# Study of Tin Doped Indium Oxide(ITO)Transparent Conducting Film by DC Reactive Magnetron Sputtering

| | |
|---|---|
| 氏　　名 | AHM Zahirul Alam |
| 生年月日 | |
| 本　　籍 | バングラデシュ |
| 学位の種類 | 博士（工学） |
| 学位記番号 | 博甲第160号 |
| 学位授与の日付 | 平成8年3月25日 |
| 学位授与の要件 | 課程博士（学位規則第4条第1項） |
| 学位授与の題目 | Study of Tin Doped Indium Oxide (ITO) Transparent Conducting Film by DC Reactive Magnetron Sputtering<br>（直流反応性スパッタにより作成した錫ドープ酸化インジュウ(ITO)透明導伝膜の研究） |
| 論文審査委員 | （主査）畑　朋延<br>（副査）渡辺一郎，長谷川誠一<br>森本章治，佐々木公洋 |

# 学位論文要旨

## ABSTRACT

Transparent conducting thin films have attracting increasing interest since they have great importance in a wide range of applications such as solar cells, liquid crystal displays and photodetectors. We have studied Sn doped indium oxide film (ITO) as a transparent film produced by the dc reactive magnetron sputtering using a metal target for high deposition rate. We have optimized the deposition parameters such as reactive gas concentration and the sputtering pressure to obtain a high transparent and a low resistivity film. A new technique has been proposed to lower the film resistivity called "Nano-scale controlled reactive magnetron sputtering" −ITO films with indium tin (IT) modulation layers. The resistivity of 1000 Å ITO film was found to be $5.8\times10^{-4}\,\Omega\cdot$cm (transmission > 90%) by this method which is 40% lower than the film produced by conventional reactive sputtering. We have also proposed highly reactive ozone ($O_3$) as a reactive gas for producing ITO film. It was found that the reaction on the substrate of growing surface at room temperature occurred in the presence of only 4% $O_3$ in $O_2$ gas. The film deposition rate was found as high as 640 Å/min whereas it was only 50 Å/min to obtained transparent film in only oxygen environment. Incorporation of ozone gas in oxygen gas was found to be very effective for producing film at low substrate temperature.

## Chapter 1. Introduction

Developement of transparent conducting coatings were discussed in this chapter. We have discussed the difference between metal and semiconductor films to evaluate film properties. Figure 1 shows the figure of merit of metal and semiconductor films.

It shows that better transparent conducting films can be obtained from thick semiconductor films. It also mentioned that good transparent conductor properties should occur in semiconductors with high mobilities and a low effective mass. A few semiconductor film properties are reviewed such as cadmium oxide (CdO), tin oxide ($SnO_2$) and indium oxide ($In_2O_3$). Our purpose of the investigation was to study Sn doped $In_2O_3$ (ITO) films which is used variety of fields. An ITO film is an n-type highly degenerated wide band gap semiconductor. Metal alloy target has been considered for fabricating ITO films by dc magnetron sputtering for several advantages over the ceramic target. In Chapter 5, the deposition parameters are optimized to obtain high quality ITO film.

A new ITO film fabrication method is proposed in Chapter 6 by introducing IT (indium tin) layer in the film and in Chapter 7, a highly reactive ozone as a reactive gas has been proposed for fabricating film at low substrate temperature and at high deposistion rate.

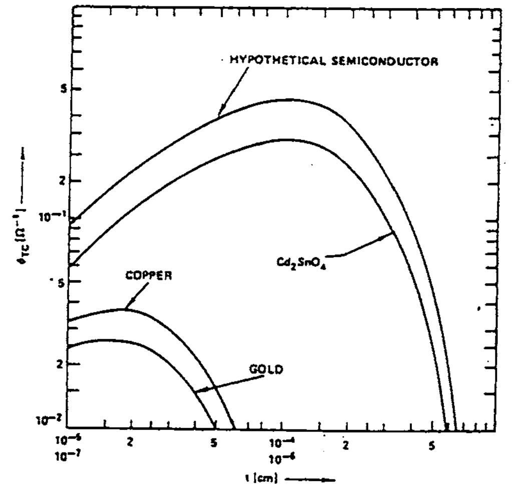

**Figure 1** : *The vaeiation of figure df merit with the film thikness for metal and semiconductor films.*

## Chapter 2. ITO films Characteristics

In this chapter we described the structure of ITO, at normal pressure an $In_2O_3$ crystallizes in a cubic structure of the bixbyite $Mn_2O_3$ (I) type. The coordinate is sixfold for the In atoms and four folds for the O atoms which are complexly oriented. The effect of tin (Sn) doping on carrier concentration in the ITO film is described to realize for getting low resistivity film. It has been shown that maximum carrier concentration in ITO film can be obtained by introducing 5% ~10% Sn doping.

## Chapter 3. ITO Film Fabrication Method

In this section we described a basic sputter deposition principle and mechanisms of ionization in plasma. Reactive sputtering (RS) phenomena along with hysteresis during discharge is briefly discussed to understand our fabrication method of ITO films. Reactive sputtering is a technique to deposit compound films such as oxide, nitride, etc. or introduced dopant into a metal or alloy. In this process target is sputtered in an atmosphere of reactive and inert gas mixtures. There are two modes of operation in the reactive sputtering : "metal" mode and "compound" mode. In metal mode, the target surface is kept metallic, and metallic films are deposited at high rate. On the other hand, in compound mode the target surface is covered with compound layers, and compound films are deposited at low rate. The transition between two modes is generally avalanche-like and non-linear to reactive gas flow rate, and further a deposition rate and discharge voltage show hysteresis for increasing and decreasing of the reactive gas flow rate. The main attractive features of RS are high deposition rate and easy fabrication of the target.

ITO films were deposited onto microslide glass substrate using dc reactive magnetron of a composite 90%In + 10%Sn metal alloy target. The experimental setup is shown in Fig. 2. The typical deposition parameters during film growth are shown in the Table I.

**Table 1** : *Typical sputtering conditons.*

| | |
|---|---|
| Substrate | Microslide glass<br>76mm × 26mm |
| Total gas pressure $P_{tot}$ | 6 mTorr |
| Sputtering gas | Ar |
| Reactive gas | $O_2$ or<br>$96\%O_2+4\%O_3$ |
| Substrate temperature $T_S$ | RT ~ 320°C |
| Film thickness $t$ | ~ 100 nm |

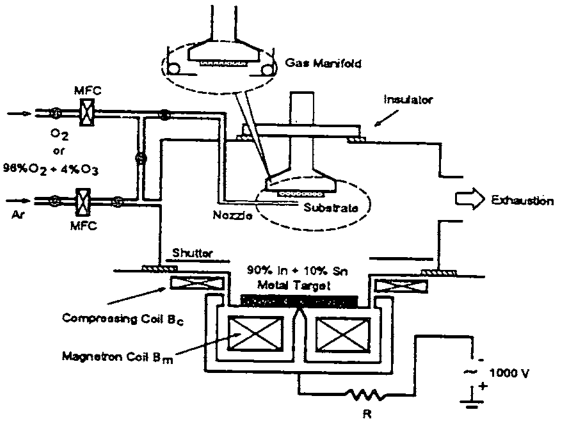

**Figure 2** : *Schematic diagram of dc magnetron sputtering system.*

## Chapter 5. How to Optimize Deposition Parameters

The property of ITO films produced by the dc reactive magnetron is strongly dependent on the deposition parameters. Therefore, some of the deposition parameters were optimized. Figure 3 shows the variation of resistivity with the percent reactive gas. In the low reactive gas concentration the films were opaque and low resistivity with metallic behavior and the film transparency increased with increasing the reactive gas concentration and the resistivity variation behavior is shown in the figure.

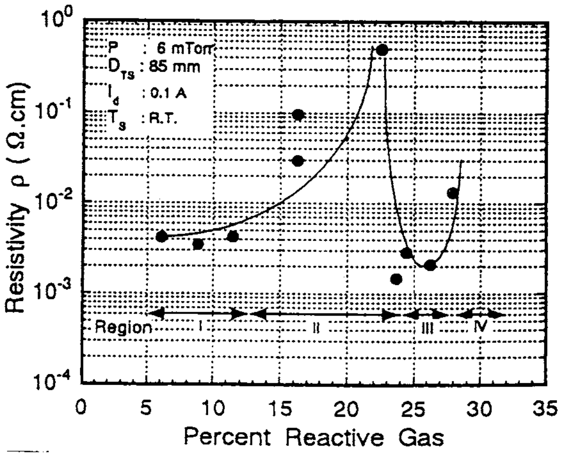

**Figure 3** : *Dependence of ITO film resistivity on $O_2$ concentration at room temperature.*

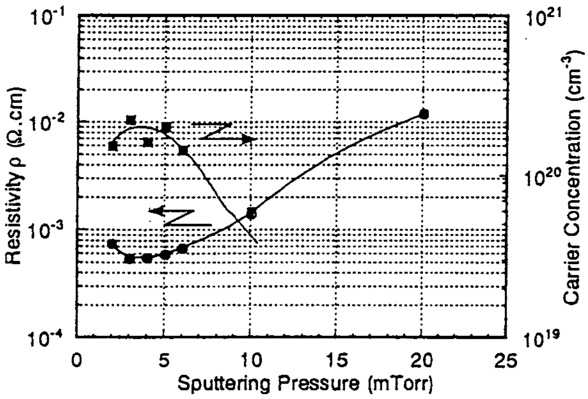

**Figure 4** : *dependence of minimum resistivity obtained at particular sputtering pressure with sputtering pressure.*

It shows that the low resistivity transparent film is delicately dependent on the reactive gas concentration, i. e., an optimum resistivity is strongly dependent on the percent reactive gas present in the sputtering gas of Ar. It was found that the percent reactive gas was also varied with the sputtering pressure and there exists a region of sputtering pressure to obtain high quality film as shown in Fig. 4.

## Chapter 6. Nano-Scale Controlled ITO Film Fabrication

In the experiment it was found that the resistivity of film was decreased with decreasing the film thickness as shown in Fig. 5. The decrease in resistivity is governed by the increase both of the carrier concentration and the Hall mobility as shown in the figure. Therefore, in-dium tin (IT) layer of layers in the film were suggested to reduce the film resistivity, so that IT layer was considered to be act as an isolation layer. IT is considered that the ressistivity of ITO film might be determined from the resistivity of surface ITO layer. Therefore in this chapter, we proposed a new method of ITO film fabrication. The schematic sketch of ITO film is shown in Fig. 6.

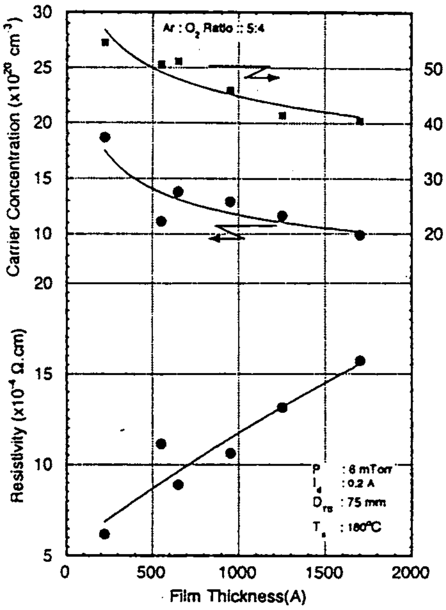

**Figure 5** : *Dependence of ITO film resistivity, carrier concentration and Hall mobility on film thickness.*

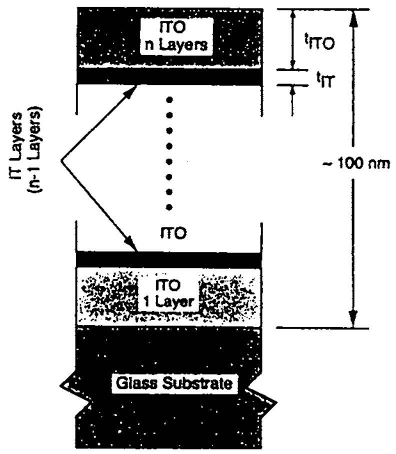

**Figure 6** : *Schematic sketch of film growth.*

The film was grown by the combination of reactive-nonreactive magnetron sputtering. The effect of inserting IT layer/s in ITO films on resistivity with the variation of thickness ratio m, IT to ITO layer thicknesses ($m=t_{IT}/t_{ITO}$) is shown in Fig. 7. These figure shows that the resistivity is decreased with increasing the number of IT layer. The resistivity is high for small and large value of m. Increasing the value of m results in the decrease of ITO layer thickness, however it does not correspond to a single structured ITO film resistivity of equal thickness. Therefore, some other factors are considered to be responsible for the variation of film resistivity.

Fig. 8 shows the variation in carrier concentration and Hall mobility with the thikness ratio m. The figure shows that the resistivity of ITO film is mainly due to the variation of carrier concentration that is originated from oxygen vacancies in the film. It is considered that the IT layers are transformed to ITO layers during subsequent growth of the film due to oxygen diffusion from ITO layers. Therefore, the total film resistivity is determined by the nature of oxidation of IT layer. Intermediate oxidation results suboxide film of high resistivity and fully oxidation results stoichiometric film of high resistivity. Therefore, there exists a optimum oxidation level of IT layer to get low resistivity film hence a optimum thickness ratio m. The minimum resistivity of 1000 Å ITO film was found to be $5.8 \times 10^{-4}\ \Omega \cdot cm$ at the substrate temperature of 180°C by inserted four equally spaced 13 Å

IT layers (m = 0.07). For this film the nominal thickness of each ITO layer was 189Å. Whereas, the resistivity of single structured ITO film was $9.8 \times 10^{-4}\,\Omega \cdot \mathrm{cm}$. Therefore, this method of fabricating ITO film was found to be effective for reducing film resistivity.

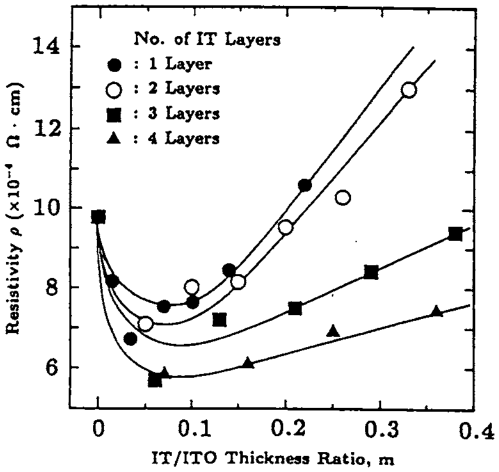

**Figure 7** : *Dependence of ITO film resistivity on the thickness ratio, m for different number of IT layers.*

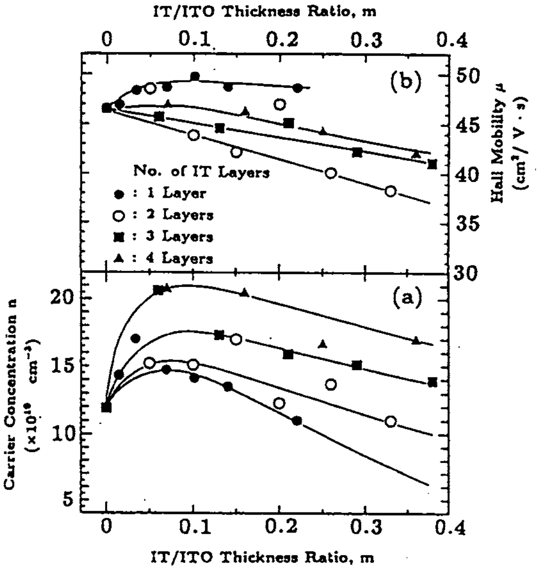

**Figure 8** : *Variation in carrier concentration and Hall mobility of ITO films with the thickness ratio, m for different number of IT layers.*

## Chapter 7. Ozone as a Reactive Gas

From the above experimental results, it was impossible to get a high quality film at low substrate temperature. Because it was considered that diffusion of oxygen atoms from ITO layers to IT layers were not possible at low substrate temperature. Moreover, the target was operated in the compound (oxide) mode hence low deposition of films. Therefore, we have tried to deposit film at the metallic mode by the aperture on the target surface to reduce the target oxidation and thereby increasing the oxygen partial pressure near the substrate. However, our attempt was failed. Therefore, we introduced $O_2$ near the substrate but failed to obtain transparent film even by increasing the substrate temperature in the metal mode i. e., at high deposition rate. This is because of less reactive nature of IT metal alloy target to oxygen.

Therefore, highly reactive ozone ($O_3$) as a reactive gas has been proposed. The effects of ($O_3$) for producing transparent ITO film at room temperature were visualized through observation of transparent circular region near the inlet of nozzle for reactive gas as shown in Fig. 9. The transparent region was increased with increasing the oxygen added ozone gas concentration. Only 4% ($O_3$) in volume concentration in ($O_2$) (checked the $O_3$ content by titration method) gas was effective to produce such transparent regions. However, no such transparent regions were observed for only oxygen as a reactive gas. Therefore, transparent oxide film was obtained at the deposition rate as high as 640 Å/min in the presence of ($O_3$) in ($O_2$) gas. Whereas, transparent film was obtained in only ($O_2$) environment at 50 Å/min for the deposition power of 45 W. The low deposition rate was due to oxide coverage on the target surface.

The effect of ($O_3$) on ITO film property was not clearly observed when the reactive gas was introduced trough the same inlet of Ar. This was due to decomposition of ozone by

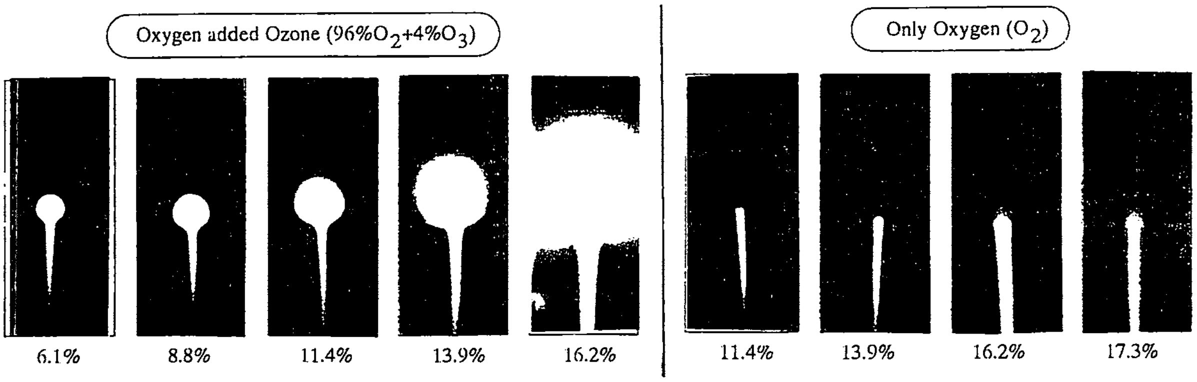

**Figure 9** : Film deposited in various concentrations of reactive gases (indicated below the photographs) of $O_2$ and $96\%O_2+4\%O_3$ introduced through the nozzle placed on the substrate.

plasma radiation. Therefore, to avoid plasma decomposition, the reactive gas was introduced near the substrate by using a enclosure. The resistivity of the film produced in different substrate temperature for both reactive gases are shown in Fig. 10. The value of resistivity shown in the figure was the minimum resistivity obtained after the optimization as discussed in Chapter 5 and the optimum reactive gases concentration are mentioned in the figure. This figure shows that the ozone added environment results a low resistivity transparent film at low substrate temperature. The reason for lowering resistivity was explained by the creation of oxygen vacancies in the film due to reaction of sputtered metal particles. At high substrate temperature the effect of ozone was not observed for the decomposition of ozone at the temperature.

The optical properties of films were observed and Burstein-Moss shift was observed. The absorption edge shifted towards higher energy at increased substrate temperature that was due to increase in carrier concentration at high substrate temperature. The intrinsic bandgap and the reduced effective mass ($1/m_r^*=1/m_c^*+m_v^*$) were found $E_{go}$=3.52 eV and $m_r^*$= $0.46m_o$, respectively. These results are in good agreement with other researchers.

## Chapter 8. Conclusions.

On the basis of our results, we can conclude the following:

1) High transparent and low resistivity film is critically dependent on the reactive gas concentration during deposition.
2) High quality films were obtained within the range of sputtering pressure from 3 to 6 mTorr.
3) Inserting IT layer/s in the ITO film was found to be very effective for reducing film resistivity. The lowest resistivity of 1000 Å film was found to be $5.8\times10^{-4}\,\Omega\cdot$cm with inserting 4 equally spaced 13 Å IT layers which was 40% lower than the film without IT layers at the substrate temperature of 180°C. The transparency of the film was greater than 90% in the visible region.
4) Ozone as a reactive gas was found very effective for producing low resistivity transparent film at high deposition rate and at low substrate temperature. The resistivity of 1000 Å film as deposition was found to be $1.5\times10^{-3}\,\Omega\cdot$cm at room temperature in the presence of only 4% $O_3$ in $O_2$ gas, whereas only $O_2$ results $6.5\times10^{-3}$

Ω·cm.

**Ackowledgments**

The author would like to thank Associate Professor Dr. K. Torei, Civil Engineering department, Kanazawa university for providing XRD measurment facilities.

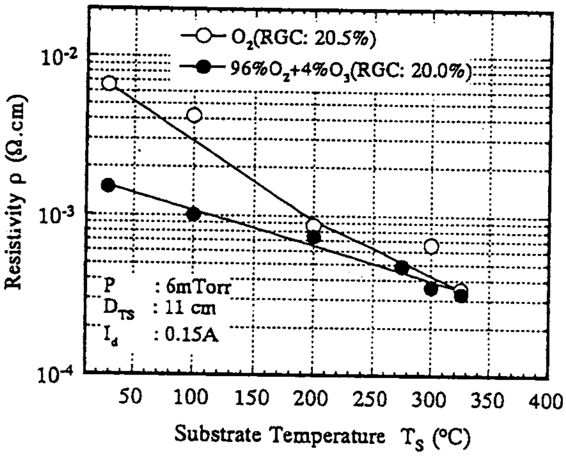

**Figure 10** : *Variation of film resistivity with the substrate temperature for both the reactive gases of $O_2$ and 96%$O_2$+4%O$O_3$.*

## 学位論文の審査結果の要旨

平成8年2月1日に論文審査委員会を開催し，提出された学位論文および口頭発表の結果をふまえ種々の意見の交換を行った。

本研究は太陽電池や液晶表示装置（LCD）に用いられる錫ドープ酸化インジュウム（ITO）透明導電膜の低抵抗化およびプロセスの低温化に関する論文である。通常はITOのセラミックターゲットを用いた反応性スパッタリング法で作製されている。しかし，堆積速度が遅い，低抵抗膜を作製するための基板温度が高いなどの欠点があり，これを改善するための研究を行った。ITOは$n$型で縮退したバンド幅の広い半導体の一種で，キャリヤの電子はドーパントの錫や酸素欠損から供給されると考えられている。特に$Sn^{4+}$ドナー密度は製膜温度とそれに伴う膜の結晶化に大きく依存する。

本研究では低抵抗ITO薄膜を作製するため，ITO薄膜の間に金属IT（インジュウムと錫の合金）の薄い層を挟んで酸素欠損を生じさせるという方法である。これを“ナノスケール制御反応性スパッタリング法”と名付け薄膜の低抵抗化を試みた。基板温度180°C，膜厚約1000ÅのITO薄膜の抵抗率は$9.8\times10^{-4}$Ω·cmであったが，ITOが約250Å，ITが約10Åを1周期とし4周期重ねると$5.8\times10^{-4}$Ω·cmにまで低下した。しかし，これを最適化することも考えたが，さらに低抵抗化するためには200°C以上の高温が必要であった。LCDパネルのカラーフィルタ上に堆積するには室温から150°Cまでが望ましい。そこで，更に酸化が容易なオゾンを用いて低温作製を試みた。

オゾナイザーに酸素を通し4％のオゾンを添加した酸素と，添加しない酸素だけの場合に基板上でのスパッタされたIT金属と酸化ガスとの反応の違いを調べた。その結果オゾン添加の場合は基板上で反応し，高速でITOは堆積するが，酸素だけの場合にはターゲットが酸化してITOにはなるが，堆積速度は遅い。室温で酸素にオゾンを添加した場合のITOは，$1.5\times10^{-3}$Ω·cmと低い値であったが，添加しない場合には$6.5\times10^{-3}$Ω·cmと高くオゾン添加の有用性が示された。オゾン添加で実際に赤，緑，青のカラーフィルター上にITOを堆積し150°Cの基板温度で赤は$9.6\times10^{-4}$Ω·cm，緑は$5.3\times10^{-4}$Ω·cm，青は$5.9\times10^{-4}$Ω·cmの低い抵抗率の膜を得ることができた。このようにITO薄膜の低温・高速作製に成功した。

これらより，本論文は博士論文として十分に値すると結論した。