World Applied Sciences Journal 10 (2): 207-213, 2010
ISSN 1818-4952

Analysis of Cu:CdS Thin Films of Three Different Copper Compositions

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Abstract: This paper presents the study of the structural, morphological and optical properties of copper doped cadmium sulfide thin films prepared by chemical bath deposition. The copper concentration in the films was varied from 0.5% to3% in atomic and it was observed that the film color changes from dark brownish to transparent yellowish. XRD patterns showed the hexagonal phase of cadmium sulfide and if the amount of copper sulphate in the deposition bath increases the preferential orientation (002) plane decreases. Compositional analysis confirmed that Cu ions replace Cd ions either interstitial or substitutional in Cu:CdS thin films. Morphological analysis confirmed that the grain size increases as doping concentration of Cu increases. Increase in Cu concentration leads to an increase in the optical transmission up to 80% and the band gap decreases with in the copper ion concentration in thin films.

Key words: CBD · X-ray diffraction · Morphology · Optical transmittance · Cu-doping

INTRODUCTION

CdS thin films have been widely studied in this decade due to their potential applications as window layers in solar cells manufacturing. Moreover Cu-CdS bilayer system is used for the preparation of metal-coated semiconductor nanocrystals which are of great interest for the fabrication of optical and electroluminescent devices [1]. Copper is reported to be incorporated as interstitial donors and mobility of interstitial Cu atoms is known to be very high [2]. Cu:CdS thin films find many applications, such as high efficiency photovoltaic cells [2] light emitters etc [3]. Chernow *et al.* [4] reported rectification characteristics and green emission of a CdS homojunction diode fabricated by Bi ion-implantation in an n-type CdS single crystal but they gave no details of the emission. As a rule, asgrown CdS films has n-type conductivity, the high dark resistivity (about 10^5 -10^8 Ω cm) and exhibit a high photoconductivity (10^4 - 10^6). Donor centers which formed in CdS during growth, were attributed to the strong self-compensation effect due to the native point defects (vacancies of the sulfur sublattice, interstitial cadmium atoms etc) caused by deviation of CdS composition from the stoichiometry. To make the as-grown CdS films useful in optoelectronic applications, the dark resistivity must be reduced from 10^5 - 10^8 Ω cm to almost 10 Ω cm. Moreover, the doping of copper changes the bandgap energy of CdS and also improves its photoelectrical properties [5]. Recently, a few reports have been published on the properties of Cu:CdS layers; for example, the analysis of Cu:CdS/CdS homojunction and its rectification property [6]. This paper presents the experimental work on to increase a few percent of Cu in CdS films and study the effect of copper on the structural, morphological and optical properties of the thin films prepared by chemical bath deposition.

EXPERIMENTAL DETAILS

The deposition of CdS thin films is based on the reaction of Cd^{2+}, Cu^{2+} and S^{2-} ions in deionised water solution. Chemical baths used for the deposition of CdS thin films consist of cadmium chloride, thiourea, triethanolamine, ammonia and copper sulphate. The pH of the solution can be adjusted by adding ammonia. Three different trials were employed by varying the molar proportions of copper sulphate for the deposition of Cu:CdS thin films and the details of chemicals used for the deposition were presented in Table 1. The deposition process mainly depends on the deposition parameters such as pH, temperature and time. The optimized deposition parameters were given in Table 2. After deposition the films were taken out and washed in deionized water to remove the unattached ions and dried naturally. The thicknesses of the deposited films were evaluated by gravimetric technique.

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Table 1: Volume and concentration of chemicals used for the deposition of Cu:CdS thin films

	Concentration (mgm)			Volume (ml)		
Chemicals	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
$CdCl_3$	1810	1810	1810	15	15	15
Thiourea	3375	3375	3375	25	25	25
$CuSO_4$	2	7	12	10	10	10

Table 2: Optimized deposition parameters

Parameter	Variation range	Optimized value
pH	10 -11	11
Temperature	60-800°C	800°C
Time	1-2 hrs	2 hrs

Characterization: A Shimadzu XRD-6000 x-ray diffractometer with vertical goniometer fitted with vanadium filter and copper radiation (λ = 1.5406 Å) was used for the structural analysis of thin films of different thicknesses. The surface morphology of Cu:CdS thin films was studied using a scanning electron microscope (JEOL JSM 6330F). A JASCO (V570: UV-VIS-NIR) double beam spectrophotometer was used for optical studies in the wavelength range 400-2500 nm. Energy dispersive x-ray analyser (LEICA.S44Oi) was used to confirm the composition of the constituents in Cu:CdS thin films.

RESULTS AND DISCUSSION

Structural Analysis of Cu:CdS Thin Films: Uniform and adherent Cu:CdS thin films have been prepared at 80°C from three different chemical baths (T_1, T_2 and T_3) containing copper sulphate, cadmium chloride and thiourea in different molar concentrations. All the films were annealed in at 100°C for 1 hour and then used for the structural analysis. Fig. 4.3 (a-c) shows the x ray diffractograms of Cu:CdS thin films prepared from chemical baths 1, 2 & 3 respectively. The lattice spacing 'd' has been determined [7] and it has been found that it is in well agreement with that of the ASTM DATA (80-0006) and are presented in Table 3. Predicted peaks (002) and (110) are reported as the characteristic peaks for Cu:CdS thin films by several workers[8-13]. From the diffraction profiles it has been found that the films are polycrystalline in nature with hexagonal structure having the preferential orientation along (002) plane. If the amount of copper sulphate in the deposition bath is increased from 2 to 12mg, the intensity of the preferential orientation plane (002) decreases. The colour of the film turned from orange to yellow and then to brownish and then to transparent yellow with increase in $CuSO_{4as}$ reported earlier [6].

The individual crystalline size (D) in the films of different thicknesses have been estimated [7] and are in the range of 540 - 890Å and are in very good agreement with the reported values [7, 14]. $CuSO_4$ crystals acts as small nucleation centres and if the concentration of Cu ion increases, the solution become denser and the crystalline size in the film also increases. Using the size of

Table 3: XRD data of Cu:CdS thin films

			2θ (Degree)		d spacing (Å)	
Trials	Filmthickness (nm)	hkl plane	Observed	JCDPS	Observed	JCDPS
T1	690	002110	26.544.9	26.644.9	3.302.01	3.3482.06
T2	775	002110	26.644.4		3.312.03	
T3	825	002110	26.644.2		3.312.05	

Table 4: Structural parameters of Cu:CdS thin films

		Lattice constant							
		a (Å)		c (Å)					
Trials	Film thickness (nm)	Observed	ASTM	Observed	ASTM	Crystalline size (Å)	Dislocation density (10^{14}/lines/m^2)	Number of crystallite per unit area (10^{15} m^{-2})	Strain(10^{-4})
T1	690	4.14	4.12	6.69	6.60	539	3.44	4.41	7.00
T2	775	4.10		6.77		635	2.48	3.03	5.94
T3	825	4.09		6.7		890	1.26	1.16	4.23

Table 5: Elemental composition of Cu:CdS thin films

Trails	Film Thickness (nm)	$a(10^6 m^{-1})[\lambda = 1000 Å]$	$k[\lambda = 1000 Å]$	Eg(eV)
T1	690	9.44	0.08	2.44
T2	775	7.74	0.01	2.33
T3	825	4.86	0.04	2.20

Table 6: Optical parameters of CdS: Cu thin films

Thickness (nm)	Trials	% Cu	% Cd	% S
690	1	0.58	62.68	36.74
775	2	1.33	41.19	57.47
825	3	2.59	37.69	59.72

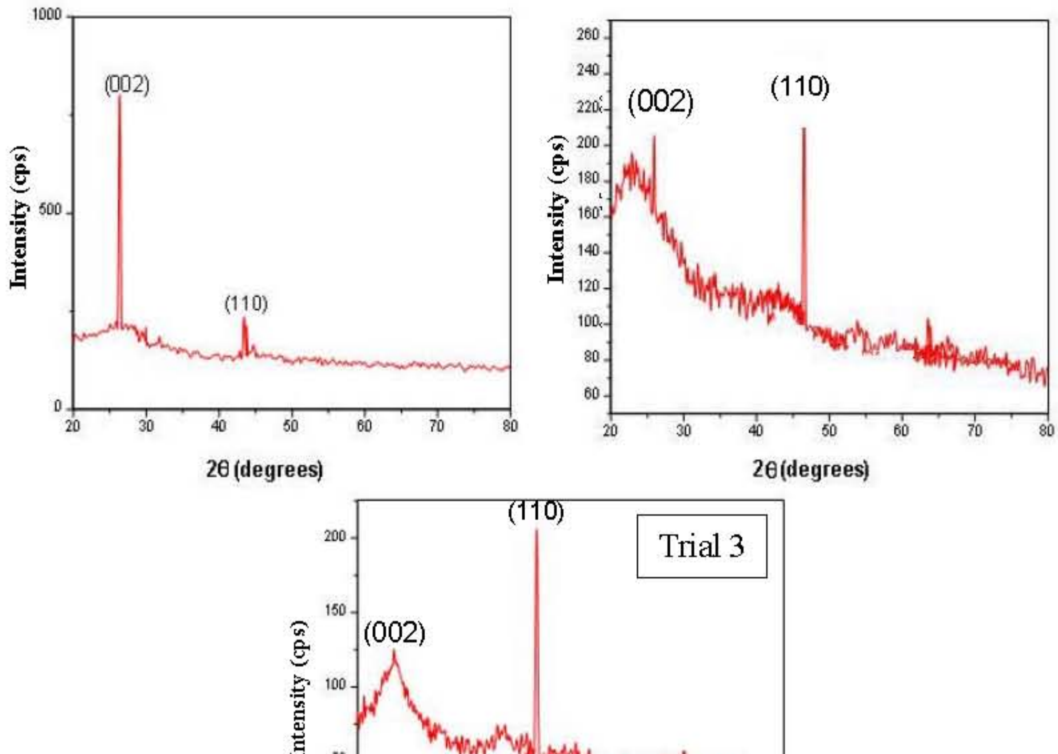

Fig. 1: X-ray diffractograms of Cu:CdS thin films

the crystallites, the dislocation density, the number of crystallites per units surface area and strain have been determined and are presented in Table 4. Irrespective of different trails (chemical baths or Cu ion concentration) the crystallite size increases and the defects such as dislocation density and strain decrease with film thickness.

Compositional Analysis: EDAX spectra and estimated elemental composition of the prepared Cu:CdS thin films are shown in Figure 2 and Table 5 respectively. As copper ion concentration increases in the bath, these ions replace interstitial as well as substitutional Cd ions and this result is also confirmed from the EDAX analysis [6] [Table 5].

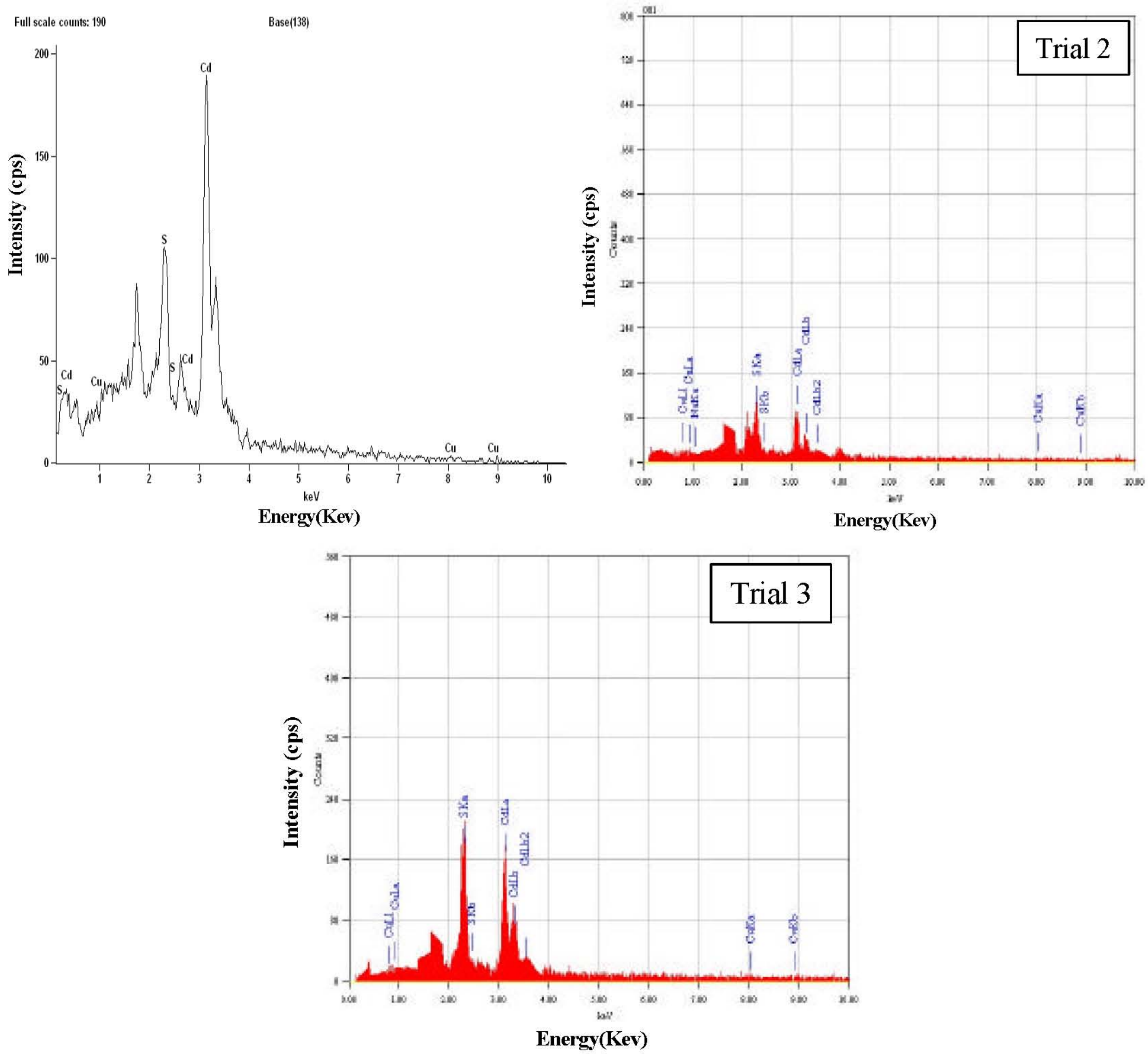

Fig. 2: EDAX spectra of Cu:CdS thin films

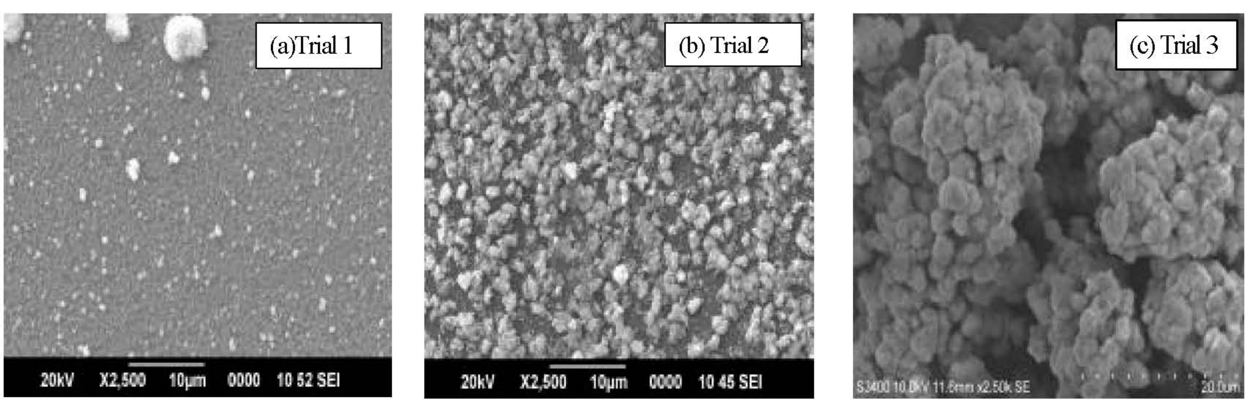

Fig. 3: SEM micrographs of Cu:CdS thin films

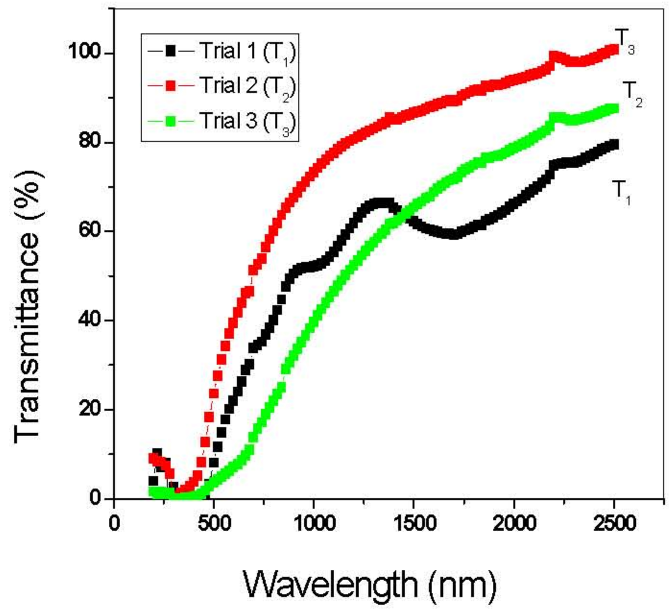

Fig. 4: Transmittance spectra of Cu:CdS thin films

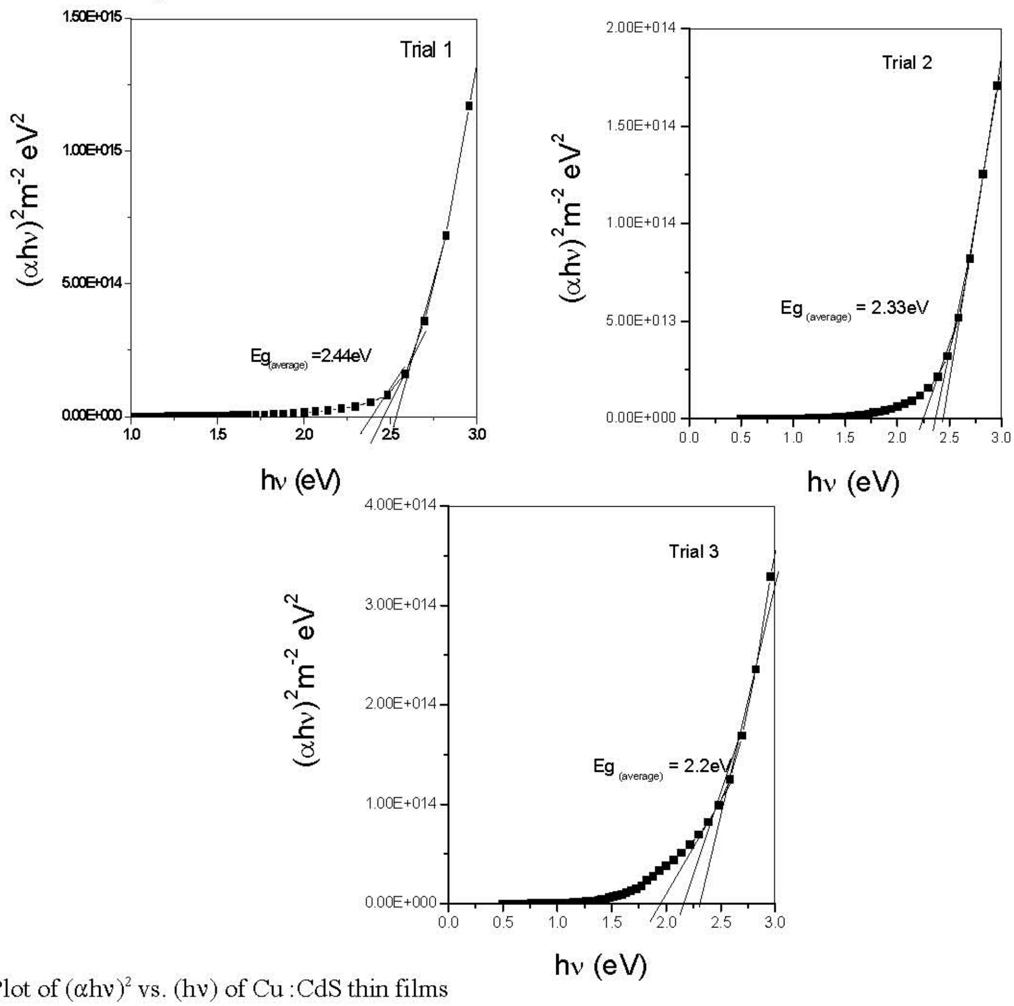

Fig. 5: Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ of Cu :CdS thin films

Morphological Analysis: SEM micrographs [Fig. 3] indicate that when Cu ion concentration increases, the morphology differs in a significant manner. The morphology changes from nanosize grain morphology [Fig. 3(a)] to spongyous morphology [Fig. 3 (b)] [6] and then to cauli- flower like morphology [Fig. 3(c)] as Cu concentration increases and the grain size also increases as doping concentration of Cu increases.

Optical Analysis: The optical transmittance spectra of Cu:CdS thin films of different trials are shown in Fig. 4. Transmittance of the films increases with thickness and Cu ion concentration in the films. The typical behavior was observed earlier researcher Petre *et al.* [6]. The optical parameters such as absorption coefficient, extinction coefficient and band gap are estimated [7] and are presented in Table 6.

Plot of $(\propto h\nu)^2$ verseus $(h\nu)$ (Figure 5) for all the three different trials Cu:CdS thin films were plotted and the straight line portion is extrapolated to cut the x axis which gives the band gap. The estimated average band gaps for the different trails are in the range 2.44 to 2.20 eV (Table 6). It was observed that the band gap decreases with increase in film thickness and increase in the copper ion concentration in thin films [6]. This decrease in the band gap of Cu:CdS thin films content can be related to the slight structural modification and surface morphology and it may be supposed that the copper ions from the deposition bath can replace either substitutional or interstitial cadmium ions in the CdS lattice [6].

Plot of $(h\nu)$ versus $(\propto h\nu)^{1/2}$ $(\propto h\nu)^{1/3}$ and $(\propto h\nu)^{3/2}$ (notshown) reveal that Cu:CdS films did not have line above $h\nu > E_g$. Since extrapolation of it did not touch the zero absorption axis which confirms the fact that Cu:CdS phase do not have indirect allowed direct forbidden and indirect forbidden transitions.

CONCLUSION

Cu:CdS thin films have been prepared by simple economical chemical bath deposition technique with three different copper ion concentrations. XRD analysis confirmed that the deposited films were polycrystalline nature with hexagonal structure. Various structural parameters of the films have been estimated and reported. From the structural analysis it was confirmed that as the doping copper concentration increases the intensity of (002) plane decreases. SEM analysis confirmed the morphological structure of Cu:CdS thin films and it was observed that the doping level of Cu ion CdS increased the size of the grain and morphology changed in a significant manner. Composition of the prepared Cu:CdS thin film is confirmed by EDAX. From EDAX it was confirmed that the copper ions in the deposition bath replaced either substitutional or interstitial cadmium ions in the CdS lattice [when Cu atomic % increases, the cadmium atomic % decreases]. From the transmittance spectra the type of transition, band gap energy and absorbance coefficient have been evaluated for Cu:CdS thin films and it was found that the band gap energy decreases with the copper ion concentration as well as film thicknesses. The investigation revealed that Cu doped CdS thin films have suitable structural as well as optical parameters in the view of solar cell applications.

ACKNOWLEDGEMENTS

The authors are grateful to the Secretary, Principal, Dean and Head of the Department of Physics, Kongunadu Arts and Science College, Coimbatore for their excellent encouragement and support. The authors B.K and B.M are grateful to express their thanks to Jawaharlal Nehru Memorial Fund and UGC, New Delhi for financial support.

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