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# Effect of $Zn^{2+}$ dopping on CuS nanocrystals

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## ABSTRACT

CuS is an important p-type semiconductor material with many interesting properties and potential applications. CuS (covellite) has been synthesized by solvothermal, hydrothermal, microwave irradiation, sol-gel, electrodeposition, solid state reaction, chemical bath decomposition, mechanochemical, sonochemical etc methods. We have taken an initial interest to synthesize CuS with Zn as dopant in different concentrations using co-precipitation technique at room temperature. The synthesized sample was structurally, chemically, optically and electrically characterized. Structural analysis shows that the particles synthesized were nanocrystals. Chemical studies show the high purity of the sample prepared. Optical studies show that these nanocrystals could be used for coatings as sun glasses and poultry roofs. Measurements of dielectric parameters confirm this nanocrystals could be used as an electrical material.



## KEYWORDS

Covellite;
Solvothermal;
Semiconductor;
Nanocrystals;
Optical properties;
Electrical properties.

## INTRODUCTION

CuS (covellite) is one of the most intensively studied p-type semiconducting material[1] owing to its technological applications in the field of solar cell devices[2], non-linear optical materials, lithium – ion batteries[3], nanometer scale switches and gas sensors[4]. It shows metallic conductivity and transforms into a super conductor at 1.6K[5]. CuS nanocrystals have been synthesized by solvothermal, hydrothermal[6], microwave irradiation, sol-gel[7], electrodeposition[8], solid state reaction[9], chemical bath decomposition, mechanochemical, sono chemical methods etc. Some of the researchers have doped $Cu^{2+}$ to ZnS and studied their properties. In the present study, we have adopted a simple co-precipitation technique at room temperature as in[10] to prepare $Zn^{2+}$ doped CuS. Doped nanoparticles of dimension below Bohr radius exhibit interesting optoelectronic properties due to quantum size effect[11]. In our sample rough estimates of nano size with Scherer formula gave their structures to be between 3-10nm. Prepared samples were characterized structurally, chemically, optically and electrically. We report here the results obtained.

## EXPERIMENTAL

### Materials used

All chemicals used in the present study were of analytical reagent (AR) grade. Copper acetate and thiourea were used as the $Cu^{2+}$ and $S^{2-}$ precursors respectively. Zinc acetate was used as the dopant. NaOH was used to adjust pH value of the solution. CTAB was used as the surfactant. Acetone was used for washing purpose.

### Preparation

1M copper acetate and 2.5wt% zinc acetate were dissolved in 250ml distilled water with constant stirring. 1M thiourea and 5wt% CTAB were dissolved in 100ml distilled water and 5 wt% sodium hydroxide was dissolved in 10ml distilled water. First, thiourea + CTAB solution was added with copper acetate + zinc acetate solution slowly with constant stirring. To maintain pH value to be 7, NaOH solution was added to the original solution drop by drop. The solution was stirred well for 30 min and left without disturbance for 24 hrs at room temperature (30°C). The colloidal solution obtained was centrifuged and rinsed many times with distilled water and acetone. The sample was annealed at 100°C for 1hr to improve ordering. The same procedure was followed for 5 wt% 7.5wt% and 10 wt% zinc acetate doping.

### Characterization

The synthesized CuS nanocrystals were characterized by X-ray powder diffractometer (XRD) (Bruker AXS D8) with monochromated Cu-$K_{\alpha}$ radiation (òλ= 1.54056 Å). The optical measurements on samples were carried out in the wavelength range 200-1000nm by UV- visible spectrometer (Varian carry 500 spectrometer). The surface features of the samples were observed by the scanning electron microscope (SEM) and purity of the prepared samples were studied with energy dispersive X-ray spectroscopy (EDS) (JEOL Model JSM 6390LV). The dielectric measurements were carried out on palletized (using 4 ton pressure) samples with a fixed frequency of 1kHz at various temperatures ranging from 40-130$^{0}$C by the parallel plate capacitor method[12,13] using a precision LCR meter (Agilent 4284).

## RESULTS AND DISCUSSION

The observed PXRD pattern of CuS corresponds to typical CuS (covellite) having hexagonal structure with space group $p6_3/mmc$[14]. The estimated lattice parameters of pure CuS nanocyrstls are a=3.806 and c=16.524 Å and JCPDS values are a=3.792 Å and c=16.344 Å. The broad peaks observed indicate the reduced size of the prepared sample. The sharp peaks of the PXRD pattern show the crystalline nature of the sample. A rough estimate of the average grain size using the Scherer formula gives a value of 2.85nm.

A comparative PXRD patterns of pure and Zn doped (2.5wt.% to 10wt.%) CuS samples are shown in Figure 1(a-e) respectively. The PXRD patterns of Zn doped CuS is in correspondence with that available in the literature[15]. An additional peak at $2\theta = 26.9^{o}$ confirms the presence of Zn in CuS lattice. A shift was observed as the doping concentration increased; that is, as the doping concentration of the zinc increased, the peaks had a higher d value which indicates that the size of the nanocrystals had been increased.

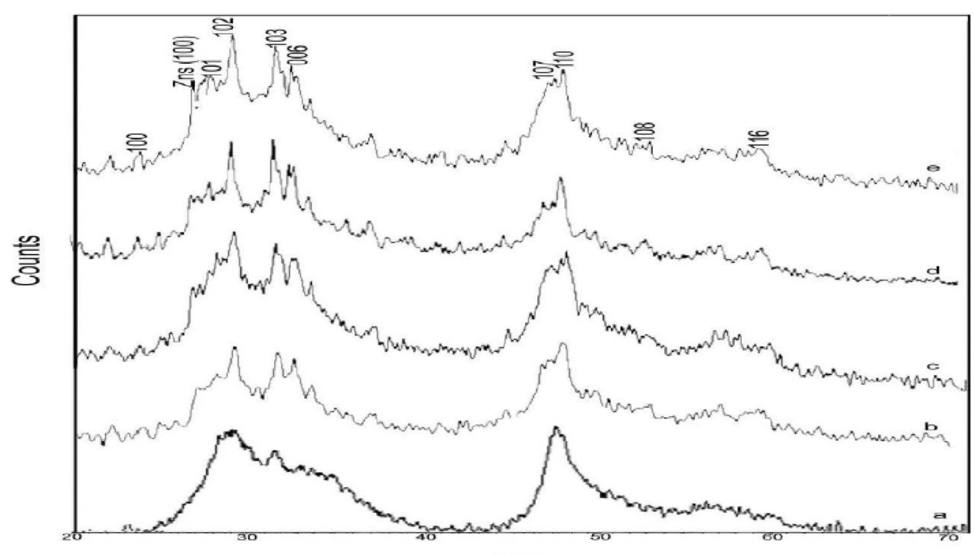



**Figure 1(a-e) : PXRD patterns of pure CuS and (2.5, 5, 7.5 and 10wt.%) Zn doped CuS nanocrystals.**

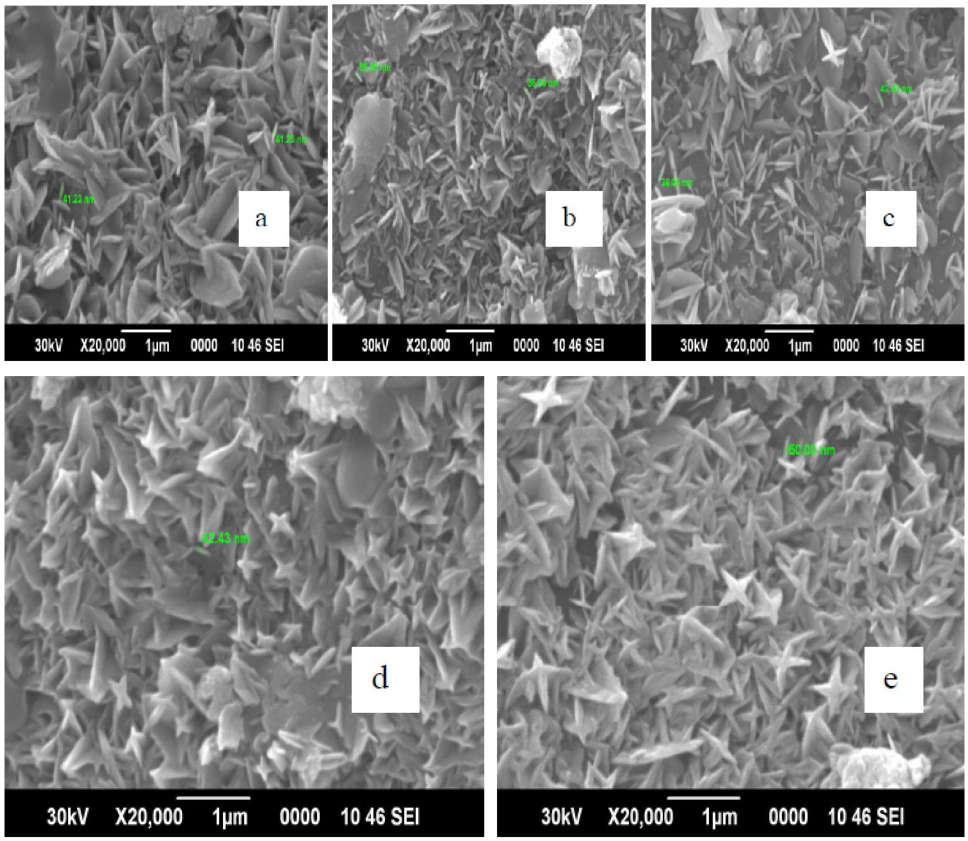



**Figure 2(a-e) : SEM images of pure CuS and (2.5, 5, 7.5 and 10wt.%) Zn doped CuS nanocrystals.**

Figure 2(a-e) gives the SEM images of pure CuS and (2.5wt.% to 10wt.%) Zn doped CuS nanocrystals. From the image it could be seen that, pure CuS nanoparticles were nanorods and nanowalls[16] of average size 41.23nm. The SEM image of Zn doped CuS nanocrystals were tetrapods. Four nanorods merged together at right angles form tetrapods. It was found that, as the doping concentration of Zn increases from 2.5wt.%-10wt.%, the average size of the samples increases from 35-50nm. The particle sizes of pure and all Zn doped CuS nanocrystals were estimated using Scherer formula and they were found to be less than 10nm.

In order to understand the chemical composition and purity of the nanocrystals prepared in the present study, we have carried out energy dispersive X-ray (EDS) spectral measurements. Figure 3(a) shows the EDS spectra obtained for pure CuS. No impurity peaks other than Cu and S were found which indicates that the CuS nanocrystals formed were phase pure. The atomic ratios of Cu:S were expected to be 1:1, but the observed ratio was 53.12 : 49.68, which may be due to excess $Cu^{2+}$ observed on the surface of CuS nanoparticles[9]. Figure 3(b) shows the EDS spectra of 2.5wt.% Zn doped CuS nanocrystals. An extra peak was found at 9.6keV, which indicates that dopant Zn is being incorporated in the host material.

Figure 4 shows the transmittance spectra of pure and CuS doped with 2.5, 5, 7.5 and 10wt.% of Zn. The UV-Vis-NIR transmittance spectrum shows that the pure CuS nanocrystals have transmittance from 0-80% in the wavelength region studied. It could be seen that the transmittance value increased with wavelength from UV region to visible region and remains constant in visible region and decreased with wavelength from visible to NIR region. The 80% transmittance in the wavelength region 300-650nm observed for CuS nanocrystals are very high compared to the transmittance of CuS film (17%)[2]. All the Zn doped CuS nanocrystals have transmittance between 35 and 70% in the Vis-NIR region. As wavelength increases in the NIR region, transmittance decreased and then became a constant. So CuS nanocrystals could be used for coating of poultry roofs and walls, which would protect young chicks from UV radiation as they have not developed protective thick feather[2]. Human eye is sensitive only in the visible region, so this could be used as UV screening material and could be used in eye glass.

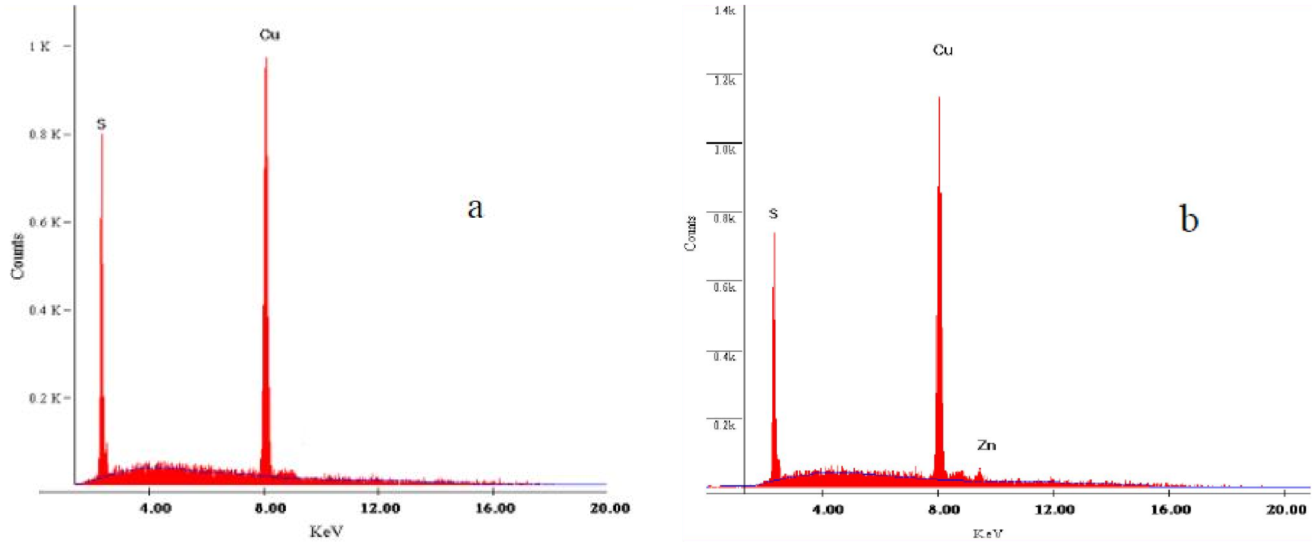
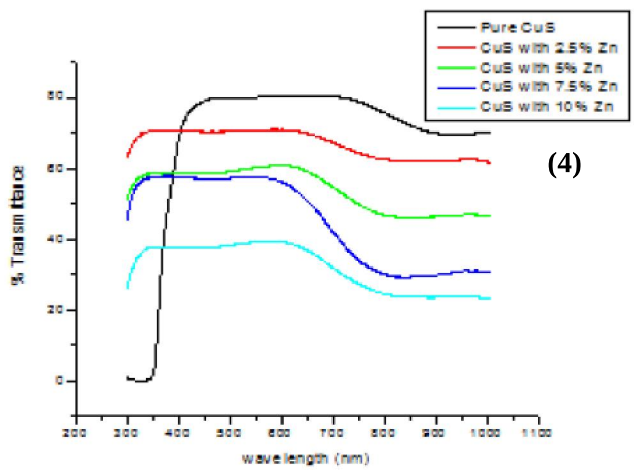



**Figure 3(a.b) : EDS images of pure CuS and 2.5wt.% CuS nanocrystals.**



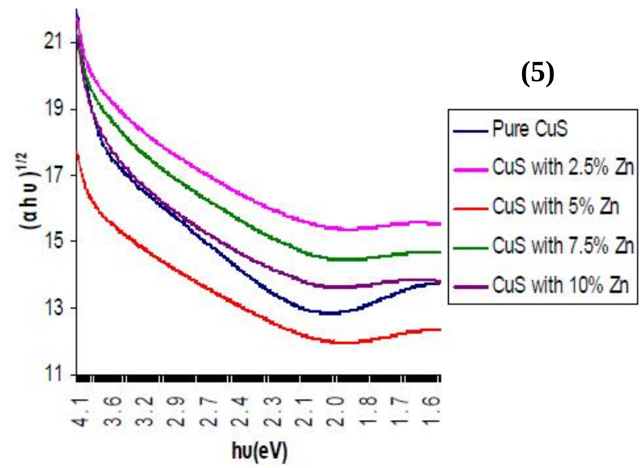




**Figure 4 and 5 : Transmittance and band gap energy spectra of pure and Zn doped CuS nanocrystals.**

Figure 5 gives the combined band gap energy of pure and Zn doped CuS nanocrystals whose values were found separately. The band gap energy is obtained by extrapolating the linear portion of $(\alpha h\upsilon)^{1/2}$ vs hυ plot to the energy axis. $(\alpha h\upsilon)^{1/2}$ vs hυ is a straight line in the domain of higher energies indicating a direct optical transition. The band gap energy for pure CuS nanocrystals was found to be 2.2eV which is less than 2.8eV that was reported by Puspitasari et al.[17]. As the concentration of doping increased from 2.5% to 10% Zn, band gap energy decreased from 2eV to 1.8eV. So it could be explained that as the concentration of doping Zn increased, the band gap energy is getting decreased. That is, the band gap energy of the nanocrystals decreased with increase in particle size. The dependence of optical band gap energy on the particle size shows the presence of quantum confinement effect.

The PL reflectance spectra of pure and Zn doped CuS nanocrystals observed in the present study is shown in Figures 6. It could be seen that the reflectance value increases above 500nm and have high reflectance in the NIR region. Figure 7 shows the band gap energy spectra for pure and Zn doped CuS nanocrystals obtained from the PL reflectance spectra. The optical band gap energy ($E_g$) can be estimated by extrapolating the linear portion of $(\alpha h\upsilon)^{1/2}$ vs (hυ) plot to the energy axis. Here,

$$\alpha = (R_{max}-R_{min}) / (R-R_{min})$$

where $R_{max}$ is maximum value of reflectance and $R_{min}$ is the minimum value of reflectance and R is the reflectance for the particular wavelength. Here also, the $E_g$ value decreases with the increase in doping concentration for all Zn dopants considered in the present study. Also, the $E_g$ values estimated from the PL reflectance spectra compares well with those estimated from the UV-Vis-NIR transmittance spectra. The band gap energy values estimated from UV-Vis-NIR transmittance spectra and PL reflectance spectra are given in TABLE 1.

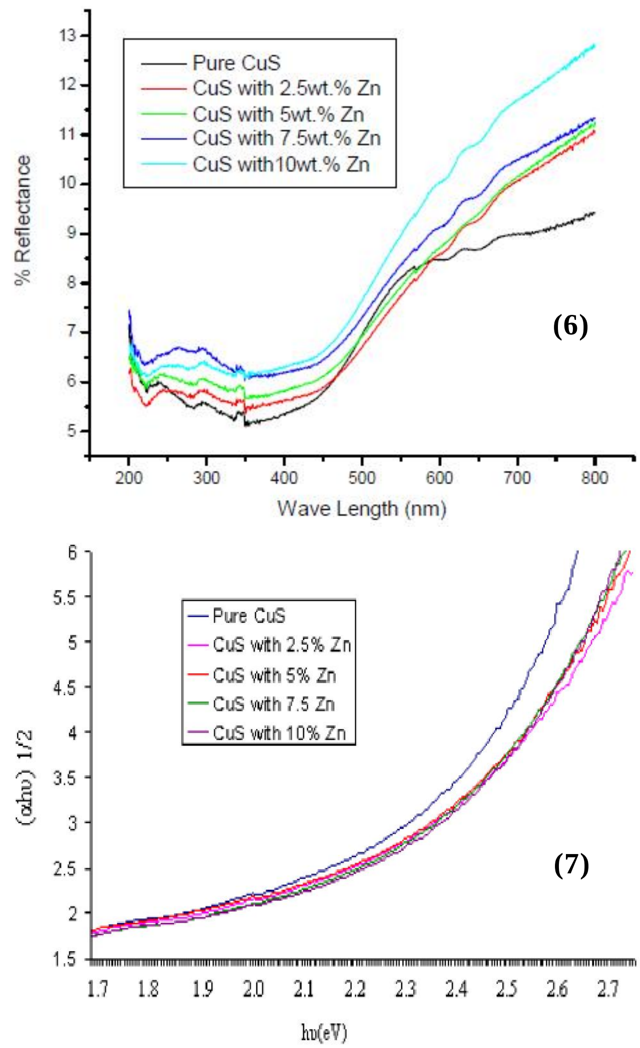



**Figure 6 and 7 : PL reflectance spectra and band gap energy spectra of pure and Zn doped CuS nanocrystals.**

Figures 8-10 show dielectric parameters of pure and Zn doped CuS samples. It was found that as temperature increases, dielectric parameters, viz. dielectric constant, dielectric loss and AC conductivity of pure and Zn doped CuS nanocrystals increase exponentially. All the three dielectric parameters considered and temperature decrease with the increase in impurity concentration. Further, the results of the present study in-

**TABLE 1 : Band gap energy from UV-Vis-NIR transmittance spectra and PL reflectance spectra.**

| Sample Name | Band gap energy | |
|---|---|---|
| | From UV abs spectra (eV) | From PL reflectance (eV) |
| Pure CuS | 2.2 | 2.2 |
| CuS with 2.5% Zn | 2 | 2.1 |
| CuS with 5% Zn | 1.85 | 2.05 |
| CuS with 7.5% Zn | 1.83 | 2 |
| CuS with 10% Zn | 1.8 | 1.95 |

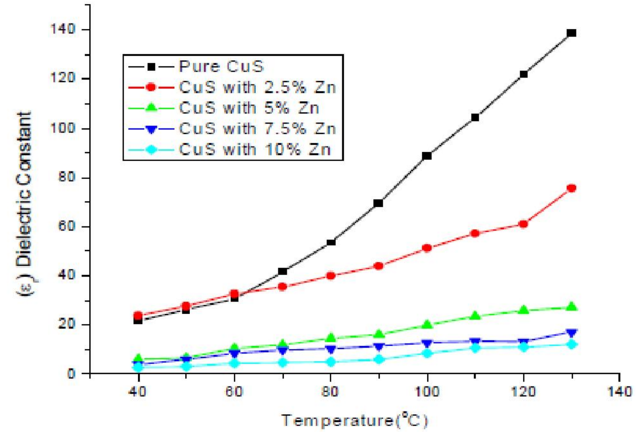



**Figure 8 : The dielectric constants.**

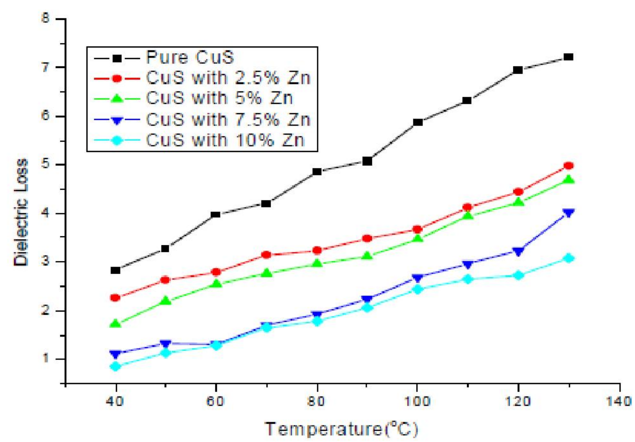



**Figure 9 : The dielectric losses.**

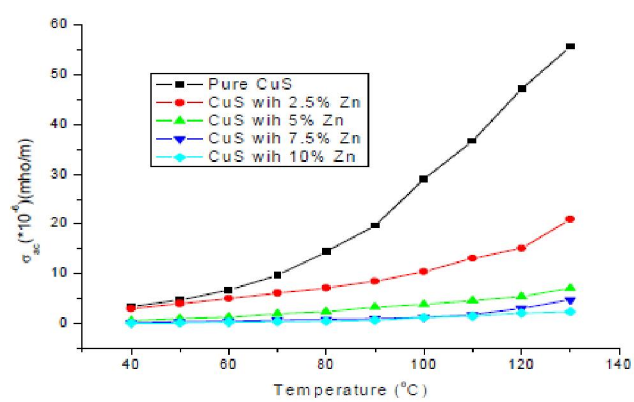



**Figure 10 : The AC conductivities.**

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dicate higher dielectric constants and lower electrical conductivities. This is in correspondence with the lower grain sizes obtained. Hence, space charge polarization and grain boundary scattering are expected to contribute more for the electrical properties of the samples considered in the present study.

## CONCLUSION

Pure and Zn doped CuS nanocrystals have been prepared successfully by a simple chemical method and found that they are of quantum size. Pure CuS nanocrystals have high transmittance in the visible region and high reflectance in the NIR region. The optical properties indicate their possible use in sunglasses and poultry roofs and in filters. Low AC conductivity indicates that the space charge polarization is playing a dominant role in the transport and polarization processes. These CuS samples can be expected to be useful in solar cell device fabrication and in other electrical devices.

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