Copper indium based solar cells are the most targeted device as it can replace the most widely used Si solar cells if low cost process are developed for large area and large scale fabrication. In this context, we developed an inexpensive, pollution free hybrid process for the preparation of CuInSe₂ films.

Of all methods, CBD is the most simple and low cost method for large area fabrication of thin films. In this method, to deposit device quality films, the parameters to be controlled are molarity of the reactants, pH and temperature of the bath. For the preparation of single phase ternary CuInSe₂ films control of these parameters is difficult as the formation of binary phases such as Cu₂Se is more probable. However, CBD is a well-suited technique for the deposition of binary films.

The first attempt was conversion of Cu₂Se prepared using CBD into CuInSe₂ by diffusing indium. Indium layer was deposited over Cu₂Se using vacuum evaporation and the resulting bilayer was annealed at 573 K in high vacuum (10⁻⁵ mbar). Indium layer of thickness up to 1300 Å was diffused into Cu₂Se film of thickness ~ 1μ until Cu/In ratio ~ 1 as obtained form XPS analysis. Structural analysis using XRD revealed that the indium-diffused film consists of mixed phases of unreacted Cu₂Se, In₂Se₃ and traces of CuInSe₂. Even though the optical absorption spectrum showed an increase in absorbance, XPS analysis revealed high deficiency of selenium in the film.

In order to compensate for the Se deficiency, we developed a novel selenisation technique using chemical bath deposited selenium thin film. However, instead of selenizing the indium diffused Cu₂Se film, we adopted Stacked Elemental Layer (SEL) technique to prepare binary and ternary selenides using the selenium thin film.
Deposition of selenium thin film through CBD was achieved by controlling pH value of the Na$_2$SeSO$_3$ solution. The optimized conditions were as follows: Well-cleaned glass substrates were dipped vertically in a 25 ml beaker containing 20 ml (0.025 M) Na$_2$SeSO$_3$ solution of pH ~ 4.5, at room temperature. Orange red coloured selenium thin films of thickness 5000 Å were deposited after 3 h of deposition. XRD analysis showed that the films were amorphous in nature. Formation of elemental selenium thin films was confirmed using XPS, SIMS and ICP. Band gap evaluated was 2.10 eV from optical absorption spectrum and electrically the films were insulator.

Photovoltaic material, indium selenide In$_2$Se$_3$ thin films were prepared by annealing the stacked layer of structure Glass/a:Se/In in high vacuum in the range of temperature 373-723 K. The films formed at different temperatures were analysed using different techniques. Films formed at 373 K and above 673 K were hexagonal γ-In$_2$Se$_3$. For films formed at intermediate temperatures were amorphous in nature.

Depthwise compositional analysis using XPS showed that interlayer diffusion was uniform due to annealing and BE values of In and Se were coinciding with that of In$_2$Se$_3$. Band gap values were estimated from optical absorption spectrum. For the films formed at 373 K, band gap was 1.8 eV and slight difference was observed for other films, which could be correlated to the structural change. Electrical conductivity was decreased with increase in annealing temperature. Both n-type and p-type films were obtained depending on annealing temperature. At room temperature maximum photosensitivity was observed for films formed at 423 K.

Copper selenide (Cu$_{2-x}$Se) films were prepared by annealing the SEL structure Glass/a:Se/Cu and characterized using XRD, XPS and optical absorption spectrum.

Copper indium selenide thin films were prepared by two different methods. First method was annealing the stacked layer structure of Glass/a:Se/In/Cu. Indium and copper layers were deposited using vacuum evaporation over selenium film. Preliminary analysis of reaction kinetics was analysed using XRD pattern of films formed at different temperatures in the range 423 K- 673 K. It was found that single-
phase (112) oriented chalcopyrite thin films were formed at 673 K. Growth of CIS film with increase in Cu/In ratio was studied using XRD. Band gap reduced with increase in Cu/In ratio and band tailing was observed for highly Cu-rich films. Electrical conductivity enhanced with Cu/In ratio and highly Cu-rich films showed semimetallic behaviour. Hall measurement studies revealed that the films were p-type and hole concentration increases with Cu/In ratio. Photosensitivity was found to be maximum for films having Cu/In ratio ~1 and decreases with increase in Cu/In ratio. Semimetallic copper rich films showed negative photoconductivity. When this type of films were treated with NaCN solution, it regained its semiconducting and photoconducting property.

Second method developed was diffused metallic Cu into In$_2$Se$_3$ film. Nature of growth of the films with temperature was similar as that of SEL technique except that formation of CuInSe$_2$ just begins at 473 K while in SEL technique significant growth was observed at 473 K. Also, pin holes were observed in films formed at 673 K. Optical properties were also similar to that of first technique. SEL technique is better than the second method, as the probability of escape of selenium is less in the first technique.

In order to avoid the wastage of material, selenium precipitate remained in the bath after deposition of the film was recovered for the use as starting material for further deposition process. Composition and purity of selenium film prepared using selenium precipitate from the bath was anlaysed using XPS and compared with that of the film prepared using powdered pellets. CuInSe$_2$ films were prepared by the SEL technique using selenium precipitate as initial material and structural, compositional and optical properties were analysed. Also, Cu$_{2+x}$Se films were prepared using the selenium precipitate by CBD technique and structure of the film was compared with that of original Cu$_{2+x}$Se film.

It is concluded that amorphous selenium thin film could be prepared using CBD. We developed a new pollution free selenisation technique using this selenium film. Indium selenide and copper indium selenide thin films were successfully
prepared using the above selenisation process. Reuse of selenium precipitate from the chemical bath minimized the wastage of material. This could be a promising option for developing much lower cost thin film technology for copper indium selenide and other selenides.