually exhibits a well-defined distribution of spots for a single crystalline phase whereas it exhibits a set of concentric rings for a polycrystalline material [19]. In the present work the SAED patterns of the samples are composed of clear rings as shown in Fig. 3e, which confirms the formation of polycrystalline ZnO nanostructures. The rings correspond to those prominent crystal planes appearing in XRD patterns. It is observed that some super lattice type structures are also created from a closely packed array of quantum wells on copper doping (Fig. 3c). We note that the shape morphology has abruptly changed from spherical to rod like structures when Al and Cu were simultaneously co-doped into ZnO as shown in Fig. 3f. This is attributed to the predominant growth behavior along c-axis. The wurtize structure of ZnO possesses polar-terminated $(0\ 0\ 0\ 1)$ and non-polar low-symmetry $(1\ 0\ \overline{1}\ 0)$ faces. The growth rate is usually the highest in $[0\ 0\ 0\ 1]$ direction having the lowest surface energy. Therefore, it shows a tendency of 1-dimensional growth in most of the growth processes.

3.3. UV-Vis study

UV-Vis-spectra of as-prepared samples are shown in Fig. 4. Absorption intensity of ZnO:Al is more pronounced in the near UV and violet region in comparison to the other samples. The lowest absorption intensity is found in case of ZnO:(Al,Cu). The UV absorption spectra of the nanostructures show clear absorption edge around 300 nm indicating blue shift from its bulk absorption at 330 nm. The blue shift is due to the quantum size effect governed by the functional groups of glucose. However, there is slight further blue shift on metal doping which can be attributed to Burstein-Moss effect because this effect is quite prominent at relatively high percentage of doping as in the present case.

Optical band gap is calculated by using Tauc relation:

$$\alpha h \nu = B(h \nu - E_g)^n \tag{3}$$

coefficient where the absorption α is $(\alpha = 2.303 \text{ A/t} \text{ where A is the absorbance})$ and t is the thickness of the cuvette), hv is the photon energy, Eg is the optical band gap and B is a function of the index of refraction. ZnO is a direct band gap semiconductor and hence n = 1/2is taken for direct transition. The optical band gap is determined from the extrapolation of the linear portion of $(\alpha h\nu)^2$ on the energy axis in the $(\alpha h\nu)^2$ vs. hv graph [20–22]. The plots of $(\alpha h \nu)^2$ against $h\nu$ for the as-prepared samples are shown in Fig. 5.

It is evident that the band structure of ZnO NPs gets modulated due to the quantum confinement [4]. Sizes of the ZnO quantum dots have been calculated using effective mass approximation (EMA) method considering parabolic band structure. The band gap of ZnO quantum dots can be expressed as:

$$E = Eg + \hbar^2 \pi^2 / 2\mu R^2 \tag{4}$$

where E_g is the band gap of bulk ZnO, μ is the effective reduced mass of exciton and R is the radius of the nanocrystallites. The observed values of band gaps, blue shifting and particle size are tabulated in Table 2 and are found to agree with the observed particle size obtained from HRTEM [23, 24]. However, the particle sizes obtained from XRD are bigger compared to that obtained from EMA. This may be due to the instrumental broadening, strain broadening or polycrystalline aggregates. Khan et al. [25] in their investigation of three Al atomic contents of 0.5 at.%, 1 at.% and 2 at.% in ZnO nanoparticles by sol-gel method observed the band gap values to be 3.37 eV, 3.40 eV and 3.44 eV, respectively. In the present work on AZO, for 10 at.% Al atomic content in ZnO NPs, the band gap value of 3.8 eV was obtained yielding blue shift of 0.33 eV. The enhancement of the optical band gap has been well explained by Burstein-Moss effect. In ZnO:Al the contribution from Al^{3+} ions on the substitutional sites of Zn^{2+} ions and Al interstitial atoms cause widening of the band gap due to an increase in carrier concentration. In such case, the Fermi level moves into the conduction band [25-27].

3.4. PL study

The photoluminescence spectra show an increase in PL intensity for Cu and Al doping over the undoped ZnO (Fig. 6). However, the PL intensity is decreased for co-doped (Al,Cu) ZnO nanostructures. It is expected that Cu and Al may form individual oxide traces which act as prime nonradiative recombination centers. Therefore, the PL intensity decreases for the co-doped sample with respect to the undoped ZnO. All the doped samples as well as undoped ones clearly show the PL emission peaks around 356 nm, 396 nm, 430 nm and 600 nm. The maximum peak at 396 nm is due to the near band gap emission of ZnO. It is stock shifted corresponding to the respective absorption. Stock shift normally occurs in semiconductors because of native defects arising from the band structure. In the present work, Al and Cu dopants exist as additional defects in the samples. Hence, the other luminescence peaks are attributed to these



Fig. 3. HRTEM images of as-prepared samples: (a), (b), (c), (d), (e) and (f).

Sample	Particle size	Particle size from	Energy	Blue shift	Particle size	
	from XRD [nm]	HRTEM [nm]	band gap [eV]	[eV]	from EMA [nm]	
ZnO	6.25	5.3	3.7	0.33	5.18	
ZnO:Al	5.67	4.1	3.8	0.43	4.52	
ZnO:Cu	9.39	5.0	3.78	0.41	4.62	
ZnO:Al,Cu	7.46	4.2	4.13	0.76	3.39	

Table 2. Particle sizes and energy band gaps of ZnO quantum dots.



Fig. 4. UV-Vis absorption spectra of synthesized nano samples: (a) ZnO, (b) ZnO:Al, (c) ZnO:Cu and (d) ZnO:(Al,Cu).

composite defect structures. Aluminium and copper have shown the capability to modulate the optical luminescence properties. However, as the codoped ZnO exhibits a slight reduction in PL intensity, it signifies the possible charge separation rather than radiative recombination. Hence, it can contribute to the conductivity which is visible in the respective I-V measurement (Fig. 9). It shows an increment in current for the co-doped ZnO with respect to others. Therefore, it can be inferred that individual single doping with Cu and Al of ZnO is more viable for their use in luminescence based devices whereas the co-doped ZnO structure may enhance the efficiency of photovoltaic based devices.

The luminescence becomes pronounced near UV region and gradually decreases for longer wavelengths. As the samples were excited with



Fig. 5. Tauc plot of $(\alpha h\nu)^2$ vs. photon energy (eV) of ZnO:Al,Cu; ZnO:Cu; ZnO:Al and pure ZnO.

325 nm light, the emission spectra were recorded from 350 nm onwards and subsequently those were analyzed. The deconvolution of the PL spectra of the as-prepared samples has been shown in Fig. 7, separately. Correspondingly, PL peak positions and the energy levels (Fig. 8) in the samples are tabulated in Table 3. In the PL spectra, the emission peaks in UV region correspond to the near band edge (NBE) emission, the violet and blue correspond to the shallow level emission (SLE) and the yellow correspond to deep level emission (DLE) [25]. Strong photoluminescence intensity in the UV region around 355 to 399 nm was found.



Fig. 6. PL spectra of synthesized nano-samples of (A) ZnO, (B) ZnO:Al, (C) ZnO:Cu and (D) ZnO:(Al,Cu).

UV emission in the near band edge emission is due to exciton recombination. In the visible region around 422 to 600 nm, weak photoluminescence intensity was observed. The broad visible emission is associated with the native defects and the OH group attached at the surface of ZnO nanoparticles by dangling bonds. As the particle size decreases on doping, the surface to volume ratios become larger which can lead to attachment of more OH groups. Similar behaviour of PL spectra was also found by other workers on doping host ZnO [16].

3.5. Conductivity study

To study electron transport behavior a conductivity experiment was performed. Thin layer of the as-prepared samples were deposited in the gap between two parallel copper coated stripes with a spacing of 3 mm. A picoammeter was used to measure the current for various potential differences applied across the copper terminals through a digital power supply (Fig. 9). Free charge carriers available at room temperature contribute to the current through ZnO film. The current-voltage (I-V) characteristics obtained at room temperature are found to be linear, indicating ohmic behavior [13]. It is seen that the current level is quite constant up to 20 V for all films but there is a slight deviation afterwards for higher applied bias. The Al doped ZnO



Fig. 7. Deconvoluted photoluminescence peaks of undoped and doped ZnO.



Fig. 8. Schematic energy level diagram of ZnO nanoparticles showing emission mechanism.

exhibits a clear reduction of current over those undoped, copper doped and co-doped ones. This implies that more Al dopants introduce deep acceptor levels which trap the electrons from the conduction band and thereby reduce conductivity.

Peak	ZnO		ZnO:Al		ZnO:Cu		ZnO:Al,Cu	
Nos.	λ [nm]	Energy [eV]						
Ι	356	3.49	355	3.50	355	3.50	357	3.48
II	395	3.15	399	3.12	396	3.14	399	3.12
III	422	2.95	468	2.66	467	2.66	439	2.83
IV	602	2.07	599	2.08	613	2.03	600	2.07

Table 3. PL peak positions and energy levels in the samples.



Fig. 9. I-V characteristics of ZnO nanostructures.

4. Conclusions

Al and Cu co-doped ZnO nanoparticles were synthesized by chemical bath deposition (CBD) method using glucose as a capping agent. XRD patterns show that all pristine and doped ZnO are polycrystalline in nature with a hexagonal wurtize type structure. Al doped ZnO exhibits in general a decrease in d-values whereas Cu doped and codoped samples show an increment in d-values. This is attributed to actual replacement of host Zn by the Al atoms; but the increment for that of Cu doped and co-doped ZnO may be caused by the non-uniform substitution as well as segregation of dopants in grain boundaries. The structure is supported by HRTEM which shows almost spherical shape of undoped ZnO nanoparticles with an average size of 5.3 nm. Doping with Al and Cu causes a small change up to 4 nm. The SAED patterns confirm the formation of polycrystalline ZnO nanostructures. The UV absorption spectra of the nanostructures show clear absorption edge around 300 nm indicating blue shift from its corresponding bulk absorption at 330 nm. However, there is slight farther blue shift on metal doping that enhances the band gap. That may be explained on the basis of Burstein-Moss effect that is especially predominant at relatively high percentage of doping. The photoluminescence spectra show an increase in PL intensity for Cu and Al doping over the undoped ZnO. But the PL intensity is decreased for co-doped (Al,Cu) ZnO nanostructures. It is expected that Cu and Al may form individual oxide traces which act as prime non-radiative recombination centers. Therefore, the PL intensity decreases for the co-doped sample with respect to undoped ZnO. All the doped as well as undoped samples clearly show the PL emission peaks around 395 nm, 467 nm and 597 nm. The maximum peak at 396 nm is due to the near band gap emission of ZnO. However, the other peaks are attributed to the incorporated defects. The linear I-V characteristics of the samples suggest ohmic behavior of electron transport properties of the material. Aluminium effectively acts as acceptor and reduces the current. Therefore, it can be inferred that individual single doping with Cu and Al on ZnO is more viable for improving the efficiency of optoelectronic devices.

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