CHAPTER 5

Influence of RF Power on the Properties of ITO Thin Films
Abstract

Highly transparent and conducting ITO thin films were deposited at room temperature by RF magnetron sputtering of ITO target (95wt%In$_2$O$_3$ and 5wt% SnO$_2$) in pure argon atmosphere. Thin films were deposited on glass substrate without any intentional heating at various RF powers ranging from 20W to 50W and the influence of RF power on the structural, electrical and optical properties of the films were investigated. The influence of fluorine doping on the properties of ITO thin films was also investigated as a function of RF power. Enhancement of crystallinity and conductivity was observed with increase in RF power. Film deposited on glass substrates at an RF power of 50W was oriented in the (100) direction and it showed a minimum resistivity of $1.27 \times 10^{-3} \Omega \text{cm}$. It has been observed that the film properties are greatly influenced by the plasma conditions during sputtering. Radio frequency (RF) plasma during sputtering was analyzed using Langmuir Probe and Optical Emission Spectroscopy (OES). The plasma parameters such as ion density and electron temperature were determined and their dependence on properties of thin film deposited under similar plasma conditions were studied. Plasma parameters were determined for different RF powers keeping the distance from the target a constant.
5.1 Introduction

The properties of Indium tin oxide thin films can be optimized by carefully selecting the process parameters during deposition. In the case of sputtered films, RF power is one of the process parameters that can be controlled during the film growth. This chapter presents the dependence of RF power on the ITO film properties.

5.2 Experimental

5.2.1 Thin film deposition

ITO films were deposited on to glass substrates at room temperature by rf magnetron sputtering of an ITO target (2 inch diameter) containing 95wt% of In$_2$O$_3$ and 5 wt% of SnO$_2$. The base pressure in the chamber was 2x10$^{-5}$ m bar. Sputtering was carried out in argon atmosphere at a pressure of 0.01 m bar. Glass slides of dimension 2.5 cm x 1 cm were used as the substrates. The substrates were kept at a distance of 4cm above the target. Highly transparent and conducting films were obtained when deposition was carried out at that distance[1]. A 13.56 MHz RF power supply was used to provide the RF field. The RF power was varied in the range 20W to 50W.

Even though the substrates were not heated intentionally during sputtering, an increase in substrate temperature was observed during sputtering. The increase in substrate temperature can be attributed to the plasma surface interactions which causes the transfer of energy to the substrate. Energy transfer from plasma to solid surface occurs through optical radiations and fluxes of neutral particles and ions. Optical radiation has components in the IR, visible and UV regions. When these radiations are absorbed by a solid surface, the radiations transforms into heat. But the energy of optical radiations is very low. At lower sputtering pressures, ion collisions become prominent [2]. During the ion bombardment, the dissipation of kinetic and vibrational energy fractions of ions causes heating.
of the substrate surface. Figure 5.1 shows the variation in substrate temperature measured at the end of sputtering as a function of RF power. The deposition rate was found to increase with increase in RF power, became maximum at 45W and then decreased slightly (Fig 5.1). The sputtering time was so adjusted that the thickness of all the films studied were 250nm.

Figure 5.1. Variation of sputtering rate and substrate temperature with RF power
5.2.2 Plasma diagnostics

Langmuir probe is one of the simplest techniques for obtaining information about the ions in plasma. An RF compensated probe was used for plasma diagnostics. The Langmuir probe assembly consists of a tungsten wire, 0.5 mm in diameter and 5 mm in length, supported by a glass sleeve (Fig 5.2) along with the RF compensating circuit. Probe current is measured for bias voltages in the range of –60 V to + 60 V. The probe voltage – current (V – I) characteristics are plotted for different RF powers (20W to 50W). Great care was taken to prevent the probe feed wires being exposed to the plasma since this will contribute to the measured probe current. To ensure a clean probe surface, the probe wire was replaced frequently.

![Figure 5.2. Experimental set up for Langmuir probe and optical emission spectral studies.](image)

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To investigate the ionic species present in the RF plasma in detail optical emission spectra (OES) of plasma plume generated during the RF sputtering of ITO target was recorded using a 0.32m monochromator and charge coupled device (CCD) detector. OES examines the light given off by species in the plasma that have been raised to excited states by electron impact. Excited species radiate at wavelengths corresponding to the quantum mechanically allowed transitions between electron energy levels. It is an attractive option for process control because it is fast, non intrusive, can monitor multiple elements simultaneously and provides information about deposition conditions in the plasma [3]. In the present investigation, the OES studies were made through the side window of the chamber (Fig 5.2). The spectral studies were carried out for different RF powers keeping the distance from the target at 4cm.

5.3 Structural characterization

The x-ray diffraction (XRD) pattern of the ITO thin films grown by sputtering at various RF powers is shown in figure5.3. All the films are polycrystalline and showed diffraction peaks of In₂O₃ [4]. The crystallinity of ITO thin films is strongly dominated by the kinetic energy of indium atoms reaching the substrate surface. The average kinetic energy of the sputtered particles is about 1 to 3 eV, which is high enough to enable the sputtered particles to migrate and to find the most suitable site to form the crystalline structure when they arrive at the substrate surface [5]. All the peaks detected were of In₂O₃ [4]. The films grown at lower RF power showed x-ray diffraction peak at 2θ = 30.6° which correspond to reflection from (222) plane indicating an orientation along the [111] direction and at 2θ = 50.5° corresponding to reflection from (440) plane indicating the orientation along [110] direction. The intensity of (440) peak increased with increase in RF power up to 35W. As the power is increased beyond 35W a new peak emerges at 2θ = 35° which correspond to (400) plane of In₂O₃ indicating a preferred orientation along the [100] direction. The increase
in RF power enhances the energy of the sputtered particles. The crystallites in the thin films deposited at higher RF powers will then try to orient in the [100] direction.

Figure 5.3. XRD pattern of ITO thin films deposited at various RF powers.

The change in preferred orientation of growth of ITO film with deposition conditions is already being reported. Some reports show that the orientation of the films change from (400) to (222) when the oxygen pressure is increased during sputtering [6,7]. Increase in substrate temperature is also reported to favor (400) orientation [8]. Though there have been controversial reports on the effect
of pressure on the film orientation, (400) peak intensity mainly decreased as the sputtering pressure is increased[9,10]. From a thermodynamic point of view, the preferred orientation of thin films is known to be the planes of lowest surface energy [11]. Also from the viewpoint of kinetics, only grains with the highest growth rate eventually survive [12]. In the case of ITO, (222) plane is known to be the most densely packed plane[13]. As a result it is the plane with highest energy and (400) plane has the lowest energy. The degree of orientation of the (400) plane is expected to be dependent on the mobility of the adatoms on the substrate[14].

The adatom mobility is found to be proportional to the diffusivity of adatoms on the substrate which is given by the expression,

\[ D_s = \frac{1}{2} a_0^2 \nu \exp \left( \frac{-E_s}{kT} \right) \]  \hspace{1cm} (5.1)

where \( a_0 \) is the atomic dimension, \( \nu \) is the vibrational frequency of adatoms and \( E_s \) is the activation energy for surface diffusion [15].

The mean square distance traveled by the adatoms in a time \( t \) is given by the expression

\[ \langle X^2 \rangle = 2D_s t \]  \hspace{1cm} (5.2)

If the adatoms have a sufficient amount of energy, then they would form nucleation centers that have thermodynamically favorable (400) orientations. The average energy of adatoms is determined by the kinetic energy of the sputtered atoms just before arriving the substrate surface and Ar\(^+\) bombardment energy. Ar\(^+\) ions that are incident on the substrate surface can supply considerable energy to the adatoms[16].

In the present study, the grains showed (222) and (440) orientations at lower RF powers and the orientation changed to (400) as the power was increased. At low
sputtering power, the energy of Ar\(^+\) ions, which collide with the target surface, is low and hence the average energy of the sputtered particles is also low. Therefore the supplied energy by ion bombardment is low and consequently the adatom mobility is very low at very low sputtering power. This favors the grain orientation along (222) and (440) planes. Increase in RF power caused increase in energy of the Ar\(^+\) ions, which in turn increases the adatom mobility. This favors the grain orientation along (400) plane. The (400) orientation is also reported to be prominent in films that are oxygen deficient [17,18]. In the present investigation, the increase in RF power resulted in an increase in oxygen vacancy which is shown by the carrier density measurements.

The full width at half maximum (FWHM) for the (440) diffraction peak was analysed as a function of RF power. A decrease in FWHM with RF power (Fig 5.4) indicates the enhancement of crystallinity. The lattice constant ‘a’ can be determined using equation (4.1). The calculated value of ‘a’ for the ITO film is slightly greater than that of indium oxide (10.117Å). According to recent reports [19] tin is incorporated into In\(_2\)O\(_3\) lattice as Sn\(^{4+}\) whose ionic radius (0.071nm) is less than that of indium. The increase in lattice parameter is attributed to the increase in repulsive forces arising from the extra positive charge of the tin cations. In the present work an increase in lattice constant with RF power was observed (Fig 5.4).
The films were also deposited at a target to substrate spacing of 2cm under the same conditions mentioned above. The XRD pattern (Fig 5.5) shows that the films are polycrystalline and are oriented in the (100) direction. The films deposited at 20W were almost amorphous in nature. The (400) diffraction peak appeared at a sufficiently low RF power of 25W. The intensity of the (400) diffraction peak increase with increase in RF power. The appearance of the (400) diffraction peak at sufficiently lower RF power compared to the case with T-S spacing = 4 cm may be because of the sharp rise in temperature of the substrate during deposition which gives the sputtered particles the sufficient energy to orient in the (100) direction. (440) diffraction peak was also present in
the XRD pattern but with lesser intensity. Also the intensity of the (440) diffraction peak decreased with rise in RF power.

Figure 5.5. XRD pattern of ITO thin films deposited at T-S spacing = 2cm and various RF powers

The influence of fluorine doping on the properties of ITO thin films were also studied. Fluorine doping was carryout by placing Indium fluoride pellets on the erosion zone of the target. The deposition was carried out at three different RF powers viz 30W, 40W and 50W at target to substrate distance 4cm. The films deposited at RF powers of 30W and 40W showed (440) diffraction peak at around $2\theta = 50.5^\circ$ indicating a preferred orientation in the [110] direction. As the power was increased to 50W the orientation of the films changed to [100] direction which can be inferred from the appearance of (400) diffraction peak in
the XRD pattern (Fig 5.6). Also we can see that the intensity of the (440) diffraction peak gets reduced as the RF power is increased from 30 to 50W.

The FWHM of the (440) diffraction peak increased with increase in RF power, which indicate that the grain size of the (440) oriented crystallites gets reduced. Figure5.7 shows the variation in FWHM and intensity of (440) diffraction peak with RF power.
The alignment of the grains along (440) plane in the lower RF power range may be due to the lower energy of the sputtered particles reaching the substrate surface. Increase in RF powers gives additional energy to the sputtered particles, which enable them to orient in the [100] direction. Fluorine doping also favors the [100] orientation. It may be because of the replacement of some oxygen sites by fluorine ions since their radii are comparable [7].
5.4 Optical characterization

The transmission spectra of the ITO films grown at various RF powers are shown in figure 5.8. The films exhibited a strong absorption in the UV region. It is caused by the excitons across the fundamental bandgap $E_g$.

All the films were highly transparent in the visible region of the electromagnetic spectrum. The average transmission in the visible region of the electromagnetic spectrum was >80%. Films deposited at higher RF powers showed a decrease in transmission at higher wavelengths (in the near IR region).
In the near IR region, the free carrier absorption becomes important for the transmittance and reflectance of the ITO films [20]. The optical phenomena in this region can be explained on the basis of classical Drude theory. According to this theory, the transition from high transmittance to high reflectance will occur for films with higher carrier concentrations. Comparing the result of the present study with the theory, it can be concluded that the carrier concentration increases with increase in RF power.

![Graph showing variation of bandgap and average transmission of ITO thin films as a function of RF power.](image)

Figure 5.9. Variation of bandgap and average transmission of ITO thin films as a function of RF power

The increase in carrier concentration with increase in RF power makes the transparent conductor to reflect the incident wavelengths in the IR region. The
average transmission in the visible range was found to decrease with increase in RF power (Fig5.9). According to Wu et al [21], the decrease in the value of transmission is related to the reduction of SnO₂ in ITO films.

The band gap of the ITO films were calculated from the transmission spectra. By assuming a parabolic band structure for the material, the absorption coefficient and bandgap can be related by the expression \( \alpha h \nu = A (h \nu - E_g)^{1/N} \) where \( E_g \) is the band gap energy and \( \alpha \) is the absorption coefficient corresponding to frequency \( \nu \). The constant \( N \) is equal to 2, for direct allowed transition. The bandgap of ITO films were determined from the plot of \( (\alpha h \nu)^2 \) vs \( h \nu \) by extrapolating the linear portion of the curve to \( \alpha h \nu \) equal to zero. In the present study, the bandgap decreased with increase in RF power (Fig 5.9) upto 40W and then increased. The increase in bandgap at higher RF powers can be attributed to Burstein - Moss effect which is a phenomenon that occurs at higher carrier concentrations. From the electrical measurements, a sharp increase in carrier density can be seen at higher RF powers which substantiate the increase in bandgap at high RF powers.

### 5.5 Electrical characterization

The resistivity of the films was determined by employing vander Pauw four probe technique. The resistivity of the films decreased with increase in RF power. Figure 5.10 shows the variation of resistivity and sheet resistance of ITO thin films with RF power for the films deposited at a target to substrate spacing of 4cm. The minimum resistivity of \( 1.27 \times 10^{-3} \) Ω cm and sheet resistance of 208 Ω/square was obtained for the films deposited at an RF power of 50W. The mobility of the films increased upto 40 W and then decreased. The increase in mobility is related to the deposition rate [22]. As a result of high deposition rate at high RF powers, atoms do not have sufficient time to complete their bondings and it causes an increase in the number of oxygen vacancies. Increase in
mobility is also associated with the increase in grain size, which causes a reduction of scattering losses. The carrier density increased sharply at 50W (Fig 5.11a). The sharp increase in carrier density at 50W causes the decrease in mobility at that RF power.

In ITO, the magnitude of conductivity results from the ability of $\text{In}_2\text{O}_3$ lattice to incorporate substitutional tin atoms without major structural modifications as well as from the scattering mechanisms for free electrons [23]. The free electrons are liberated from the substitutionally entered tin atoms in the cation sub lattice and from doubly charged oxygen vacancies. When $\text{Sn}^{4+}$ replaces $\text{In}^{3+}$ in the $\text{In}_2\text{O}_3$ lattice, one free electron is created. Doubly charged oxygen vacancy
creates two free electrons. The increase in number of free carriers with increase in RF power reduces the resistivity of the films.

The figure of merit of the films was determined using the relation devised by Haacke[24]. The figure of merit increased with increase in RF power and showed a slight decrease corresponding to the RF power of 50W (Fig5.11b). This decrease is due to the decrease in the value of average transmission in the visible range corresponding to 50W.

Figure 5.11. Variation in (a)mobility and carrier density and (b)figure of merit of ITO thin films with RF power.
The resistivity of the films deposited at a target to substrate spacing of 2cm also decreased with increase in RF power. It got almost saturated after 35W. But the minimum value of resistivity observed was less than that in the case of T-S = 4cm. The electrical properties of the fluorine doped ITO films also showed a similar trend with increase in RF power.

Resistivity and sheet resistance decreased with increase in RF power (Fig 5.12) while mobility and carrier density increased with increase in RF power (Fig 5.13). However, there was much reduction in the value of sheet resistance for the
fluorine doped ITO films. A sheet resistance of 65 $\Omega$/square was obtained when film deposition was carried out at an RF power of 50W.

![Image](image1.jpg)

**Figure 5.13.** Variation of mobility and carrier density of ITO:F thin films with RF power

### 5.6 Plasma characterization

#### 5.6.1 Langmuir Probe

Probe current ($I$) was measured for bias voltage ($V$) in the range $-40$ to $+40$V. The measurement was carried out at different RF powers ranging from 20W to 50W. Figure 5.14 shows the probe I-V characteristics for an RF power of
20W with the probe placed at a distance of 4cm. This characteristics is normally determined by the plasma properties in the immediate vicinity of the probe [25].

As mentioned in section 3.5.1a three separate regions namely region I, region II and region III can be seen in the I-V characteristics. From the characteristics we can determine the plasma potential ($V_p$) and floating potential ($V_f$). The difference between plasma potential and floating potential ($V_p - V_f$) gives a measure of energy of the sputtered particles bombarding the substrate. $V_p - V_f$ is plotted in the figure 5.15 as a function of RF power. In the present investigation $V_p - V_f$ shows a slight decreases with increasing RF power.
5.6.1a Ion Density

The saturation ion portion of the characteristics is used to determine the ion density[26]. The ion current drawn by the probe is given by the equation

\[ I_i = \frac{A e^{\frac{3}{2}} N}{2\sqrt{\pi}} \left( \frac{3T_e}{m_i} \right)^{\frac{1}{2}} \left( 1 - \frac{V - V_f}{T_e} \right)^{\frac{1}{2}}, \]  

(5.3)
where \( A \) is the surface area of the probe, \( N \) is the plasma density, \( m_i \) is the ion mass and \( T_e \) is the electron temperature in electron volts. Taking the derivative of \( I_i^2 \) with respect to \( V \) and rearranging we get

\[
\frac{\partial I_i^2}{\partial V} = \frac{4\pi n_i m_i}{3 A^2 e^3} \left( \frac{\partial I_i^2}{\partial V} \right)
\]  

(5.4)

Where \( n_i \) is the ion density, \( m_i \) is the ion mass and \( A \) is the collection area of probe which is given by

\[
A = 2\pi rl + \pi r^2,
\]

(5.5)

where \( r \) is the radius of the probe (100 \( \mu \)m) and \( l \) is the probe length (5 mm). Ion mass was taken as \( m_i = 40m_p \) (where the \( m_p \) is the mass of the proton (1.667x10^{-27} Kg)), on the assumption that the major contribution of ions are given by Argon. This equation is based on the fact that \( n_i \) is equal to electron density \( n_e \) because plasma is neutral.

Figure 5.16 shows the dependence of ion density on RF power. Ion density is found to increase linearly with increase in RF power. The increase in ion density is due to the greater ionization resulting from collisions that may occur at higher RF power.
5.6.1b Electron temperature

The state of plasma is essentially specified if the composition of the plasma is known and if the energy of each constituent can be determined. Electron temperature can be determined from the I-V characteristics [26]. The electron temperature can be determined from the plot of natural logarithm of current (\( \ln I \)) versus probe voltage in the region between floating potential and plasma potential. The graph will be a straight line. The reciprocal of the slope of the straight line plot will give the value of \( kT_e \). In the present investigation, electron temperature decreased with increase in RF power (Fig 5.17 (a)). The drop in electron temperature and \( V_p - V_f \) is due to the increase in ion density[27].
The electron velocity and ion velocity\cite{28} were calculated using the equations,

\[
\nu_e = \left( \frac{8kT_e}{\pi m_e} \right)^{1/2} \tag{5.6}
\]

\[
\nu_i = \left( \frac{8kT_e}{\pi m_i} \right)^{1/2} \tag{5.7}
\]

where \( k \) is the Boltzmann constant, \( T_e \) is the electron temperature, \( m_e \) is the mass of electron and \( m_i \) is the ion mass.

Figure 5.17. Variation of (a) electron temperature and (b) electron and ion velocity with RF power.
Ion velocity is of the order of $10^3\text{m/s}$ and electron velocity is of the order of $10^6\text{m/s}$. Both ion velocity and electron velocity decreased with increase in RF power (Fig 5.17(b)). The variation of velocity with RF power showed a similar behaviour as that of electron temperature.

5.6.2 Optical Emission Spectral Studies

RF plasma generated during the sputtering of ITO target was analysed by recording the optical emission spectra, in order to identify the ionic species in the plume.

![Optical emission spectrum](image)

Figure 5.18. Optical emission spectrum of RF plasma generated with ITO target at an RF power of 20 W and at a distance of 4 cm from the target. Inset shows the variation of integral intensity of argon (I) at a wavelength of 811.5 nm with RF power.
The spectral analysis revealed that the ionic species is mainly composed of argon ions. The identified species [29] essentially comprises argon neutrals (ArI), singly ionised argon (ArII), doubly ionised argon (ArIII), Indium neutral (InI), Oxygen neutral (OI) and tin neutral (SnI). Figure 5.18 gives a typical OES spectrum taken at an RF power of 20W. The spectral data is collected from the plasma at a distance of 4cm from the target.

The OES shows that the intensity of emission lines increases with increase of RF power. The variation of integral intensity of Argon (I) at a wavelength of 811.5nm with RF power is given in the inset of figure 5.18. The integral intensity is found to increase linearly with RF power. Increase of RF power causes more ionization, which in turn increases the population of various energy levels associated with the ions leading to the increase in integral intensity.

5.7 Conclusion

Highly transparent and conducting indium tin oxide thin films were deposited by RF magnetron sputtering at room temperature. The influence of RF power on the structural, electrical and optical properties were evaluated. Enhancement of crystallinity with increase in RF power was observed. The films deposited at an RF power of 50W were oriented in the (100) direction. An increase in lattice parameter with increase in RF power was also observed. The films were highly transparent in the visible range of the electromagnetic spectrum. The average transmission in the visible range was greater than 80%. The minimum resistivity of $1.25 \times 10^{-3} \Omega \text{cm}$ was obtained for the films deposited at an RF power of 50W. Langmuir probe and Optical Emission Spectroscopic (OES) studies were done to investigate the plasma parameters. Different ionic species in the plasma were identified from the spectrum. The plasma parameters such as electron temperature, electron & ion velocity and ion density were determined by the Langmuir probe technique for various RF powers. The observed plasma
parameters were correlated with the properties of thin films deposited under similar plasma conditions. The ion density and electron temperature was the highest for an RF power of 50W.
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