

Present Understanding and Problems of ITO Thin Films

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The ITO thin film is widely used for the electro-optical applications among many transparent conductors because of ease of making and fine pattern generation. Being transparent and highly conductive can be achieved by the presence of plenty amount of free electrons in the conduction band which is separated by roughly 3.5eV from the valence band. Effort of understanding this material and thin film processes for the making is still being continued to have further improvement along with the market needs.

An overview about the present understanding of the material will be made from very practical and scientific point of view, including discussion about the basic but controversial concepts of improving the electrical properties.

1. The History of Discovery

Georg Rupprecht is well recognized to have reported for the first time in 1954 the electrical properties of evaporated indium oxide films [1]. He got transparent indium oxide films after annealing "metallic" thin films evaporated from indium metal. The thickness of these films were 500~2500Å.

There seems to have been some good and unintentional combinations of factors that had led to fairly low resistivities if we take into consideration that the vacuum attained at that time was at most in the range of 10^{-4} torr because the outgassing systems in early 50s must have consisted of a mercury diffusion pump of poor capability. No metallic film with thin continuous structure was possible on glass or quartz substrates if the indium metal was evaporated in the vacuum of 10^{-6} torr, very common today. The "metallic" films in his description were undoubtedly oxidized to such an extent that the films did not assume discontinuous island structures.

The resistivity of indium oxide films thus annealed at 700~1000 C were ranged from 10^5 to 10^{-1} Ωcm. We now well recognize that the oxidation proceeds from surface to inside of the film, and that the more the oxygen vacancy in the film, the higher the electrical conductivity becomes. The resistivities of thicker films must have been lower than those of thinner films even if they were as clear and transparent as thinner films. Rupprecht noticed some very interesting behavior of resistivity changes in the experiments carried out in vacuum. It can be summarized as follows:

(1) The conductivity decreased with decreasing temperature and increased with increasing temperature for the temperature range roughly less than 100 C. This change was reversible.

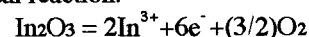
(2) The conductivity increased with increasing

temperature for the temperature range higher than 100 C. This change was irreversible.

(3) The conductivity decreased or increased as observed in (1), namely reversibly, when the specimens were allowed to cool from any temperatures above 100 C.

(4) The conductivities of the specimen restored original values by leaving them in an ordinary ambient for hours after taking them back from vacuum.

Figure 1 shows schematic changes observed. In brief it indicates that the reversible change can be explained in terms of the thermal excitation of free carriers, while the irreversible changes had to be caused by the desorption of gas(es) that might have trapped electrons when adsorbed. According to the observation the conductivity was uniquely determined by the oxygen partial pressure for the temperatures higher than 450 C. The dependence was $\sigma \sim P_{O_2}^{-0.19}$, the value -0.19 being very nicely reflecting the theoretical expectation of $\sigma \sim P_{O_2}^{-3/16}$. This was derived by applying the mass-action law to the chemical reaction:



A conclusion drawn at this point was that the material was a n-type defect semiconductor with an excess amount of electrons. The irreversible changes observed in the 100 to 450 C range were attributed to the desorption of oxygen in the forms of O or O². They also reported the fundamental absorption edge^{1x} at around 350 nm and the refractive index of roughly 2.

In summary it was mid 50s that we became aware of the indium oxide as a transparent conductive thin film material and got knowledge of the method of controlling resistivity by choosing

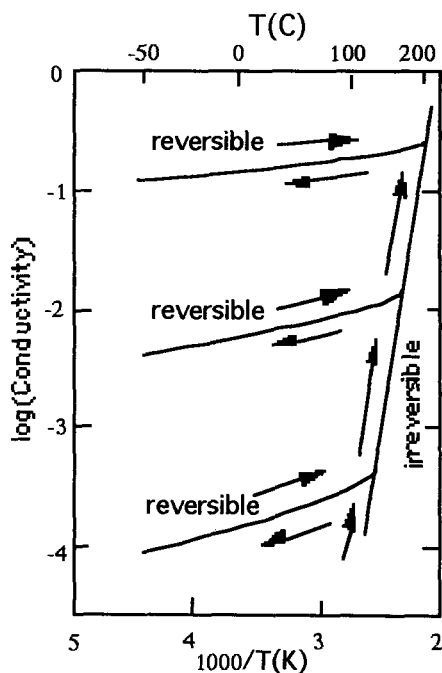


Fig. 1 Thermal behaviors of an Indium Oxide Film measured in vacuum

simply a pair of parameters, temperature and oxygen partial pressure. From the resistivity we can calculate easily the sheet resistivity²⁷. No one could imagine, however, at the time of Rupprecht that such a low resistivity become achieved.

2. Technical Progress : ever lasting competition with tin oxide

In the history of transparent conductors more attention and effort had been paid to the development of high quality SnO₂ until early 70s. This was because tin was much more abundant and hence popular material than indium. Acidic alcoholic solution of stannic chloride, SnCl₄, has been a well known formulation for such applications. Spraying the solution onto glass substrates heated up to 600 C could yield SnO₂ films very easily with a specific resistivity of mid 10⁻³ Ωcm.

Further progress in lowering the resistivity was made in late 60s by applying a new knowledge of the valence control that the conductivity of semiconductors could be controlled intentionally by introducing an appropriate amount of dopant whose position in the Periodic Table is adjacent to the (elemental) semiconductor in concern. In the case of SnO₂ it is antimony. The doping effect arises from the creation of excess charges in the form of electron or hole that can freely move around inside

the semiconductors. In the case of SnO₂ excess electrons are released from antimony ions on the tin position in the lattice points because it liberates 5 electrons. Four of 5 electrons are used to form bonds with 4 oxygen ions just like as tin atoms do in the lattice, and hence one electron becomes free to move inside the crystal.

Quantitatively, 1 mol% addition of Sb₂O₅ results in the formation of 2.7×10^{20} electrons per cm³ if all the antimony atoms occupy the tin positions and fully ionized. This level of carrier density gives rise to a conductivity of $2.7 \times 10^{20} \times 1.6 \times 10^{-19} \times \mu = 43.2 \mu$ [(Ωcm)⁻¹], where μ is the mobility of charge carriers, ordinarily 20 to 40 cm²/V.s. Thus the resistivities can attain 10⁻⁴ Ωcm on doping, roughly one order of magnitude lower than those of non doping cases. Actually the degree of full ionization is dependent on the degree of crystallinity and the degree of segregation of dopant into the grain boundaries. In terms of experiment it depends on the substrate temperature, glass composition, duration of spray process and the composition of spraying solution. The probability for full ionization seems to have been 1/3 to 1/5.

Now we return back to indium oxide. The Rupprecht's finding had been forgotten for more than 10 years. In 1968 new work was reported by H. J. J. van Boort and R. Groth of Philips, Holland [2]. They got a resistivity as low as 3×10^{-4} Ωcm by spraying the solution onto heated Pyrex glass substrate with a thickness of 6 mm. In the alcoholic solution were dissolved indium chloride, InCl₃, and small amount of tin tetrachloride, SnCl₄. The substrates were heated up to 600 C or more. Two points to be noticed are the glass thickness and fewer alkali content of the substrate. It would have provided sufficient heat that was necessary for the oxidation reaction and fewer alkali on glass surface was also favorable for the formation of good crystallites. The impact of this value was great because it was one order of magnitude lower than that of "best" tin oxide films at that time. Main stream of research has changed to indium oxide from tin oxide.

The conductive material has become to be called "indium tin oxide" or "ITO" by American research people. Now this lazy American expression is prevailing all over the world, though it must technically be called "tin-doped indium oxide".

From mid 70s began the first generation of liquid crystal displays. They were alpha-numeric displays driven by the dynamic scattering mode of the homeotropic phase of liquid crystals. This display mode forced to lower the resistivity because

the patterned display segments could be seen to unaided eye (you could see a number 8 in this case) even when the segments are not turned on if the thickness of ITO film was more than 500Å. The sheet resistivity requested at that time was 100~250 Ω/sq. This means the specific resistivity of (5~12.5) $\times 10^{-4}$ Ωcm, which was impossible for tin oxide to attain. Tin oxide seemed to have given up its position.

The methods of ITO thin film formation at that time were the vacuum evaporation and diode sputtering. In Japan the development of production technology was lead by the Osaka Industrial Testing Laboratory. Its achievement was transferred to private industries[3]. Large area vacuum deposition technique as a mass production technology was established at around 1980 and capable of making 200~300 thousand square meters a year. The diode sputtering had been replaced by the magnetron sputtering until up to 1985. Application of liquid crystal displays began to expand from calculator, games to consumer electronic products such as word processors and lap top computers. A rough estimation of production amount in 1985 was a little more than a million square meters (4 times increase in 5 years). This year must be memorized as the beginning of word processor applications, the era of the dot matrix based on the STN (super twisted nematic) mode. Thereafter growth of ITO production has become more accelerated to reach 10 million square meters a year in 1995 in Japan.

Demand on "more information in a limited display area" led to finer dot pitches, which forced us to produce ITO coated glass with lower resistivities. Today the sheet resistivity must be less than 10 Ω/sq in most sophisticated color LCDs based on the STN mode and even 5 Ω/sq in cases of developing some new types of displays. This means that it is necessary to improve the specific resistivity by 40% in a close future if the customers do not allow us to increase the film thickness.

3. The Differences of Indium Oxide from Tin Oxide

It would be worth noting the presence of an intervening layer which is deposited prior to the deposition of ITO film. Not necessarily explicitly described about conducting glass is that the sheet glass has been coated with an amorphous silica film. Ordinary processing position of silica coating is just before the ITO deposition in the same vacuum chamber although it was previously an independent processing line in the form of CVD or sol/gel.

The silica surface acts as alkali barrier to

prevent the out-diffusion of alkali ions from the sheet glass which contains about 14 wt% sodium oxide. The presence of alkali on the glass surface, even if it is very small, causes not only an unfavorable increase in the specific resistivity of growing film but also a possible decomposition of liquid crystal material through the electrochemical process, which shorten the service term of displays.

3.1 Specific resistivity

It is well recognized that there is always some delay in the production side in establishing the best values that has been achieved in the research area. In the case of ITO notable research works on the electrical properties are summarized in Table 1. The specific resistivity of ITO thin films coated on the sheet glass had been almost unchanged to be 2×10^{-4} Ωcm in both sputtered and evaporated products [3,4]. During 1991-93 a great deal of development effort have been concentrated at many firms in Japan to achieve the level of less than 1.8×10^{-4} Ωcm. The low resistivity grades of the order of 1.5×10^{-4} Ωcm has been available in commercial basis since around 1994, though the 2×10^{-4} Ωcm grade is still being mostly produced.

We are still behind the experimental achievement by more than 10 years. We know that we can reach the value 0.7×10^{-4} Ωcm someday, but we do not know when it will be. In addition we may have a new record low in some close future. Then the new goal shall be set forth.

Figure 2 shows an experimental result of the dc magnetron sputtering. The substrate temperature during the sputter deposition has a dramatic effect on the resistivity, especially in the range of 100 to 200 C. Resistivity attained at 400 C was 1.4×10^{-4} Ωcm. Lower resistivities at higher temperatures have been often attributed to the improvements in crystallinity. However, the meaning of crystallinity is not necessarily well-defined. Does it mean the average size of microcrystals as a constituent of thin film? Does it mean the distribution of grain sizes? Does it mean some kind of reduction in the internal force field generated either by the presence of impurities at unlike sites in the crystal lattice, or by

Table 1 Important Progresses in ITO resistivity

year	first author	method	resistivity $10^{-4}\Omega\text{cm}$	ref.
1968	van Boort	spray	2.5	2
1971	Katsube	evaporation	2.0	3
1972	Fraser	sputter	2.0	4
1980	Nath	ion plating	0.7	5
1983	Ray	sputtering	0.7	6

the expansion mismatch? All of them are possible causes to degrade the crystallinity of microcrystals in different manners.

Figure 3 shows the effect of cathode voltage on the resistivity. Three curves from the upper correspond to three substrate temperatures: room temperature, 200 and 350C. This figure enables us to recognize the bird's eye view of the situation including the result obtained in figure 2. The values in figure 3 are a little bit better than those shown in figure 2. The lower the sputtering voltage and the higher the substrate temperature, we can get lower resistivities. Also we can read from this figure that the tendency towards low resistivities becomes weak as the sputtering voltage is lowered and hence the resistivity of $0.7 \times 10^{-4} \Omega\text{cm}$ seems to be a good limit to ultimately attain within the framework of magnetron sputtering.

However, there have been a very few theoretical works so as to be able to predict the ultimate lowest possible value of specific resistivity. We know two papers reporting the lowest value of $0.7 \times 10^{-4} \Omega\text{cm}$ by the activated reactive evaporation [5] and magnetron sputtering [6], but we do not know persuasive evidences responsible for why such values were possible. The lack of theoretical works on the ITO material is undoubtedly due to the complex and crowded structure in the very big unit cell with the lattice constant of 10.12 \AA . Such a structural complexity gives rise to difficulties in calculating the stability of the crystal structure and formation of impurity levels due to doping elements.

In this sense we still need to characterize the crystallographic structure of ITO grains in more detail. Similarly the examination of the possible field effect of the grain boundary on the electrical properties must be explored more than ever. Of course we have been getting better understandings about the structure [7, 8]. Nevertheless, it should be more in order to recognize the relations between the structure and the other properties.

The ITO films formed by evaporation tend to have more regular grain structure compared to the indium oxide films with no tin addition [9]. Figure 4 shows the result of plotting the size of the large grains observed in the area of $1.5 \mu\text{m}$ by $1.5 \mu\text{m}$ of SEM images. As clearly shown in the figure, grain size is bigger for the high temperature case at 450 C and the rate of grain size decrease with tin oxide content is higher for the low temperature case at 400 C. Very curious is that it shows an exponential dependence on the dopant concentration.

Another feature of interest in the electrical properties is the temperature dependence. The

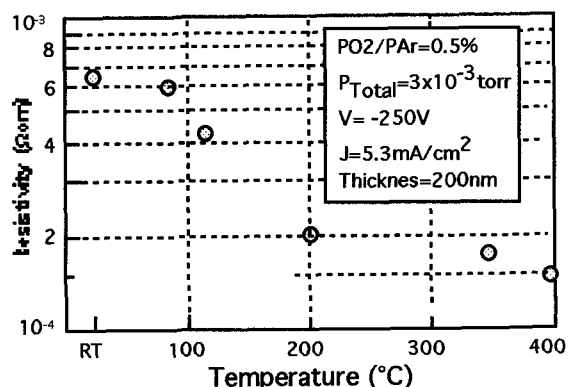


FIG.2 Substrate temperature dependence of specific resistivity

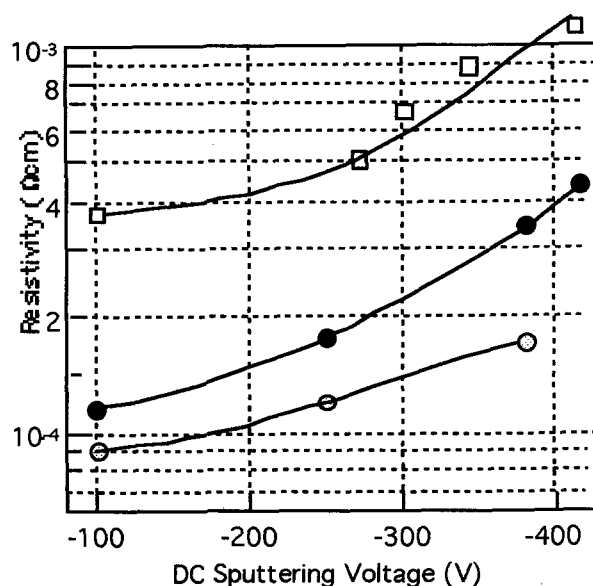


Fig.3 Acceleration voltage dependence of specific resistivity of magnetron sputtered ITO thin films

change indicated by a dashed curve in figure 5 was observed on the two In_2O_3 single crystals by Weiher [10]. Because the carrier densities of these crystals were very small compared to those observed on ITO films and on the border of the degeneracy, they showed very clear temperature dependence in the mobility and carrier density while highly degenerated ITO films showed only a slight changes. Note that the mobility of single crystals is very high, $200\text{--}600 \text{ cm}^2/\text{V}\cdot\text{s}$ at low temperatures and about 150 at room temperature, while typical ITO films have 40-45. The mobility, according to the solid state physics, decreases monotonically with increasing carrier density. The relation of the mobility with the carrier density in ITO films seems to be also reasonable as an extension from the single

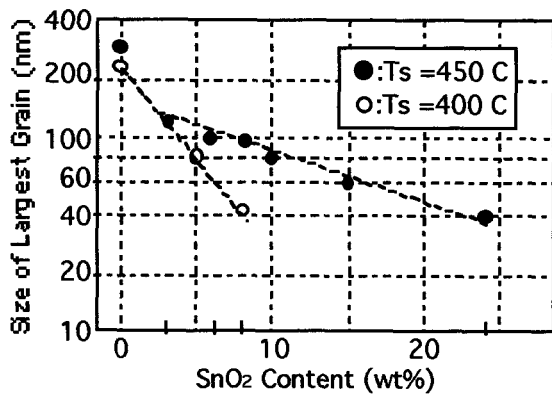


Fig.4 Effect of SnO₂ content on grain size of evaporated 700Å thick ITO films .

crystal values. Also note that the carrier density and mobility of typical ITO films are mid 10^{20} to lower 10^{21} cm^{-3} and 40-45 $\text{cm}^2/\text{V}\cdot\text{s}$, respectively.

3.2 Transparency

Figure 6 shows a comparison of transparency of sputtered ITO and CVD SnO₂ films with the same thickness of 200 nm, but with different carrier densities. Very clearly shown is the effect of free carrier density. Four times increase in carrier density in the case of tin oxide makes the film more than twice absorptive. A question of why not a four time increase in absorption must be examined in detail with more accurate measurements. The second feature is that the ITO is very much transparent in the blue to green region of the spectrum. Observed increase in absorption towards infrared is due to the free carrier absorption. This absorption increasing

towards infrared makes the hue of ITO films slightly bluish. Taking into account the fact that the spectral sensitivity of the eye has a sharp maximum at around $\lambda=555$ nm, it can be said that the transparency of ITO film is almost equal to that of SnO₂ films with carrier density of 1×10^{20} cm^{-3} . The third feature is that ITO seems to show smaller optical band gap in comparison to SnO₂.

This infrared absorption is understood as a result of the collective motion of free carriers conforming a solid state plasma with positive charges on the lattice points. Electromagnetic waves with frequencies near the plasma frequency³ is resonantly absorbed to excite electrons in the plasma⁴. Electrons in the system can responses easily for the light of longer wavelengths. This means that the system of high free carrier density shows high reflectivity for the wavelength region longer than the plasma wavelength.

As a result of so many (10^{20} cm^{-3}) free carriers in the bulk semiconductor we can observe the Burstein-Moss shift [11, 12]. The effect can be observed as a result of increase in the distance between the top of the valence band and the bottom of conduction band. This gives rise to an apparent broadening of the optical bandgap. The amount of increase is given by the expression;

$$\Delta E_{opt}^{BM} \equiv E_{opt} - E_G = \frac{\pi^2 \hbar^2}{2m_r^*} \left(\frac{3n_e}{\pi} \right)^{2/3}$$

$$= \frac{0.3641}{m_r^*/m_0} n_e^{2/3} \times 10^{-14} [eV]$$

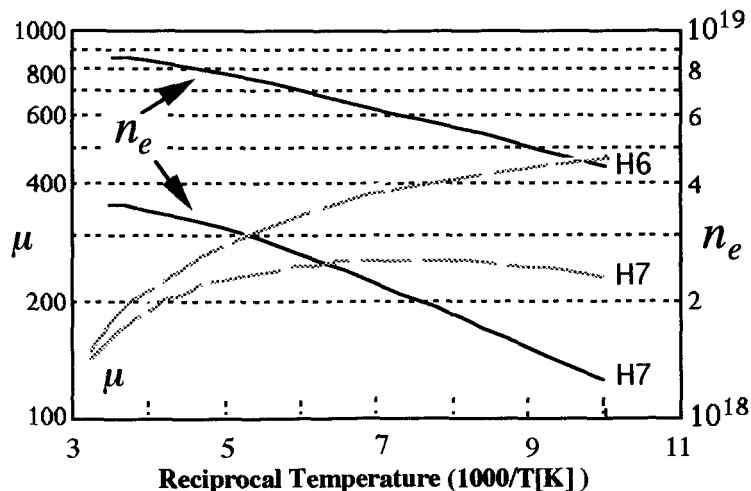


Fig.5 Temperature dependence of the carrier density and mobility of two single crystals of indium oxide

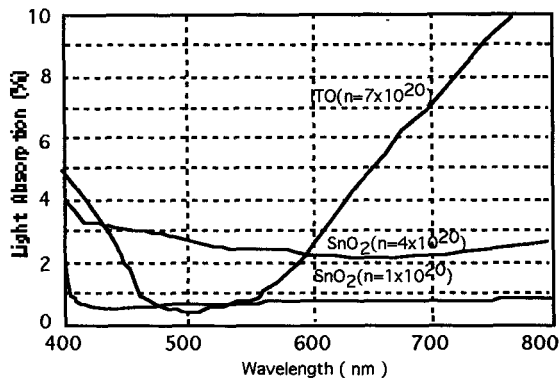


Fig.6 Comparison of light absorption of an ITO and two SnO₂ films with different carrier densities at a normalized thickness of 200nm.

where n_c is the carrier density. m_e^* is the reduced mass of electrons given by where $m_e^* = [m_c^* + m_v^*] / m_c^*$, m_c^* is the reduced mass of electrons on optical transition and roughly $0.55m_0$, and $m_v^* = 0.3m_0$ the effective mass of conduction electrons.

Figure 7 shows very clearly the above mentioned optical properties of semiconductors as represented by IO and ITO films. The carrier density and mobility of the films are ($n_1 = 1 \times 10^{20} \text{ cm}^{-3}$, $\mu_1 = 40 \text{ cm}^2/\text{V}\cdot\text{s}$) and ($n_2 = 9 \times 10^{20} \text{ cm}^{-3}$, $\mu_2 = 30 \text{ cm}^2/\text{V}\cdot\text{s}$), respectively. The film thickness is 160 nm for the IO film and 200 nm for the ITO film. We can notice with respect to the ITO curve that the plasma resonance absorption centered at $1.8 \mu\text{m}$ extends its tail down to the 800 nm region, while there appears no such an absorption band in the case of IO film.

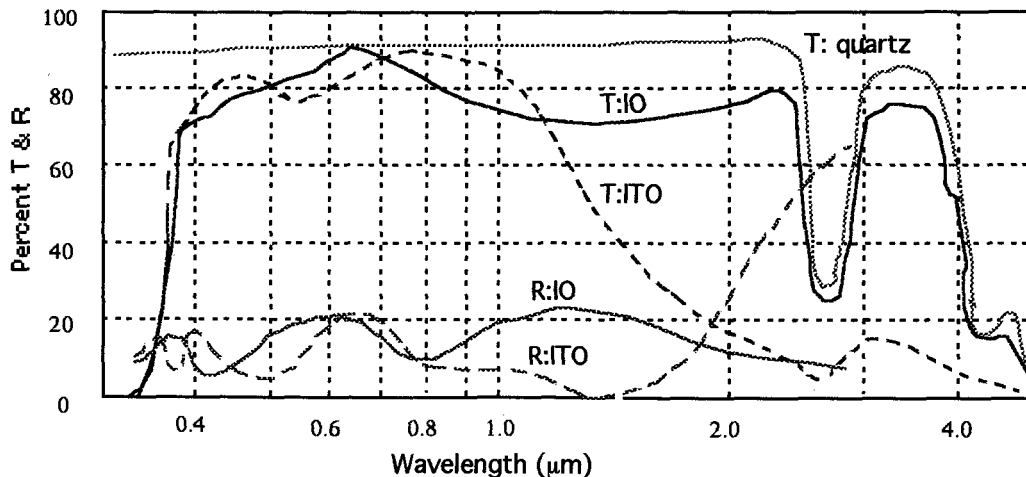


Figure 7 Transmission & reflection of poor conducting IO and highly conducting ITO films

3.3 Ease of pattern generation

ITO is much easier to remove by using acidic etchant such as $\text{FeCl}_3 + \text{HCl}^{\text{sr}}$ while atomic hydrogen evolved from the reaction of zinc powder and HCl has to be used to etch the tin oxide films in order to have a reasonable etch rate. Such a process is inferior to that adopted in ITO etching in controllability and very dusty even if Zn powder is used in a wet paste form. In more detail the acidic solution is reducing in nature, i.e. ferric ion tends to capture an electron. Thus indium oxide film is easily reduced to become In^{2+} which is soluble to HCl acidic solution. This reaction proceeds quietly at the surface. Thus bubble-free high definition pattern can be formed, in contrast to the situation of etching tin oxide with zinc powder and HCl solution.

The pattern thus obtained is normally of high accuracy and enough sharpness, though, of course, it depends on the etching conditions such as the concentration and temperature. Etching process for ITO films is normally finished in 20~90 seconds. On the other hand it takes 2~5 min for the removal of tin oxide films with Zn powder plus HCl solution.

Important factors in the evaluation of pattern generation are the cross-sectional shape, sharpness, in-depth and lateral etch rates, ease of outwashing and ease of treating reagents from the pollution control point of view. The ITO film seems to be best fit to these requirements. Etchability of ITO can be adjusted to some extent by changing deposition conditions such as substrate temperature, gas pressure, deposition rate etc. in sputtering or

evaporation. This makes the ITO more adaptable to the panel production process of LCDs.

In a few specific area tin oxide film are dominantly used : the electrode of plasma displays and amorphous Si solar cells. The former industry had established its first production process before the development of ITO, and the latter needed tough material which withstands the strongly reducing ambient of hydrogen plasma at the beginning of a-Si deposition.

There has occurred a new demand of generating high accuracy patterns, though the technology is not new, but has been used in the production of LSIs. High accuracy of the order of 2~3 μm is of vital importance for smaller active devices to come, such as finder screen of video camera, head-mount display for the virtual reality or high precision / high density LCD panels for giant projection screen. For this purpose dry etch processes have been tested using various gas etchants. Methane [13,14], methanol [15,16], ethanol [13], and halogen compounds [17,18,19,20] were explored. Very recent report[21] clarified that halogenated hydrogen gases such as HI and HBr showed higher etch rate of roughly 100 nm/min without any harmful deposits on and around the intended areas while organic gas etchants are probably not suited because of the deposit formation and rather slow etch rates.

3.4 Thermal stability

This property like the etchability reflects the chemical stability against the acids and alkalis. In the case of ITO it is rather unstable compared to tin oxide. This may be due to the complexity of the unit cell, namely the presence of similar or almost equivalent positions for oxygen atoms, and ease of releasing or capturing O_2 in and out of the unit cell. Nevertheless, many of ITO thin films can withstand up to 300 C if 30% increase in resistivity is admitted. There has been found no countermeasure to overcome this limitation, whereas it lies at around 550 C in the case of tin oxide. Fortunately the highest temperature met in the LCD panel production process has been 300 C and will be unchanged for the time being.

Requirement on thermal stability arises from the requirement imposed to peripheral seals. We know that even very small amount of water inside the LCD panel damages the liquid crystal materials through the electrochemical process. It is not a sealant body but the sealant interfaces through which moisture comes in because sealants based on the epoxy resin are almost impervious to the

penetration of moisture. Then the most important from the long term stability point of view of LCD pane is to provide tight adherence at the interface.

On the other hand tin oxide thin films well withstand the temperatures mentioned above. In many cases it does not undergo the resistivity change up to 600 C. It seems to be satisfactory when looking only at this subject. But the requirement on the specific resistivity excluded the possibilities for this material to be applied to the LCD field.

3.5 Pinholes

Almost all ITO films are now used for making LCD panels. More than 70% of them are the dot matrix type. The dimension of a dot is 0.3 by 0.1 for color displays normally seen on the lap top computers and 0.21 by 0.07 for high resolution displays. This means that the defect dimension must be smaller than the half of the smallest dimension. It is about 30 μm . Defects of such smallness can be detected only by very sharp eyes of skilled examiners.

Pinholes stem from many causes such as insufficient cleaning of glass substrate, sticking of dust particles and lints in a clean room or even in a vacuum chamber. Occurrence of pinholes cannot be perfectly avoided even if we know how and wherefrom they come, just like as we cannot escape from the effects of moisture or oxygen on the earth.

A typical specification for pinhole is something like the following : no pinhole that is greater than 0.2 mm; less than 2 that is greater than 0.05 mm and must be confined to the peripheral zone of the glass substrate; less than 5 that are greater than 0.03 mm over entire glass substrate.

This is truly a technical skill in the production areas of washing, cleaning, drying, transporting, coating, handling and packaging. The vacuum deposition method now prevailing over the world is actually much suited to such a clean work than the chemical methods like CVD. Inherent disadvantage of CVD process may be the formation of particles as a result of gas phase reaction.

4. The Methods of Making

The deposition method adopted as a first step of production was evaporation because it was cheap and reliable in mid to late 70s. Of course, the investment allowed to respond to a fragile and smaller market had to be as small as possible. However the situation now is the predominance of dc magnetron sputtering owing to the big growth in market size.

Lower resistivities achieved in recent few

years seem to be due much to so-called high density targets. They are tightly sintered at a high temperature in some reduced pressures. This makes the bulk resistivity of the sputter target low, due to proper replacement (i.e. substitution) of indium sites with tin atoms and reduces the amount of unwanted gases trapped or absorbed inside the target.

The reactive dc magnetron sputtering in which oxygen is fed to keep the pressure at a few 10^{-4} torr seems to be more suitable than evaporation because of smaller possibility of spitting, a typical source of pinholes. However the process is not necessarily calm and stable enough to any sputtering conditions. When we put higher voltages to get higher deposition rates, violent arc discharges begin to take place on and between target and glass substrate, which in general cause many serious defects on the ITO film. The situation is improving owing to the effort of power suppliers through the development of highly sensitive surge absorber to be installed inside the power supply units already purchased.

The sputtering has been considered to have advantages over the evaporation. They are, for example, expectations of fewer process parameters to be controlled in the production process and no particular skill even on a large substrate, say 1 meter by 1 meter. In addition there had been some critical improvements without which no overwhelming situation was given to. The first one is densification technique with keeping appropriate level of chemical reduction state over entire bulk, the second is bonding to release heat from the target, the third may be to form uniform magnetic field on a big target surface in order to achieve uniform distribution of thickness over entire substrate.

The problem still left behind from the production cost point of view is the low efficiency of target utilization. The target undergoes erosion caused by the bombardment of argon ions attacking from the plasma, resulting in a formation of rather narrow and deep erosion zone. This limits the efficient use of target material at most up to 20%. Developments of milder erosion technique are now going on at every production site.

5. Discussion of Concepts towards

Improvements

Any trial towards higher conductivities face a trade-off that the increase in the carrier density is ordinarily accompanied by the decrease in the mobility⁶⁷. The lowest resistivities in the present production level would be $1.2 \times 10^{-4} \Omega \text{ cm}$ with $n_e = 1.4 \times 10^{21} / \text{cm}^3$ and $\mu = 37 \text{ cm}^2 / \text{V} \cdot \text{s}$.

It may be worth reexamining the meaning of

impurity addition, i.e. the meaning of the carrier density and mobility. In the case of complete substitution of In^{3+} sites with Sn^{4+} , 6.02×10^{22} tin atoms occupy the $2 \times 6.02 \times 10^{23} \text{ In}^{3+}$ sites. This yields the carrier density of $1.88 \times 10^{21} / \text{cm}^3$ with $\rho_{\text{In}_2\text{O}_3} = 7.12 \text{ g/cm}^3$. This is in good proximity to the highest values reported ($1 \sim 1.4$) $\times 10^{21} / \text{cm}^3$ [22, 23]. However, it has been considered that actual contribution of intentionally added tin atoms is less than one third of 1.88×10^{21} because it decreases sharply to $(2 \sim 3) \times 10^{20} / \text{cm}^3$ when heated in air at temperatures higher than 300 C [24]. Another contribution must be from the existence of oxygen vacancies. Hence this contribution from oxygen vacancies is more effective.

Scattering mechanisms that affect the carrier mobility are the ionized impurity scattering, phonon scattering, electron-electron scattering in single crystals, and grain boundary scattering in polycrystalline thin films. The last factor has been recognized to be minor because no appreciable misfit or mis-alignment has been detected on the lattice image photographs [23, 25], though segregation of tin had been observed at the grain boundary zone [26].

In addition it has been clarified in the case of heavily doped semiconductor such as ITO that the presence of neutral impurities as an atom or cluster of atoms must have affected the resistivity through the scattering process [22, 27, 28]. We will also have to pay attention to the contributions from off-site ionized impurities of the Frenkel type and gas molecules occluded in the film during the deposition. The detail and quantitative evaluation of the scattering mechanisms including neutral species will unveil the key factor(s).

Some recent papers discuss a concept of increasing the mobility. Point of discussion is to search a class of materials in which electrons assume smaller effective mass than in indium oxide. Basis of the concept is clearly given by the equations [29]:

$$\mu \propto T^{-3/2} m^{*-5/2}$$

or

$$\mu = \frac{e\langle\tau\rangle}{m^*} = \frac{e}{m^*} \frac{\ell}{v_e}$$

These kinds of expression are said to be too crude for quantitative discussion, though it is clear that the effective mass has a significant effect. It must be noted that the former equation can be derived from phonon scattering under the assumption of small

changes in k -vector upon scattering while the latter still remains in a classical regime of the free electron theory. Discussion of its validity is necessary for the ionized impurity scattering. Practically most important then is to achieve such a crystal structure with highest possible perfection. In this sense our present situation may be still far from achieving.

It should be mentioned as a whole that such improvements in the electrical properties must be consistent with the optical properties of ITO. Therefore, the best measure is to increase the mobility only. Lower resistivities based on the increases in carrier density inevitably result in transmission decreases due to increase in free carrier absorption.

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NOTES

1*(p.2) The fundamental absorption edge means an abrupt increase in the absorption coefficient up to 10^5 cm^{-1} towards shorter wavelengths, by the transition of valence electrons.

2*(p.2) The sheet resistivity $R(\Omega/\text{square})$ is defined as ρ/d , and derived from

$$R = \rho(a/bd)$$

when $a=b$, where a , b and d are the width, length and thickness.

3*(p.6) The following expression gives the plasma resonance frequency inside the solids:

$$\omega_p = \frac{2\pi c}{\lambda_p} = \sqrt{\frac{e^2 n_e}{\epsilon_o \epsilon_L m^*} - \frac{1}{\tau^2}}$$

$$\tau = \frac{300 \mu m^*}{e}, \quad \epsilon_o = \frac{1}{4\pi}$$

Putting $\epsilon_L=4$, $\epsilon_o=1/4\pi$, $m^*=3 \times 10^{-28} \text{ g}$, $n_e=7 \times 10^{20} \text{ cm}^{-3}$, $e=4.8 \times 10^{-10} \text{ esu}$ and $\mu=45 \text{ cm}^2/\text{V}\cdot\text{s}$, then $\omega_p=1.33 \times 10^{15} \text{ s}$ or $\lambda_p=1.42 \mu\text{m}$.

At ω_p the real part of the dielectric constnt is 0.

4*(p.6) The energy absorbed is finally released to the lattice in the form of heat.

5*(p.7) Acid mostly used is HCl. Alcohol can be methanol, ethanol, propanol and their mixtures.

6*(p.8) Köstlin described the dependence of mobility on the carrier density as

$$\mu = (4e/h)(\pi/3)^{1/3} N^{1/3}$$

If we use $e=4.8 \times 10^{-10} \text{ esu}$, $h=6.6 \times 10^{-27} \text{ erg}\cdot\text{sec}$, and $m^*=0.3m_o$, then $\mu=2.91 \times 10^{17}/N^{1/3}$. Putting $N=10^{21} \text{ cm}^{-3}$, then we have $\mu=2.91 \times 10^3 \text{ cm}^2/\text{V}\cdot\text{s}$.