Synthesis of Cu doped ZnO nanorods for photosensitive UV detection application

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Abstract

We report the fabrication and characterization of photosensitive heterostructure device using pure and Cu doped ZnO nanorods on n-Si substrate using a low cost hydrothermal technique. Special techniques like Rutherford backscattering spectroscopy and Proton Induced X-ray emission (PIXE) were used to confirm the doping of Cu in ZnO nanorods. The PIXE measurements confirm the absence of any foreign element in parts per million level, except pure Cu doping in ZnO. The compressive stress in (002) peak develops after Cu doping is indicating the successful substitution of Cu^{+2} ions into Zn^{+2} lattice sites. The I-V measurement of 5% Cu doped ZnO device shows five orders of magnitude increase in current flow compared to 1% Cu doping. Under ultraviolet (UV) light exposure further enhancement of the photocurrent in the devices has been observed, which demonstrates the capability of Cu doped ZnO nanorods as a potential UV photodetector. Copyright © 2017 VBRI Press.

Keywords: ZnO nanorods, UV photodetector, hydrothermal, RBS, PIXE, XRD.

Introduction

Among all the oxide materials studied, zinc oxide (ZnO) has emerged as one of the most promising materials due to their unique physical and opto-electronic properties [1–13]. Depending on the size, shape, and structure, it has multifunctional potential applications in gas sensors [1], biosensors [2], light emitting devices [3], solar cells [4] and photocatalyst [5]. In particular, low dimensional ZnO nanostructures are considered as promising candidates for UV detection [6] due to their large surface-to-volume ratio for which they exhibit high photoconductive gain restricting from the spatial separation of photogenerated carriers [7]. The UV detection is important for many applications such as bio-medical applications, chemical sensing, and short- range communication. Moreover, it is inexpensive and environmental friendly as compared to other metal oxides. Properties of ZnO can be tuned according to the research interest, by doping with various metal atoms to suit specific needs and applications. Previously, many elements such as Al, Ga, Co, Ni, S, and Cu have been doped into ZnO and demonstrate tunable properties [8-18]. Among those, the Cu dopants could modify the properties of ZnO crystals by creating localized impurity levels [15]. Cu doped ZnO nanomaterials or thin films have also been reported as dilute magnetic semiconductors [17-19]. Moreover, the Cu doping acts a shallow acceptor level in ZnO crystals,

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which makes it a promising candidate for producing ptype ZnO [16]. Such p type ZnO NRs grown on n-Si can also be treated as typical p-n junction device. Similar studies on p-ZnO/n-Si were reported by Mandalapu *et al.* [20] and Dutta *et al.* [21] where they have studied Sb doped and Al-N doped p-ZnO thin films on n-Si substrates respectively and studied the heterojunction photodiode properties for photoresponse applications.

The Cu impurity penetrates through the lattice during growth process, via diffusion by replacing either substitutional or interstitial zinc ions in the ZnO lattice, which create the structural deformation. ZnO nanorods (NRs) can be synthesized by a variety of techniques including vapor-phase transport, chemical vapor deposition, sol-gel, condensation, spray pyrolysis, and hydrothermal method. However, most of the reported Cu doped ZnO nanomaterials were synthesized by vapor deposition at high temperatures in the range of 650–1150 °C which is an expensive method and restricts the samples for many applications. In this work we report on the synthesis and its structural and optical properties of Cu doped ZnO NRs produced by a simple, low-cost efficient hydrothermal method [**22**] at a low temperature of 90°C.

In the present study, we emphasize the composition and elemental confirmation of Cu doping into the ZnO crystal structure on n-type Si substrates by investigating through the depth sensitive methods Rutherford Backscattering Spectroscopy (RBS) and Proton induced X-ray emission (PIXE) respectively. The photoresponse study of Cu doped ZnO nanorods shows higher order of current flow under UV light which makes it a promising candidate for UV photo detector applications.

Experimental

Materials

Undoped and Cu-doped ZnO NRs were grown by the hydrothermal method on a Si substrate using hexamethylenetetramine (HMT) ((CH₂)₆N₄), zinc nitrate (Zn (NO₃)₂.6 H₂O) and Copper (II) Acetate Monohydrate (Cu(CH₃COO)₂.H₂O) for hydroxide, zinc (Zn), and copper (Cu) precursors, respectively. The nanorod growth was accomplished by dipping the substrates in the aqueous solution that was prepared equimolar concentration of zinc acetate (0.01 M) and HMT (0.01 M). Before dipping the samples, the aqueous solution was magnetically stirred for 30 min. The flask that contains the equimolar aqueous solution was placed in a hot water bath at 90 °C for 3 hours. After the nanorods were grown, the samples were removed from the beakers, rinsed in deionized water several times to remove the residuals, and then finally dried in an oven at 60 °C for 2 hours. In order to introduce the Cu dopants, Copper (II) Acetate Monohydrate (0.01 M) was added to the sample precursor solution. The undoped ZnO nanorods (sample S1), 1 at. % (sample S2) and 5 at. % (sample S3) of Cu doped ZnO nanorods were grown for different analyses.

Characterizations / device fabrications /response measurements

The morphology and structure of the hydrothermally grown ZnO nanorods were investigated by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) measurements. The impurity and composition analysis was carried out by Particle induced X-ray emission (PIXE) and Rutherford backscattering spectrometric (RBS) measurements using the 3 MV pelletron accelerator facility at Institute of Physics, Bhubaneswar with 3 MeV H⁺ and 2 MeV He²⁺ ion beam respectively. The current–voltage (I–V) characteristics of the fabricated n-Si/Cu doped ZnO nanorods (p-type) heterojunction were measured both in dark and under illumination by a keithley electrometer using an UV lamp emitting at 325 nm with a power density of 0.3 mW/cm².

Results and discussion

Fig. 1 shows the FESEM images of the undoped, 1% and 5% Cu-doped ZnO NRs. The length and diameter of the undoped ZnO nanorods found to be approximately 10 micron and 0.9 micron respectively as shown in **Fig. 1(a)**. A higher density and diameters of the NRs are found in case of Cu doped ZnO NRs as shown in Fig. 1(b)-(c). It can be realized that the average rod diameter increases from approximately 0.9 micron (sample S1) to ~ 1.2 micron for 1 at.% Cu doping (sample S2) and ~ 2 micron after 5 at.% Cu doping (sample S3).



Fig.1. SEM images of (a) undoped, (b) 1% Cu-doped, and (c) 5% Cu-doped ZnO nanorods.

These variations in case of Cu doped ZnO NRs are due to the availability of more nucleation sites during the growth, which depends on the nucleation centers. The reason why the nanorods doped with Cu(CH₃COO)₂ exhibited a larger diameter compared to the bare ZnO nanorods is that, the release of Cu²⁺ ion concentration during growth process enhances the nucleation sites as shown in Equation 1. In the hydrolysis process of CH₃COO⁻, the occurrence of OH⁻ will be more (Equation 2), which improves both lateral and vertical growth rates of ZnO nanorods with increasing the Cu (CH₃COO)₂ precursor.

 $Cu (CH_3COO)_2 \rightarrow Cu^{2+} + 2CH_3COO^-$ (1)

$$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$$
 (2)

Therefore, introducing Cu dopants into the reaction path would increase the nucleation density and hence enhance the density and diameter of the NRs [23].



Fig. 2. XRD patterns of (a) undoped, (b) 1% Cu-doped, and (c) 5% Cu-doped ZnO nanorods.

Fig. 2 shows the XRD patterns of the undoped, 1% and 5% Cu-doped ZnO NRs. The XRD pattern of these samples clearly show the formation of the hexagonal wurtzite structure of ZnO (a = 0.3249 nm, c = 0.5206 nm) (JCPDS # 89-7102). For the Cu-doped ZnO nanorod samples, no other diffraction peaks are observed, only ZnO-related peaks [24, 25] are found in the XRD spectra. This indicates that the Cu ions have substituted Zn sites without affecting the crystal structure of ZnO much. This is important to observe (002) peak for ZnO material because it decides the orientation and the phase of the sample. As shown in Fig. 3, the intensity of (002) plane for the undoped ZnO nanorods is more pronounced than that of Cu doped ZnO nanorods, which again establish that the incorporation of Cu dopants into the ZnO lattice induces more crystallographic defects and hence degrades the crystal quality [24, 25]. As shown in Fig. 3, the (002) peak positions of the Cu-doped ZnO nanorods have shifted towards higher angles as the percentage of doping increases. The shift in (002) peak positions are due to the substitution of Zn²⁺ by Cu²⁺ as the ionic radii of Cu²⁺ (0.73 Å) is much smaller than the Zn $^{2+}$ ionic radii (0.74 Å) [26]. The effect of substitution of Zn $^{2+}$ ions by Cu $^{2+}$ ions could be significant in changing the c-lattice parameters in this ZnO atomic arrangement. The shifts in (002) peak positions also well agree with previous reports [27, 28]. The shift in (002) peak positions, results a small lattice deformation in the Cu-ZnO lattice. The deformation in lattice constant may be assigned to the diminishing of Cu-Zn-O bonds. In this study, we have observed that with 1% and 5 % Cu doped ZnO nanrorods, neither the Cu nor CuO phases are observed in the XRD measurements, which indicates that the Cu impurities are dissolved completely in the ZnO crystal lattice. The unit cell parameters 'a' and 'c' obtained from the XRD data undoped and Cu-doped ZnO nanorods samples

are tabulated in **Table 1**. For Cu doped sample, lattice parameters 'a' and 'c' have been found to be smaller as compared to those of undoped ZnO. We can explain these observations from the view of dimension of ZnO nanorods and the arrangement of Zn $^{2+}$ and O $^{2-}$ ions in the crystal plane.

Table 1. The peak position and FWHM of (002) peaks from XRD and corresponding a, c, c/a. and strain from undoped and Cu doped ZnO nanorods.

Sample ZnO NRs	XRD (002) peak position	FWHM (002) peak	a (100)	с (200)	c/a	Strain ε _z (%)
Un-	34.10	0.369	3.25	5.21	1.604	0.08
doped						
1%Cu-	34.35	0.928	3.25	5.20	1.604	-0.01
doped						
5%Cu-	34.65	1.24	3.25	5.17	1.591	-0.7
doped						

ZnO crystals grow faster in c-axis, attributed to its lowest surface energy as compared to other directions. As seen from SEM image [(**Fig. 1** (c)], the longer dimension of Cu doped ZnO nanorods could be possible when more Cu dopants found in the c-axis as compared to its a-axis. Therefore, the accumulation effect of Cu²⁺ ions to reduce the c-lattice parameter of ZnO nanorod was relatively significant than in its a-lattice parameter. Similarly, the c/a parameter of bare ZnO nanorods has also been found to show a good match with the value 1.602 for ideally close packed hexagonal structure where as it deviates more for Cu-dopped ZnO nanorods. The lattice constants a and c of Wurtzite structure ZnO were calculated, according to Bragg's law [**29**]:

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

where, n is the order of diffraction, λ is the X-ray wavelength and d is the spacing between planes of given Miller indices h, k and l. In the ZnO hexagonal structure, the plane spacing is related to the lattice constants a, c and the Miller indices by the following relation [**30**]:

$$a = \frac{\lambda}{\sqrt{3}\,Sin\theta}\tag{2}$$

$$c = \frac{\lambda}{\sin\theta} \tag{3}$$

The lattice strain of the undoped ZnO nanorods and the Cu-doped ZnO nanorods was calculated using Equation 4.

$$\varepsilon_z = \frac{c - c^0}{c^0} \times 100 \tag{4}$$

where, c is the lattice constant of the ZnO nanorods calculated from the XRD measurements, and $c^0 = 5.206$ Å is the lattice constant of the standard unstrained ZnO. Compressive strain of 0.1 % and 0.7 % have been observed in case of 1% and 5% Cu-doped ZnO nanorods

respectively. XRD data clearly show the effect of Cu doping in the ZnO lattice and that does not contribute to phase segregation, which is an important issue for further sensor applications.



Fig. 3. XRD patterns of (002) peak of undoped, 1% Cu-doped and 5% Cu-doped ZnO nanorods. Lines are fits for the experimental data.

As there are small number of atoms introduced to host material during doping of nanostructured semiconductors, inclusion of this doping material will influence the changes in their properties [**31**]. It is therefore, essential to ascertain the presence of the doping material in nanostructured semiconductors. Hence, PIXE analyses were carried out in order to ascertain the presence of Cu in ZnO nanorods sample. PIXE spectra of bare ZnO nanorods sample and the Cu-doped ZnO nanorod samples are shown in **Fig. 4**.



Fig. 4. The PIXE spectra of (a) undoped, (b) 1% Cu-doped and (c) 5% Cu-doped ZnO nanorods.

Si (Li) detector was used to detect the X-ray coming out from the sample due to inner shell ionization. After calibration with known standard sources, presence of Zn and Cu in Cu-doped ZnO nanorods is clearly identified as shown in Fig. 4(b). The respective X-rays emission from different atomic levels of Zn and Cu caused by inner shell ionization are marked as Zn K_{α} , Zn K_{β} and Cu K_{α} are clearly resolvable. Note that only Zn K_{α} and Zn K_{β} peaks are present in undoped ZnO nanorods sample (S1) as shown in Fig. 4 (a). The Cu K_{β} peak could not be resolved due to low concentration of Cu in ZnO nanorod samples. This observation suggests that the Cu doping is successful in ZnO nanorods and absence of any foreign impurity in ZnO nanorods sample even at ppm level. However, Si (Li) detector is not able to detect the low Z (<11) elements. Hence, the presence of Oxygen in the ZnO nanorod sample cannot be ruled out. RBS is an important tool for estimating the composition, thickness and surface roughness [32] of the sample and was performed using 2.0 MeV energy He²⁺ ion beam. The back scattered particles were detected by a surface barrier detector kept at 165° angle to the incident ion beam. RBS measurements were carried out for both the samples keeping both beam energy and current constant. A current integrator was used to maintain constant charge passage through the target. Then Zn to O ratio was calculated by taking the area under the peak of Zn, O and scattering cross sections into considerations. The RBS spectra along with the simulated curves for ZnO nanorods and Cu doped ZnO samples on Si substrates are shown in Fig. 5.



Fig. 5. RBS spectra of (a) undoped ZnO nanorods sample and (b) Cu doped ZnO nanorods sample. The solid line is the theoretical fit to the experimental data.

The RBS spectra show the presence of Zn, O and Cu in the sample marked by their respective peaks. From the simulated data, the thickness of the undoped ZnO nanorods samples found to be 2.5 μ m, whereas Cu doped ZnO nanorods sample found to be 2.7 μ m. As discussed in the previous section, the inclusion of Cu ion into ZnO crystal with 5 % Cu doping increase the nucleation density and enhance the growth rate which tends to increase the total thickness on Si substrates. The increased thickness of doped samples as observed from RBS is in well agreement with the findings of SEM. As shown in **Fig. 5**, the Si and Zn edge do not match well, because the undoped samples have random distribution of ZnO and less dense with respect to the Cu doped ZnO samples. The experimental and simulated RBS spectra of undoped sample shows mismatch in Si edge, because of random distribution of ZnO with wider empty areas to see Si edge by backscattered He ions, whereas the Cu doped ZnO nanorods, Si edge is well matching with experimental data because of high density of nanorods. This result confirms the Cu doping improves the close pack growth, hence the density of ZnO nanorods.

The photosensitivity measurement of both Cu doped and undoped ZnO samples were carried out by fabricating the heterostructure (P-type Cu doped ZnO/ n-type Si) device using 2 probe point contact method. An Indium contact was formed on top of the Cu doped ZnO nanorods and Au contact was formed on n-Si for electrical measurement as shown in the inset of the Fig. (6). A good ohmic contact was confirmed between our Cu doped ZnO and the Indium metal film and Si with Au metal films. Fig. 6 (a) shows I-V characteristics of all the devices measured in the dark. In the dark condition, the values of current are ~9.4×10⁻¹⁰A and ~8.45×10⁻⁵A for 1% and 5% Cu doped ZnO samples respectively at +2 V. Such notable drop in current value for 1% Cu doped ZnO sample is expected as the Cu dopants in ZnO can often act as a deep acceptor trap centers for electrons [33]. Upon increasing the doping concentration of Cu to 5% in ZnO, it can be observed that there is an appreciable improvement in the current which is almost five orders of magnitude compared to 1% Cu doped ZnO NRs. The rectifying I-V characteristics were obtained at a forward threshold voltage of 2V. Moreover, 5% Cu-doped ZnO sample shows much better rectifying behaviour than 1% doped and pure ZnO samples. Meanwhile, the heterostructure consisting of the n-Si/Cu doped ZnO nanorods behaves like a well-defined p-n junction diode, showing rapid current increase under forward bias and blocking of the current flow under reverse bias, as shown in Fig. 6(a). In addition, 5% doped device shows a forward bias turn-on voltage of about ~ 2 V, and a low leakage current of about 4.91×10^{-6} A at reverse bias of 2V. The current observed in S3 is 5 orders of magnitude higher as compared to S2, suggests that 5% doped sample is a good candidate for heterostructure device application. For S3 the turn-on voltage of the diode exhibits a relatively low value indicating that the diode has fairly low power consumption. The ideality factor can be calculated from the slope and intercept the straight line region of the forward bias in ln (I)-V plot, as shown in Fig. 6(a). The calculated ideality factor found to be 2.4. The ideality factor larger than the value of an ideal diode (n = 1) suggests that the transport mechanism is not dominated by the thermionic emission. The presence of surface states and/or vacant space in between the ZnO nanorods could be the possible reason to have higher ideality factor as compared to the thin films based hererojunction.

Fig. 6 (b) shows the *I-V* measurements performed under UV light (wavelength 325 nm) illuminations for both Cu doped and undoped ZnO nanorod samples. From these measurements, we have noticed that the values of current at +2 V for 1% and 5% Cu doped ZnO sample are found to be 4.8×10^{-9} A and 5.65×10^{-4} A respectively. Under UV light, the 5% Cu doped ZnO nanorod sample is also found to generate five orders of magnitude higher currents than the 1% Cu doped ZnO nanorod sample in the same voltage region, which marks the 5% Cu doped ZnO sample a better UV photo detector. However, I –*V* characteristics of un-doped ZnO nanorods sample under UV light did not show notable enhancement in the current (Figure not shown here).



Fig. 6. *I-V* characteristics of the 1% and 5% Cu doped ZnO nanorods/n-Si heterojunctions under dark shown in (a) and under UV illumination shown in (b). *I-V* characteristics of undoped ZnO NRs is shown in the inset of 6 (b). *I-V* characteristics of the *n*-Si/ 5% Cu doped ZnO nanorods heterojunction using UV lamp on and off during forward biases shown in (c), and the schematic of the performed *I-V* measurement under UV light shown is shown in the inset of 6 (c).

Fig. 6 (c) shows photo response of n-Si/Cu doped ZnO heterojunction for S3. As we switched the UV lamp on and off during the *I-V* scan the forward bias current became sensitive. It was found that the dark current and photocurrent were varying with switching off and on the UV lamp. We performed the I-V measurements while switching the UV light from ON to OFF and vice versa to observe the switching/ response of the device at any given level of voltage. This measurement demonstrates the UV light detection of Cu doped ZnO nanorods. Under the dark condition, the free electrons from the surface of ZnO nanorods are captured by oxygen molecules, which are then absorbed on the surface of ZnO nanorods forming a low conducting depletion layer near the surface.

It has been understood that under 325 nm UV light illumination, Cu doped ZnO nanorods absorb UV light and electron -hole (e-h) pairs are generated. These photogenerated holes take part in the conduction process, which may be responsible for the increase in current exponentially. The obtained results are comparable with the previous results reported in reference [6]. The photo current is two orders higher in case of 5% Cu doping as compared to 1% doping, because of higher thickness of ZnO nanorod layer which creates more holes for photo conduction. It has been noted that the thickness of the 1% Cu doped layer is much less as compared to 5% Cu doped ZnO samples as confirmed from RBS data and SEM images. For higher thickness, the UV light is absorbed by ZnO nanorods before it reaches the Si layer. For lower thickness, the quantum well region at the interface and the depletion region extend into the Si layer start the absorption and reduce the photocurrent. From the analysis of above results, we conclude that the higher percentage of Cu doping in ZnO nano rods would result in enhancement of the photoresponse under the UV light. Such enhancement in the photo response of Cu- doped ZnO NRs make them potential candidates for the UV photo detection applications.

Conclusion

In conclusion, Cu doped ZnO nanorods were grown on n-Si substrate by hydrothermal technique to fabricate heterostructure device for UV light detection and compared with undoped ZnO. The (002) XRD peaks of ZnO shifting to higher angles as percentage of Cu doping increases in ZnO nanorods, because of the ionic radius of Cu^{2+} (0.73 Å) being smaller than that of Zn^{2+} (0.74 Å). Substitution of a smaller Cu²⁺ ion into the ZnO lattice reduced the c-lattice parameter of ZnO, which confirms the development of compressive strain in its hexagonal wurtzite structure. The I-V measurements performed in dark reveals that the 5% Cu doped ZnO nanorods/n-Si heterojunction shows the better characteristics of rectifying diodes than the 1% Cu doped and pure ZnO NRs. Moreover, the 5% Cu doped ZnO nanorod sample draws much higher current almost four orders of magnitude more than the other samples in the same applied bias regime. Under the UV light, 5% Cu doped ZnO generates the highest currents among all the samples.

Further, the UV sensing of the forward bias is more sensitive than that of the reverse bias. The photocurrent was around 5 times larger than the dark current at 2 V. Therefore, we conclude that, the Cu-doped ZnO nanorods, might be an important material for nano-optoelectronic device application and the phenomenon may enable a novel platform for large scale and cost-efficient engineering of sensitive UV photodetectors.

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Author's contributions

SNS conducted most of the experiments and written the manuscript.VS performed RBS measurements in the samples and assisted in the analysis. PKS helped in analysis part and writing the manuscript. BKP helped SNS in conducting the experiments. All the authors read the manuscript and agreed for the publication.

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