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## Investigation of Pure and Transition Metal Doped ZnO Nanoparticles for Photovoltaic Applications

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**Abstract :** Among the various binary metal oxide materials, ZnO is a very important II – VI semiconductor material with a direct band gap of 3.37eV at room temperature and a large exciton binding energy of 60meV. Good crystallization and electrical conduction of transition metal doped ZnO materials can be advantageous for using it as a transparent electrode in solar cells, gas sensors and photonic devices. Nanocrystalline ZnO was prepared by employing a simple hydrothermal route at low temperature of 160°C without any additives or surfactants. The effect of Cu and Sn doping on ZnO was investigated. The prepared pure and TM-doped ZnO nanocrystals were subjected to structural, morphological, compositional and optical characterization. X-ray diffraction spectra exhibit wurzite structure for pure and TM-doped ZnO nanocrystals. The average particle size calculated using XRD data were found to vary between 12 nm and 17 nm. SEM micrograph shows that the prepared samples consist of an assembly of hexagonal nanoplate structure. Composition of the samples observed using EDX spectrum reveals that the prepared samples are free from impurities. The absorption edge of TM-doped ZnO shift towards shorter wavelength when compared to pure ZnO indicating blue shift from the bulk counterpart. This may be due to the small size of the particles exhibiting quantum confinement effect.

**Keywords:** ZnO, nanoparticles, hydrothermal, TM-doped, optical properties.

### Introduction

The continuously increasing energy consumption has created an urgent need for alternative energy sources. The direct conversion of sunlight to electricity is doubtlessly a budget-effective and environment friendly solution<sup>1</sup>. Semiconductors with dimensions in the nanometer realm are important because their electrical, optical and chemical properties can be tuned by changing the size of the particles. Important class of metal oxides is transparent conducting oxides, which possess two diametrically opposite characteristics: high optical transparency in visible region and high dc electrical conductivity. Among the nanostructured metal oxides, ZnO is considered to be one of the best metal oxides that can be used at a nano scale level. ZnO itself has normally a hexagonal or wurzite structure and it is well-known as an n-type II-VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV. From this point of view, nanostructured ZnO powders display a great power in many applications such as gas sensors, solar cells, varistors and photo catalyst with high chemical activity. Oxygen deficient off-stoichiometric ZnO shows n-type conductivity, which can be enhanced by doping<sup>2,3</sup>. In the synthesis part, high cost equipment like pulsed laser deposition, electron beam evaporation, electro spinning method, have been used to synthesize and grow

different zinc oxide nanostructured powders and films. All these techniques either demands stringent reaction condition such as high temperature and pressure, and hazardous chemicals or both. However solution growth method can produce good nanostructures, without using metal catalyst or templates, that too with better crystal quality. In the present work a simple hydrothermal method was presented to synthesize undoped and TM-doped ZnO nanostructures without the assistance of additional surfactant or high temperature annealing. It is one of the most convenient, reliable, simple and inexpensive method.

## Experimental

All chemicals reagents used in the present work were of analytical grade. In a typical procedure, 1 M of zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2$ ) and 1.5 M of sodium hydroxide (NaOH) were dissolved in 100ml of deionized water and magnetically stirred until a homogenous solution was obtained. Then the solution was transferred into Teflon lined autoclave and maintained at  $160^\circ\text{C}$  for about 5 hours and then air cooled at room temperature. The precipitates were filtered out, washed with deionized water and ethanol to remove the impurities. The white precipitate was dried in air at  $60^\circ\text{C}$  for 3 hours to obtain monodisperse ZnO nanoparticles. TM-doped ZnO nanoparticles were synthesized using Sn and Cu ions as dopants. Tin chloride ( $\text{SnCl}_4$ ) and copper chloride ( $\text{CuCl}_2$ ) were used as tin and copper precursors, Sn-doped and Cu-doped ZnO nanoparticles were synthesized by adding appropriate amount of tin and copper precursor with Zinc precursor at the beginning of the reaction.

## Results and Discussions

### Structural analysis

The crystal structure and phase of the pure and TM doped ZnO nanoparticles were investigated using Rigaku X-ray diffractometer (XRD) with  $\text{CuK}\alpha$  radiation ( $1.5418\text{\AA}$ ) in the  $\theta$  range  $20^\circ$ - $80^\circ$ . XRD spectra of ZnO, Sn and Cu doped ZnO samples are shown in fig (1.1 and 1.2, 1.3). The sharp peaks at scattering angle  $2\theta$  of  $31.91^\circ$ ,  $34.74^\circ$ ,  $36.60^\circ$ ,  $47.66^\circ$ ,  $56.89^\circ$ ,  $62.99^\circ$ ,  $66.67^\circ$ ,  $68.08^\circ$  and  $69.23^\circ$  corresponds to the reflection from: (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes, indicating crystalline ZnO with hexagonal wurzite structure, consistent with the standard JCPDS (Card No.89-0510). No characteristic peaks of impurities could be detected within the precision limit of XRD measurement, which confirms the highly pure and single phase nature of ZnO. The substitution of tin and copper does not affect the structure of ZnO. Similar results were observed<sup>4</sup>.

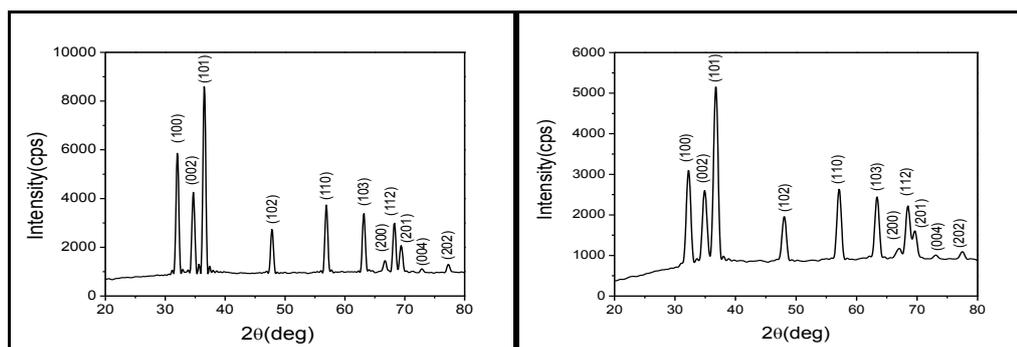


Fig 1.1 XRD spectra of undoped ZnO Fig 1.2 XRD spectra of Sn doped ZnO

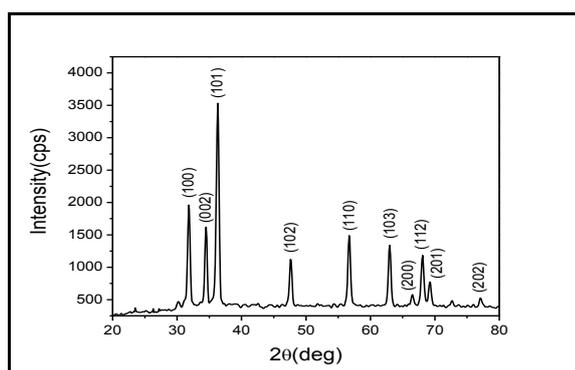


Fig 1.3 XRD spectra of Cu doped ZnO

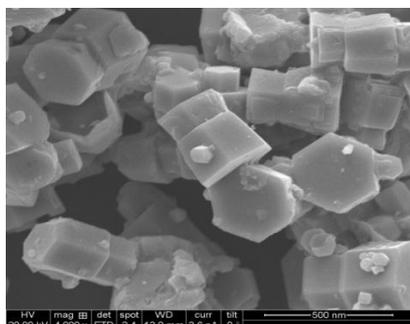
The mean crystallite sizes of the ZnO, ZnO: Sn and ZnO: Cu was estimated from Scherer's formula and the values are given in the table 1. It can be observed that the mean crystalline size of Sn-doped ZnO nanoparticles was reduced when compared to undoped ZnO nanoparticles. The *c/a* ratio of TM doped ZnO nanoparticles were found to increase compared to undoped ZnO nanoparticles, which can cause lattice distortion (slight expansion of unit cell) confirming the successful incorporation of Sn<sup>4+</sup>, Cu<sup>2+</sup> ions into the ZnO host lattice<sup>5</sup>.

**Table 1: Mean crystalline size and lattice parameters of undoped and TM doped ZnO nanoparticles**

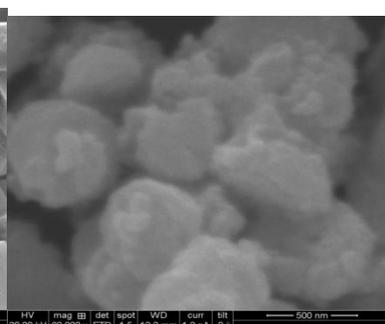
sample	mean crystalline size (nm)	lattice constants (nm)		c/a ratio
		a	c	
pure ZnO	15	0.3252	0.519	1.59594
Sn: ZnO	13	0.3236	0.5196	1.60569
Cu: ZnO	17	0.3257	0.5217	1.60239

### Morphological analysis

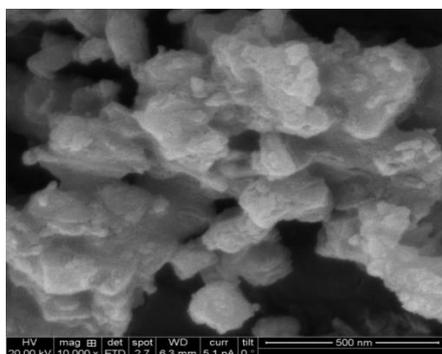
The scanning electron micrographs of the prepared pure and TM doped ZnO nanoparticles are shown in Fig (2.1, 2.2 and 2.3). The SEM micrograph of undoped ZnO showed that the ZnO nanocrystals form a well-defined nanoplate like appearance having hexagonal cross-section, hexagonal nanodiscs from Zinc acetate precursor is reported<sup>6</sup>. Doping of Sn and Cu ions into the ZnO lattice does not alter the morphology of ZnO nanoparticles. The surface of Sn doped ZnO particles become rough compared with the smooth surface of undoped ZnO nanoparticles, indicating that the Sn doped ZnO nanoparticles have higher specific surface area than the undoped ones. SEM image of Cu doped ZnO does not appear to be fragile: does not show any broken particles. Due to incorporation of Cu ions into the ZnO lattice the ZnO crystals got agglomerated. The morphology of the Cu doped ZnO fig (2.3) shows that the size of Cu doped ZnO nanoparticles is greater than that of the Sn doped ZnO nanoparticles which are consistent with the result of the XRD.



**Fig 2.1 SEM of undoped ZnO**



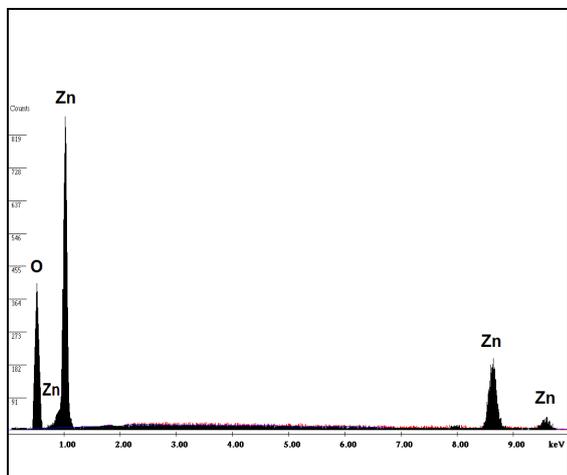
**Fig. 2.2 SEM of Sn doped ZnO**



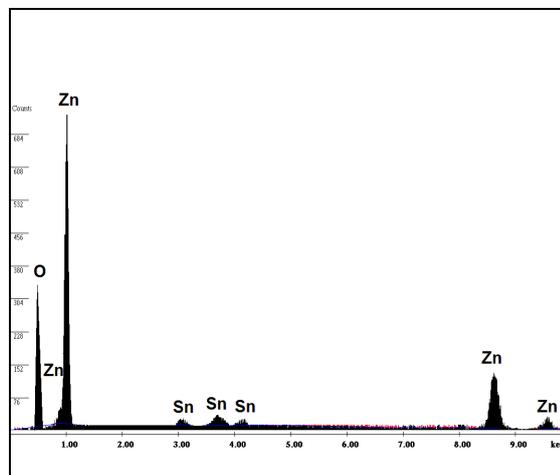
**Fig 2.3 SEM of Cu doped ZnO**

### Compositional analysis

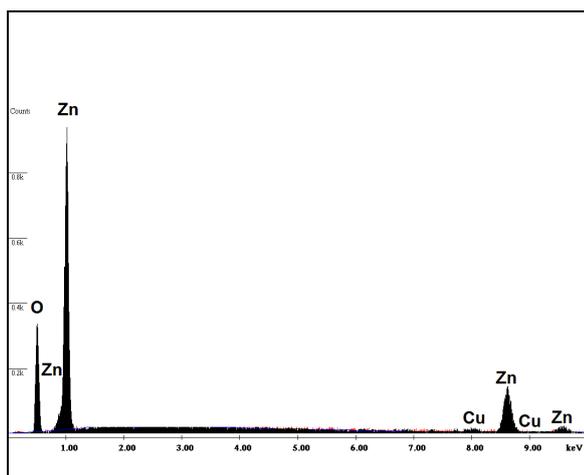
The compositional analysis of as prepared ZnO nanoparticles was investigated using EDX. Fig (3.1-3.3) shows the EDX spectra of ZnO, Sn and Cu doped ZnO nanoparticles. EDX analysis confirms the presence of zinc (Zn) and oxygen (O) in undoped and the presence of zinc (Zn), oxygen (O), tin (Sn) and (Cu) in TM doped ZnO nanocrystals. EDX spectrum shows that prepared samples are free from impurities. Atomic percentage of Zinc, Oxygen in undoped ZnO and copper and tin in Cu doped Sn doped ZnO nanoparticles are given in table 2.



**Fig 3.1** EDX spectrum of undoped ZnO



**Fig 3.2** EDX spectrum of Sn doped ZnO



**Fig 3.3** EDX spectrum of Cu doped ZnO

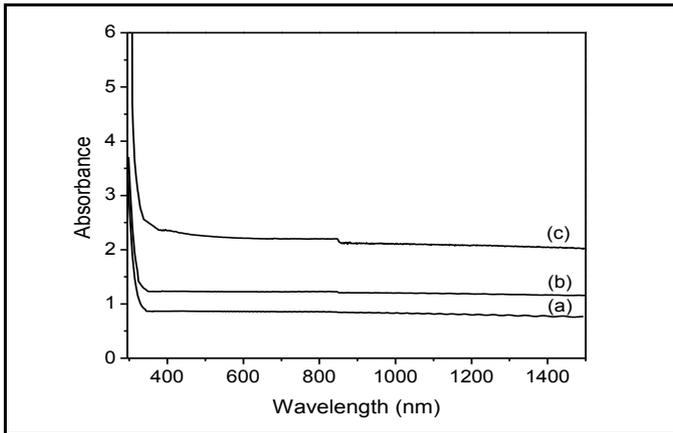
**Table 2:** Atomic percentage of undoped and TM doped ZnO

Compound	Atomic percentage			
	Zinc (Zn)	Oxygen (O)	Tin (Sn)	Copper (Cu)
pure ZnO	51.23	48.77	0	0
Sn: ZnO	50.47	48.01	1.52	0
Cu: ZnO	50.32	48.07	0	1.61

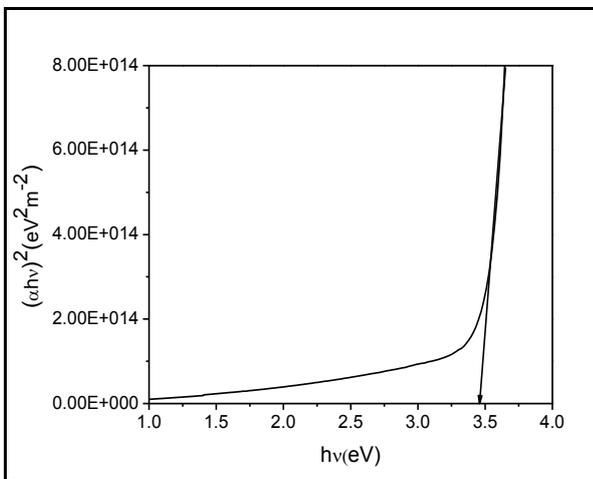
## Optical analysis

### UV-Visible Spectroscopy

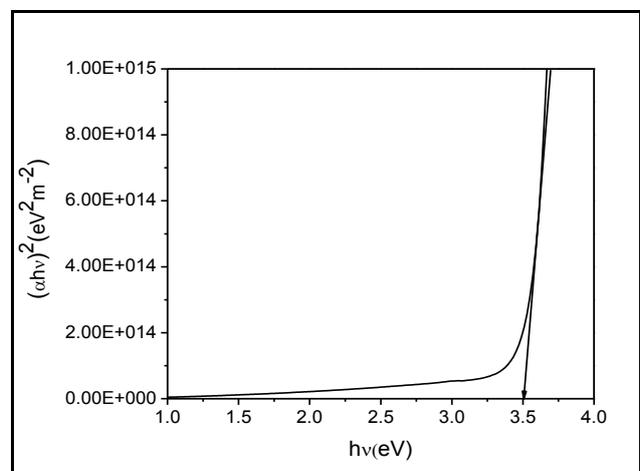
It is well known that dopant can cause crystal imperfections as well as change the band gap of semiconductor. The optical absorption properties of undoped and TM doped ZnO nanoparticles were characterized using UV-visible spectroscopy. The room temperature UV-visible absorption spectra of ZnO, Sn doped ZnO and Cu doped ZnO samples are shown in fig4.1.



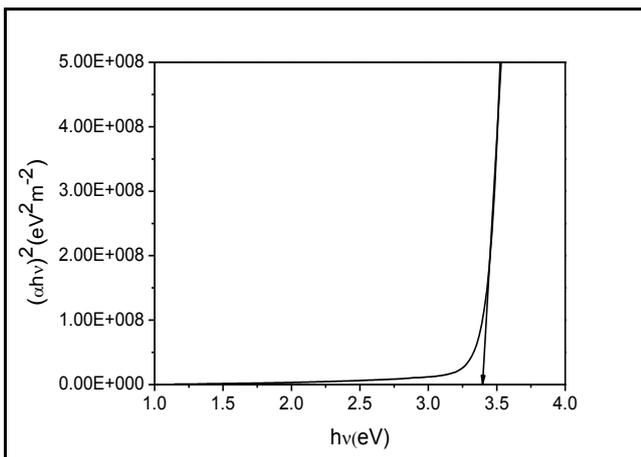
**Fig 4.1** Absorption spectra of (a) Pure, (b) Sn doped and (c) Cu doped ZnO



**Fig 4.2**Tauc plot of undoped ZnO



**Fig 4.3**Tauc plot of Sn doped ZnO

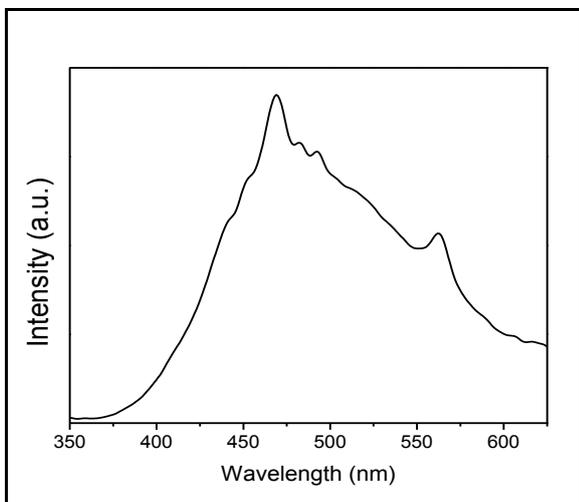


**Fig4.4**Tauc plot of Cu doped ZnO

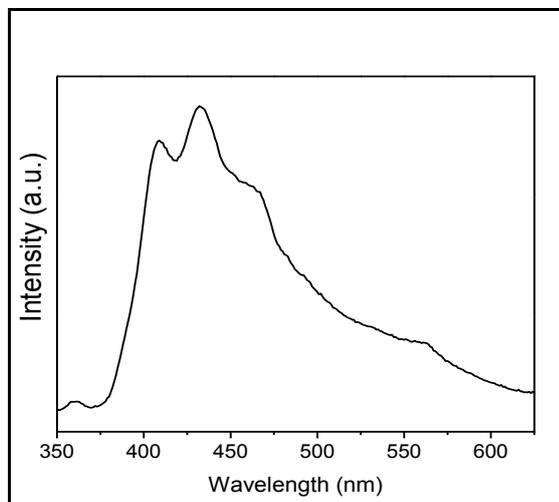
The spectrum reveals a maximum absorption around 330 nm for both undoped and TM doped ZnO samples indicating blue shift from the bulk counterpart. This blue shift in absorption spectrum, caused by doping process suggests an increase in optical band gap energy. The absorption edge of Sn doped ZnO shift towards shorter wavelength when compared to undoped ZnO which confirms the existence of doping states of ZnO<sup>7</sup>. The enhancement of the band gap energy was attributed to the strong quantum confinement of the electrons at nanoscale as well as the incorporation of dopant ion into the ZnO host structure. The UV emission peak of Cu doped ZnO showed a small red shift (approx. 8nm) relative to undoped ZnO, which can be attributed to the shift in the levels of Valence and Conduction bands relative to the coupling of localized Cu<sup>2+</sup> ion and band electron<sup>4</sup>. The optical band gap energy ( $E_g$ ) of samples were calculated by fitting the Tauc plot. From the

plot it is found that the band gaps of undoped ZnO (Fig. 4.1) and doped ZnO (Fig.4.2,4.3) samples are 3.46eV, 3.51eV (Sn: ZnO) and 3.40eV(Cu: ZnO) respectively.

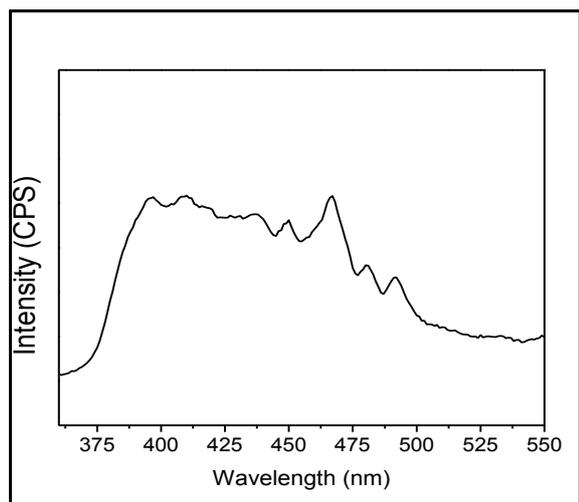
### Photoluminescence Spectroscopy



**Fig 4.5** PL spectra of undoped ZnO



**Fig 4.6** PL spectra of Sn doped ZnO



**Fig 4.7** PL spectra of Cu doped ZnO

Room temperature PL measurement is the effective way to study the defect structure of the semiconductor nanocrystals. PL spectrograph showed the occurrence of energy transition from ZnO to dopant sites. A strong peak around 465 nm was observed for pure and Cu doped ZnO which can be attributed to the recombination of electron at zinc interstitial and a hole in the valence band<sup>4</sup>. The presence of Sn in ZnO host lattice could increase the intensity of deep trap emission of bulk ZnO as well as the intensity of optical band gap emission of doped ZnO<sup>5</sup>. After the incorporation of Cu ions into the ZnO lattice, peak shifted to lower energy. This blue emission might come from intrinsic defects<sup>6</sup>. Cu behaves as an acceptor level with a deep energy of about 0.17 eV, below the conduction band. The peak around 563 nm called deep-level emission in pure and Sn doped ZnO originates due to the recombination of electron in oxygen vacancy with the photo excited holes in the valance band<sup>8</sup>.

### Conclusion

Highly pure and TM doped ZnO has been prepared using simple hydrothermal route. XRD analysis showed hexagonal wurzite structure for pure and doped-ZnO nanocrystals. Doping of Sn and Cu ions into the ZnO lattice does not altered the hexagonal phase nature of ZnO. EDAX spectrum shows only the sharp peaks of Zn, O, Cu and Sn which confirming the high pure nature of prepared undoped and TM doped ZnO nanoparticles. The blue shift in the UV absorption spectrum, caused by the doping suggests an increase in band

gap energy which indicates the quantum confinement effect. PL spectrum of TM doped ZnO show Prominent near band edge emission due to the increase of electron population in conduction band with doping of donor impurities.

## References

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