7.1 Introduction

The ever-increasing demand for the storage of electrical energy in portable and multi-functional device such as transparent displays, touch screens with transparent energy storage systems and multi-energy harvesting devices, using hybrid photovoltaic supercapacitor-battery systems drives technological improvements in supercapacitors and research on flexible and transparent electronics. Supercapacitors are very attractive for portable electronics as well as automotive applications due to their high specific power and durability. Although some supercapacitors built on carbon nanotubes as transparent supercapacitor have been reported, the performance of these supercapacitors is usually not as good as redox supercapacitors made of metal oxide materials (e.g., RuO$_2$, MnO$_2$, and IrO$_2$). On the other hand; these supercapacitors are usually neither transparent nor flexible, which greatly limit their real applications in flexible or transparent electronics [1]. It is still of great interest to develop transparent and flexible supercapacitors. The transparent electrode can be obtained by (i) fabricating the nano material (ii) doping the metal and non-metal in the semiconductor [2-4].

Very few results are available on non metal like nitrogen doped in metal oxide thin films. Boron is generally doped in diamond use for the electroreduction of compounds that are difficult to reduce. Here we tune the band gap of CuO thin films by boron doping in order to get transparent CuO thin films for transparent supercapacitor.
7.2 Experimental section

The colloidal solution route was used to synthesize the nanostructured boron doped CuO thin films. The following route was used to obtain monodispersed and highly stable CuO Colloidal solution at low temperature: 0.0125 M Copper acetate solution was prepared in reducing solvent dimethylformamide (DMF). The reaction was carried out at 100-120°C temperature with constant stirring using a magnetic stirrer. After 20 minutes heating processes the stable colloidal suspension of CuO nanoparticles was obtained. The depositions of the thin films were performed on steel and glass substrates by a few drops of the colloidal dispersion were placed on the top of the substrate for spin coating (3000 rpm). For synthesis of boron doped CuO thin films, borax was used as dopant precursor. The volume weight percent of the boron dopant (5-15 %) were varied for the study the effect of doping on the CuO thin films for optical properties. For convenience named as B1, B2 and B3 for 5, 10 and 15% Boron doped films. Fig.7.1 shows the photograph of a flexible and transparent supercapacitor fabricated using boron doped CuO films.
Fig. 7.1 Photograph of a flexible and transparent supercapacitor fabricated using boron doped CuO films.

7.3 Result and discussion

X-ray photoelectron spectroscopy

Fig. 7.2 shows representative XPS survey spectra of pure CuO and boron doped CuO films. Intense core-level lines of Cu, shown as Cu2p doublet at (Cu2P\textsubscript{1/2} and Cu2P\textsubscript{3/2}) at 930-955eV, Cu 3s at 123 eV, Cu 3p at 77eV and Cu3d at 10eV, are present. In addition, an Auger Cu LMM triplet, which represents energy levels of the Cu Auger processes, was observed.
between 567 and 750 eV. O1s at between 531-531 eV were observed and correspond to oxidation of copper respectively.

Fig. 7.2 shows representative XPS survey spectra of films pure CuO and boron doped CuO

A High resolution Cu2p and O1s XPS spectra was used for the qualitative investigation of pure CuO and boron doped CuO thin films. Fig.7.3 shows the core level spectra for the Cu2p peak over the binding energy ranges from 930-970 eV. The peaks observed for B-CuO at (i) 934.05 eV and (ii) 954.25 eV, were assigned to Cu2p1/2 and Cu2p3/2 respectively. Additionally, two satellite peaks were observed at 944.74 and 962.9 eV respectively. The satellite peaks were positioned at higher binding energies as compare to main peaks was found. This indicated the formation of the CuO phase. The shift into the binding energies and decrement in intensity of the Cu2P peaks of the boron doped CuO thin film with respect to pure CuO films was observed.
Fig. 7.3 shows the core level spectra for the Cu2p peak over the binding energy ranges from 930-970 eV.

The Fig. 7.4 (a and b) shows O1s core level spectrum for pure CuO and boron doped CuO thin films. The peak O1s of boron doped CuO is deconvoluted with three components at 531.49, 532.40 and 532.71 eV, which were assigned to the carbonyl groups, hydroxyl groups and O$^{2-}$ respectively in CuO phase. The spectrum also indicates that Cu$_2$O phase does not exist with CuO as the main peak of Cu$_2$O in O1s spectrum usually appears at 530.2 eV. The shift in binding energy of the peak Cu2p and O1s core spectrum with respect to the pure CuO sample revealed the doping of boron takes place.
Fig. 7.4 (a and b) O1s core level spectrum for pure CuO and boron doped CuO thin films.

Fig. 7.5 shows B1s core level spectrum for B-CuO thin film. The peak observed at 191.55 eV was assigned to B1s core line. From this spectrum we revealed that the boron doping takes place in the B-CuO film.

Fig. 7.5 shows B1s core level spectrum for B-CuO thin film.
The valence band spectra of pure CuO and boron doped CuO thin films measured by XPS were displayed in Fig.7.6 In spectrum the d spectral spread over a very wide energy range of 1-12 eV. Similarly, the O2p characters were present in wide range of 1-6 eV in pure CuO and boron doped CuO respectively. The structure at 8-12 eV in the CuO spectrum is due to the d$^8$ final states. The blue shifts in spectral peaks of valence band spectra are observed for boron doped CuO thin films with respect to pure CuO thin film.

Fig.7.6. Valence band spectra of pure CuO and boron doped CuO thin films measured by XPS.

**FT-Raman studies**

The Raman spectra recorded over 35 – 4000 cm$^{-1}$ of pure CuO and boron doped CuO thin films are shown in Fig.7.7 (a and b). Three Raman active modes are observed at about 164.28 cm$^{-1}$(Ag), 339.8 cm$^{-1}$(Bg) and 563.53 cm$^{-1}$ (Bg) respectively. The band at about 1099.72 cm$^{-1}$ was assigned to multi-phonon transition. The blue shift of Ag mode vibration was observed with respective the boron doping concentration in films. Also, three extra peaks were observed for boron doped CuO thin films. For B1 sample only two
extra peaks were observed at 1371.67 and 1485.46 cm\(^{-1}\) compared to pure 
CuO film. The extra peaks for sample B2 were observed at 1354.31, 1491.25 
and 1595.40 cm\(^{-1}\) respectively. And for sample B3 these extra peaks 
observed at 1352, 1504.75 and 1593.47 cm\(^{-1}\) respectively. From these peaks 
we revealed that the first peaks show red shift, second peaks show blue shift 
and third peaks show red shift respectively with concentration of boron in CuO 
thin films.

Fig.7.7 The Raman spectra recorded over 35 – 4000 cm\(^{-1}\) of (a) pure CuO 
and (b) boron doped CuO thin films.
Optical band gap studies

UV-visible absorption spectra of the pure CuO and boron doped copper oxide thin films were measured, and a classical tauc approach was employed to estimate their optical energy band gaps. It has been found that n=1/2 (allowed direct transition) gives the best description for absorption measurements. Fig.7.8 (a and d) shows representative plots of $(\alpha h\nu)^2$ versus $h\nu$ based on the direct transition for pure CuO and boron doped CuO thin films. The extrapolated value (the straight lines to the x-axis) of $h\nu$ at $\alpha=0$ gives an absorption edge energy corresponding to $E_g$. The band gap energy 2.6 eV was observed for pure CuO sample and it is larger than the bulk CuO (~1.2eV). The increase of the band gap energy is due to the quantum size effect, which is usually observed for nanomaterials. The band gap energy 2.8, 3 and 3.06 eV observed for sample having 5, 10 and 15% boron doping respectively. The blue shift in band gap energy with respect to the concentration of boron was observed.
Fig. 7.8 (a and d) Plots of $(\alpha h \nu)^2$ versus $h \nu$ based on the direct transition for pure CuO and boron doped CuO thin films.

**Scanning Electron Microscopy (SEM)**

Fig. 7.9 shows SEM images of B3 sample. From this image we revealed that the sample is highly dense. Monodispersed nanoparticles are observed on the hierarchical nanostructure.
Fig. 7.9 shows SEM images of B3 film.

**Cyclic voltammetry studies**

To evaluate the rate capability of the electrode, the CVs at different scan rate were recorded for sample B3 in 6 M KOH at different scan rate and is shown in fig. 7.10. The specific capacitance 31.5 F/g was observed for sample B3 at 40 mV/s scan rate. As the scan rate increased 40 to 900mVs\(^{-1}\), the shapes of the CV curves of films B3, still keep nearly square, indicating the good high rate capability.
In order to increase the specific capacitance of the flexible and transparent boron doped CuO film (B3), 0.1 M [NMP] [HSO₄] used as electrolyte. The specific capacitance 132 Fg⁻¹ is observed for 40 mV/s. The area under curve is increased with scan rate as expected for supercapacitor and the shape of the CVs does not change with respect to scan rate revealed the high rate capability of the film as is shown in fig.7.11.
Fig. 7.11. CVs at different scan rates recorded in 0.1 M [NMP][H$_2$SO$_4$] for B3 film.
Conclusions

A prototype of flexible and transparent supercapacitor electrode by using boron doped CuO film is made. Boron doped CuO thin films were successfully synthesized by simple and cost effective colloidal solution method on flexible substrate (PET). The effect of boron concentration on the band gap energy of CuO thin films were studied by using tauc approach. The blue shift (from 2.6 to 3.06eV) in band gap energy of CuO thin films were observed with respect to the concentration of boron. The specific capacitance 31.5 F/g was observed for B3 sample in 1M KOH. The improvement in specific capacitance upto 132 Fg$^{-1}$ is obtained by using 1 M [NMP] [HSO$_4$] electrolyte. From this study we conclude that transparent and flexible B doped CuO film as electrode and [NMP] [HSO$_4$] IL as electrolyte are useful in developing green chemistry approach for better supercapacitors. This approach could work as the platform for future transparent and flexible nanoelectronics.
## References

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