Chapter 6
Summary and scope for future work

Abstract
The chapter gives the summary of the work carried out and a brief outlook for future work in the area of transparent electronics.
Chapter 6
6.1 Summary

Transparent electronics is an emerging area. Transparent conducting oxides with electrons as carriers are well known. The carrier concentration in these n-type TCOs can be controlled either by doping or by varying the stoichiometry. However, the progress of the field of transparent electronics is hindered by the lack of suitable p-type TCOs. Recently, co-doping of ZnO has been proposed to achieve p-type conduction [1]. The advantage of co-doping is that an increase in solubility of introduced dopants creates shallow acceptor levels in the band gap. This technique has been applied to ZnO to realize p-type conduction in ZnO thin films [2]. The reproducibility of p-type ZnO remained a difficult task for quite a long time. Recently, the researchers have been successful in establishing techniques that will result in reproducible p-type ZnO and thereby facilitating the fabrication of ZnO based homojunctions. [3-5] In 1997 Kawazoe et al from Tokyo Institute of Technology reported another class of materials in thin film form that exhibits p-type conductivity [6]. Followed by this report there were numerous reports on various copper delafossites, grown in thin film form which are reasonably transparent and conducting [7-10] Wide band gap semiconductors are difficult to be doped particularly to p-type [11] and there is no report on p-type silver delafossite in thin film form, except for AgCoO2 [12] The AgInO2[13] films doped with tin shows n-type conductivity.

In the present studies, various copper delafossite materials viz; CuAlO2, CuGaO2, CuFeO2, CuGa1-xFe2xO2, CuYO2 and CuCaY1-xO2 were synthesised by solid state reaction technique. These copper delafossite materials were grown in thin film form by rf magnetron sputtering technique. In general copper delafossites exhibit good optical transparency. The conductivity of the CuYO2 could be improved by Ca doping or by oxygen intercalation by annealing the
film in oxygen atmosphere. It has so far been impossible to improve the p-type conductivity of CuGaO$_2$ significantly by doping Mg or Ca on the Ga site. The p-type conductivity is presumed to be due to oxygen doping or Cu Vacancies [6]. Reports in literature show, oxygen intercalation or divalent ion doping on Ga site is not possible for CuGaO$_2$ thin films to improve the p-type conductivity. Sintered powder and crystals of CuFeO$_2$ have been reported as the materials having the highest p-type conductivity [14, 15] among the copper and silver delafossites. However the CuFeO$_2$ films are found to be less transparent in the visible region compared to CuGaO$_2$. Hence in the present work, the solid solution between the CuGaO$_2$ and CuFeO$_2$ was effected by solid state reaction, varying the Fe content. The CuGa$_{1-x}$Fe$_x$O$_2$ with Fe content, $x=0.5$ shows an increase in conductivity by two orders, compared to CuGaO$_2$ but the transparency is only about 50% in the visible region which is less than that of CuGaO$_2$.

The synthesis of $\alpha$-AgGaO$_2$ was carried out by two step process which involves the synthesis of $\beta$-AgGaO$_2$ by ion exchange reaction followed by the hydrothermal conversion of the $\beta$-AgGaO$_2$ into $\alpha$-AgGaO$_2$. The trace amount of Ag has been reduced substantially in the two step synthesis compared to the direct hydrothermal synthesis. Thin films of $\alpha$-AgGaO$_2$ were prepared on silicon and Al$_2$O$_3$ substrates by pulsed laser deposition. These studies indicate the possibility of using this material as p-type material in thin film form for transparent electronics. The room temperature conductivity of $\alpha$-AgGaO$_2$ was measured as $3.17 \times 10^{-4}$ Scm$^{-1}$ and the optical band gap was estimated as 4.12 eV. A transparent p-n junction thin film diode on glass substrate was fabricated using p-type $\alpha$-AgGaO$_2$ and n-ZnO.
AgCoO$_2$ thin films with 50% transparency in the visible region were deposited on single crystalline Al$_2$O$_3$ and amorphous silica substrates by RF magnetron sputtering and p type conductivity of AgCoO$_2$ was demonstrated by fabricating transparent p-n junction diode with AgCoO$_2$ as p-side and ZnO: Al as n-side using sputtering. The junction thus obtained was found to be rectifying with a forward to reverse current of about 10 at an applied voltage of 3 V. The present study shows that silver delafossite thin films with p-type conductivity can be used for the fabrication of active devices for transparent electronics applications.

### 6.2 Scope for future work

The pn junction fabricated in the present study shows that, the diode ideality factor deviates very much from normal diode behaviour. This is mainly due to the poor interface between the p and n-type TCOs. The conductivity of n-type ZnO TCO used for the fabrication of pn junction mainly depends on oxygen deficiency, whereas the conductivity of p-type delafossite increases on oxygen intercalation. Hence the growth conditions of one are detrimental for the other. It is expected that the epitaxial growth of both n-type and p-type oxide layers will result in a better junction. Since both these oxides have band gap greater than 3 eV, UV light emitting diodes can be fabricated using all oxide transparent heterojunctions. The transparent pn junction can also be used as smart windows which can utilise the ultraviolet part of the sunlight for photovoltaic generation while depending on the plasma frequency of the TCOs IR part can be made reflecting.

The transparent thin film transistor (TTFT) is another active component in the field of transparent electronics. There are numerous reports on TTFT using n-type TCO as the channel layer [16]. The delafossite p-type TCO can be used
for the fabrication of p-channel TFTs. The main drawbacks of these p-type TCOs are their much lower carrier mobility and high carrier concentration. Various growth techniques have to be employed to get better crystalline films which can lead to better mobility for the carriers. Cu(I), Ru(III) oxide, lanthanum copper oxysulphides, lanthanum copper selenides etc have been investigated as p-type materials. The hole mobilities of p-type channel layers are very low compared to the electron mobilities of n-type channel layers. Considerable material development remains a task, before high performance devices can be realised. The transparent electronics calls for the development of new materials especially p-type TCOs and growth techniques for realising active and passive components with high performance efficiency. Another research area with high prospects is the study of magnetic impurity doped delafossite materials. The ZnO based dilute magnetic semiconductors which are transparent are widely being investigated for spintronics applications. The transition metal dopants can be easily incorporated into the delafossite materials and this technique offers the possibility of applications in the field of spintronics.

References

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