Indium tin oxide (ITO) deposition, patterning and Schottky contact fabrication

Jianming Zhou

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Indium Tin Oxide (ITO) Deposition, Patterning, and Schottky Contact Fabrication

By
Jianming Zhou

A thesis submitted
in partial fulfillment
of the requirements for the degree of
Master of Science
in
Microelectronic Engineering

Approved by:
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DEPARTMENT OF MICROELECTRONIC ENGINEERING

COLLEGE OF ENGINEERING

ROCHESTER INSTITUTE OF TECHNOLOGY

ROCHESTER, NEW YORK

DECEMBER, 2005
Indium Tin Oxide (ITO) Deposition, Patterning, and Schottky Contact Fabrication

By

Jianming Zhou

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__________________________  _______________________
Jianming Zhou  Month Date, Year

03/31/2006
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I would like to thank my thesis advisor, Prof. Dale E. Ewbank, who has given me numerous instructions about this project. He helped me develop the ability to carry out a project from an engineering point of view, plan a project systematically, and be efficient. This thesis is the culmination of a number of discussions I have had with Prof. Ewbank since joining Microelectronics Engineering Department of RIT.

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Abstract

As a transparent conductive material, indium tin oxide (ITO) has been utilized as electrodes in liquid crystal displays, solar cells, heat reflecting films and gas sensors. In general, the desired properties are high conductance and transmission. However, due to the complexity of ITO, the film properties strongly depend on the deposition processes. In this study, the deposition conditions for ITO film were optimized to get both high conductivity and transmission. The emphasis was on investigating the effects of various deposition parameters, such as oxygen partial pressure, total gas flow, annealing conditions and power. These are the most critical parameters for ITO deposition. A mathematical model to describe the material properties as functions of these parameters for a CVC model 601 Sputterer was developed utilizing JMP IN software. Films with resistivity $3 \times 10^{-4} \Omega \cdot \text{cm}$ and transmittance above 90% were achieved on glass and silicon substrates with 20 hours of annealing. The processing window (power: 120-150W, oxygen ratio: 6-10%) is, to the author’s knowledge, the largest reported by literature. However, the ITO film properties (electrical and optical) variation between runs needs to be further reduced.

Patterning of ITO was also investigated. High but controllable etch rates are desired. Both wet and dry etch processes were developed. The etch rate of 48nm/min was achieved by using HCL aqueous solution (4:1 HCl to DI water volumetric ratio, where HCl is the standard 37% HCl solution) with almost infinite selectivity between the ITO film and the photoresist. For dry etch, the etch rate is 1nm/min with just
argon as the working gas and the etching selectivity between the photoresist and the ITO film is 13.02. To etch 100nm ITO film, the photoresist needs to be at least 1.5um to serve as etching mask. This dry etch process still needs to be improved.

A Schottky contact was successfully fabricated by using ITO as the metal. The electrical barrier height was calculated to be 1.01eV. The current-voltage characteristics were investigated as well.
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<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid Crystal Display</td>
</tr>
<tr>
<td>MS</td>
<td>Metal-Semiconductor</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etch</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>DOE</td>
<td>Design Of Experiment</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>ANOVA</td>
<td>ANalysis Of VAriance</td>
</tr>
<tr>
<td>VASE</td>
<td>Variable Angle Spectroscopic Ellipsometer</td>
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Chapter 1

Introduction

1.1 Motivation

Since 1907, when reports of transparent and conductive cadmium oxide films first appeared, interest in transparent conductors has rapidly increased [1]. Indium Tin Oxide (ITO) is one of the most attractive of these materials due to its high conductivity and transmission in the visible range. It is suitable for various applications such as transparent heating elements [2], antistatic coatings over electronic instrument [3,4], electro-optic devices [5,6], liquid crystal displays [7,8,9], transparent electrodes for various display devices [10,11], and transparent contact [12,13]. The most commonly used methods for ITO deposition are sputtering, thermal evaporation, spray pyrolysis, pulsed laser deposition (PLD) and screen printing technique [14-21]. However, due to the complexity of crystal structure, tin doping level, and composition, the properties of ITO films produced by different processes vary significantly. Table 1.1 shows some of the results of previous research. From this table, we can see that the resistivity, transmittance and carrier concentrations vary significantly. This indicates that properties of ITO film strongly depend on individual processes. Electro-optic technology requires a greater understanding of the optical and electrical properties of ITO, so it is necessary to characterize an ITO film deposition process.

In 1938, Schottky suggested a model for the rectification mechanism for metal-
semiconductor (MS) contact. Since ITO can be used as transparent contacts, it is useful to investigate the MS contact formed with ITO as the conductor. This will demonstrate the feasibility of using the ITO as electrode material in device fabrication.

Table 1.1: The properties of ITO films prepared by different techniques.

<table>
<thead>
<tr>
<th>Deposition Technique</th>
<th>Thickness (Å)</th>
<th>Carrier concentration (cm⁻³)</th>
<th>Resistivity (ρ·cm)</th>
<th>Transmittance (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>r.f. Sputtering</td>
<td>7500</td>
<td>6.0x10⁻²⁰</td>
<td>3.0x10⁻⁴</td>
<td>90</td>
<td>[14]</td>
</tr>
<tr>
<td>r.f. Sputtering</td>
<td>5000</td>
<td>1.20x10²¹</td>
<td>4.0x10⁻⁴</td>
<td>95</td>
<td>[15]</td>
</tr>
<tr>
<td>Pulsed laser deposition</td>
<td>14000</td>
<td>1.0-1.2x10²¹</td>
<td>8.0x10⁻⁴</td>
<td>90</td>
<td>[16]</td>
</tr>
<tr>
<td>Magnetron Sputtering</td>
<td>800</td>
<td>6.0x10⁻²⁰</td>
<td>4.0x10⁻⁴</td>
<td>85</td>
<td>[17]</td>
</tr>
<tr>
<td>d.c. Sputtering</td>
<td>1000</td>
<td>9.0x10⁻²⁰</td>
<td>2.0x10⁻⁴</td>
<td>85</td>
<td>[18]</td>
</tr>
<tr>
<td>Reactive evaporation</td>
<td>2500</td>
<td>5.0x10⁻²⁰</td>
<td>4.0x10⁻⁴</td>
<td>91</td>
<td>[19]</td>
</tr>
<tr>
<td>Ion Beam sputtering</td>
<td>600</td>
<td>2.0x10⁻²⁰</td>
<td>1.2x10⁻³</td>
<td>-</td>
<td>[20]</td>
</tr>
<tr>
<td>Spray Pyrolysis</td>
<td>3000</td>
<td>5.0x10⁻²⁰</td>
<td>3.0x10⁻⁴</td>
<td>85</td>
<td>[21]</td>
</tr>
</tbody>
</table>

1.2 Aims and objectives

The primary objectives of this work were to optimize the ITO film deposition and to fabricate Schottky contact with ITO as the conductor. With these objectives in mind, the ITO film deposition based on a DC reactive magnetron sputtering technique
was first studied and then optimized. Extensive work involving the characterization of the sputterer was carried out to understand the effects of various conditions on the ITO films. These films were then characterized for their electrical conductivity, optical transmittance, refractive index, surface roughness and uniformity. Post-deposition annealing techniques were also used to achieve desired properties.

Once it was established that satisfactory ITO films could be produced, the work was extended to the fabrication of the Schottky contacts. A patterning process was then developed to enable the device fabrication involving ITO film. Schottky diodes were realized on n-type silicon substrates.

1.3 Summary and Layout of Thesis

This thesis is composed of seven chapters. The background theory and the relevant literature overview are presented in the second chapter. This is followed in chapter three by a description of various deposition processes, especially DC magnetron sputtering. Chapter four consists of the details of the equipment involved. Chapter five contains the detailed experimental results including initial screening process and optimized sputtering process. Finally, chapter six constitutes the second part of this study, namely that of the Schottky contact fabrication and characterization, etching is discussed in this chapter since it is part of device fabrication. The conclusion of the work is presented in chapter seven.
Chapter 2

Theory

2.1 General properties of ITO

The unique properties of ITO come from its structure and composition. Indium oxide has a cubic bixbyite structure which is shown in Fig. 2.1. One unit cell contains 16 units of In$_2$O$_3$. Therefore, for defect free In$_2$O$_3$ crystal, there are 80 atoms in one unit cell. The lattice constant is reported to be 10.118Å [22]. The theoretical density is 7.12g/cm$^3$. Two kinds of non-equivalent indium sites are present in In$_2$O$_3$ crystal structure which are shown in Fig. 2.2 [23]. In Fig. 2.2 (a), the separation between indium and oxygen atoms is 2.18Å, and the oxygen atoms are positioned at the corners of the cube with two body-diagonally opposite corners unoccupied. In Fig. 2.2 (b), the In-O separations are 2.13, 2.19 and 2.23Å, where the oxygen atoms occupy positions at the corner of the cube with two face-diagonally opposite corners unoccupied. Based on the description above, both indium sites can be viewed as an incomplete body centered cubic structure with an indium atom located at the center and oxygen atoms at the corners. One fourth of the anions are missing. To vary the material properties, In$_2$O$_3$ can be extrinsically doped with tin. When tin atoms substitute for indium atoms, it forms either SnO or SnO$_2$. The material retains its bixbyite structure. However, if the doping level is extremely high, the tin atoms may enter interstitially and distort the lattice structure. As a polycrystalline structure, the ITO crystal grain size depends on various processing parameters such as substrate temperature and deposition rate.
Fig. 2.1: $\text{In}_2\text{O}_3$ crystal structure [22].

Fig. 2.2: Two indium sites of ITO films [23].
2.1.1 Electrical properties of ITO

Indium oxide is a wide gap semiconductor. The band gap of In$_2$O$_3$ was reported to be 3.75eV [24]. Generally, In$_2$O$_3$ crystal structure is not ideal since oxygen vacancies are present. The accurate formula of indium oxide is In$_2$O$_{3-x}$(V$_O$)$_x$, where V$_O$ is donor-like doubly-charged oxygen vacancy, and x is the oxygen vacancy portion and depends on the oxidation state. The typical value of x is less than 0.01. Under room temperature, the excitation of electrons from valence band to conduction band is negligible. Oxygen vacancies dominate the conduction mechanism of In$_2$O$_3$ and the free charge carrier concentration has been reported to be in the range $10^{19}$-$10^{20}$ cm$^{-3}$. Extrinsic doping can vary the electrical properties of indium oxide significantly. If In$_2$O$_3$ is doped with tin atom, tin atoms will replace indium atoms and form tin oxide in either SnO or SnO$_2$ depending on the valence. If SnO is formed, tin acts as an acceptor since it accepts an electron. Otherwise, when SnO$_2$ is formed, it acts as donor since it gives off an electron. Usually, SnO$_2$ dominates, and tin atoms act as donors. Both tin and oxygen vacancies contribute to the conductivity of ITO. The free carrier concentration can be expressed as $n = [Sn\cdot]_A + 2[V_O\cdot\cdot\cdot]$, where [Sn\cdot]$_A$ is the active tin atom concentration.

The doping level is critical for electrical properties. As the tin concentration increases, the carrier concentration increases until a saturation level is reached. An increase in the tin concentration above this saturation level causes a decrease in the free carrier concentration. This is due to an increased probability of the occupation of adjacent cation positions by two or more tin atoms, which can deplete the active tin
concentration. The carrier concentration as a function of tin doping level is well illustrated in Fig. 2.3. The highest carrier concentration, which corresponds to the lowest resistivity, occurs when the tin doping level is about 10%. The solid solubility of tin in indium oxide is approximately 8%. Beyond this range, tin oxide phase will be formed and distort the lattice structure. This will eventually cause a decrease of free carrier concentration.

In order to get conductivity $> 10^3\text{ohm}^{-1}\text{cm}^{-1}$ and avoid the formation of tin oxide phase, the doping level is typically chosen to be 8-10%. This doping level will produce degenerative ITO [24]. Fig. 2.4 shows the energy diagram of In$_2$O$_3$ and ITO. ITO has metal like electrical properties because the carrier concentration is typically around $10^{20}$ to $10^{21}\text{cm}^{-3}$. For heavily doped indium oxide, the contribution of oxygen vacancies to the conductivity is negligible.

Fig. 2.3: The experimental and calculation of the carrier concentration as function of the tin doping level [22].
2.1.2 Optical properties of ITO

The theoretical treatment of the dielectric function of ITO was derived by Bender, et. al. [25] From the imaginary part of the dielectric constant, the absorption coefficients of the films were derived (see Fig. 2.5). Two absorption edges can be seen, one at photon energies below 1eV (far infrared region), which is due to the free electrons, and one at photon energies above 4eV which is caused by the excitation of the valence electron into the conductance electron. In the region between 1 to 4eV, the imaginary part of the dielectric constant is negligible which corresponds to a high transmission region in the visible and NIR region.
2.2 ITO-Semiconductor contact

2.2.1 The energy band diagram analysis of MS contact

The ITO-Semiconductor contact is essentially an MS contact since ITO has metal like electrical properties. MS contact was the first semiconductor device ever studied (in the year 1874). The contact between ITO and semiconductor can be characterized as either an ohmic contact or rectifying contact. Ohmic contacts are defined as a metal-semiconductor contact with a linear or near linear current voltage characteristic; current can be passed in either direction with a negligibly small voltage drop. Rectifying contact, also known as Schottky contact, corresponds to the contact where current can only easily flow in one direction.

Contact analysis can be done by establishing the equilibrium energy band...
diagram for metal-semiconductor contact. We consider a one-dimensional structure of
the MS contact as shown in Fig. 2.6. Fig. 2.7 shows the energy band diagram of metal
and an n-type semiconductor which are separated from each other. The work function
is defined as the energy difference between the Fermi level and the vacuum level. The
energy difference between the conduction band edge and the vacuum level is defined
as electron affinity \( q\chi \), where \( q \) is charge of an electron, \( \chi \) is the potential difference
between the conduction band edge and the vacuum level. The metal working function
is specified as \( q\Phi_m \), the potential difference between the metal Fermi level and the
vacuum level, which is an invariant fundamental property of the specified metal. The
semiconductor work function \( q\Phi_s \) is expressed as

\[
q\Phi_s = q\chi + (E_c - E_\beta)
\]  

(2.1)

where \( E_\beta \) is the Fermi level of the semiconductor. When the metal and semiconductor
are put together, the Fermi levels in the two materials must be equal at thermal
equilibrium; the vacuum level must be continuous. This leads to the unique band
structure, which is shown in Fig. 2.8. For the ideal case, there are no surface energy
states, the space between the metal and the semiconductor is infinitesimally small.
When \( \Phi_m > \Phi_s \), it will form a potential barrier for the electrons to move between the
semiconductor and the metal. The barrier height is simply the difference between the
metal work function and the semiconductor electron affinity, which is

\[
q\Phi_{bn} = q\Phi_m - q\chi
\]  

(2.2)

When \( \Phi_m < \Phi_s \), as shown in Fig. 2.9, there will be a highly conductive layer at the
metal semiconductor interface. The contact has a negligible resistance. This type of
contact is called ohmic contact. For the case of ideal contact between a metal and a p-type semiconductor, the analysis is similar, when $\Phi_m < \Phi_s$, the barrier height is now given by

$$q\Phi_{bp} = E_g - (q\Phi_m - q\chi)$$  \hspace{1cm} (2.3)

where $E_g$ is the bandgap of the semiconductor. When $\Phi_m > \Phi_s$, it will behave as an ohmic contact. The electrical natures of ideal MS contacts are summarized in Table 2.1.

![Fig. 2.6: One-dimensional structure of a MS contact.](image)

![Fig. 2.7: Energy band diagram for a metal and n-type semiconductor. [26]](image)
Fig. 2.8: Energy band diagrams for ideal MS contacts between a metal and an n-type semiconductor under equilibrium condition, $\Phi_m > \Phi_s$. [26]

Fig. 2.9: Energy band diagrams for ideal MS contacts between a metal and an n-type semiconductor under equilibrium condition, $\Phi_m < \Phi_s$. [26]
Table 2.1: Electrical Nature of Ideal MS contacts.

<table>
<thead>
<tr>
<th></th>
<th>n-type semiconductor</th>
<th>p-type semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_m &gt; \Phi_s$</td>
<td>Rectifying</td>
<td>Ohmic</td>
</tr>
<tr>
<td>$\Phi_m &lt; \Phi_s$</td>
<td>Ohmic</td>
<td>Rectifying</td>
</tr>
</tbody>
</table>

According to Eq. 2.2, the barrier height increases with the metal work function. However, in reality, the dependence is not as strong as predicted by Eq. 2.2. This is because of the non-ideality of the semiconductor. At the semiconductor surface, the crystalline structure might be damaged due to metal deposition. A large number of surface energy states locate in the forbidden band of the semiconductor. For n-type silicon, these surface states are usually donor like. Therefore, Eq. 2.1 generally underestimates the barrier height.

The work function of ITO varies due to the complexity of its structure. For an isolated atom, the electrons can have discrete energy levels. If a large number (N) of atoms are brought together to form a solid, the orbits of the outer electrons of different atoms overlap and interact with each other. The discrete energy levels will split into N separate but closely spaced levels. When N is large, the result is an essentially continuous band of energy. This band of N levels can extend over a few eV depending on the inter-atomic spacing for the crystal [26]. This is shown in Fig. 2.10. Fig. 2.11 illustrates the formation of a silicon crystal from N isolated atoms. Both the conduction band width and the valence band width depend on the inter-atomic spacing, so does the forbidden band gap width. For ITO, the reported crystal constants
are different from different sources [22], so the $E_c$, $E_v$ and $E_g$ may vary since the inter-atomic spacing varies. The inter-atomic spacing variation is a result of different doping level, oxygen vacancies, crystallization, and damage due to sputtering. The typical value of ITO work function falls in the range of 4.6-5eV. To form a Schottky contact, the work function of the silicon substrate must be less than the work function of ITO. A lightly doped n-type substrate typically has work function around 4.2eV. ITO and n-type silicon contact should be a Schottky contact.

![Fig. 2.10: The splitting of a degenerate state into a band of allowed energies.](image1)

![Fig. 2.11: Formation of energy bands of silicon crystal. [26]](image2)
2.2.2 The I-V characteristic of Schottky contact

For a pn diode, the current is carried by minority carriers. A Schottky contact is a majority carrier device. At room temperature, the dominating transport mechanism for a Schottky diode is thermionic emission of majority carriers from the semiconductor over the potential barrier into the metal.

The energy diagrams of different biasing conditions are summarized in Fig. 2.12. Let \( J_{ms} \) be the current density flowing from the metal into the semiconductor while \( J_{sm} \) is the current density flowing from the semiconductor into the metal. For an n-type semiconductor, when the bias is zero, the band diagram is under a thermal equilibrium condition and \( J_{sm} = J_{ms} \). This is shown in Fig. 2.10 a). The current density is

\[
|J_{sm}| = |J_{ms}| = A'T^2 \exp(-q\Phi_{Bn} / kT)
\]

(2.4)

where \( A^* \) is called the effective Richardson constant, and \( T \) is the absolute temperature. The value of \( A^* \) are equal to 110 and 32AK^{-2}cm^{-2} for n- and p- type silicon, respectively [26]. When a forward bias is applied, the built-in potential \( \Phi_i \) will decrease. This will make it easier for the electron to move from the semiconductor into the metal. As a result, \( J_{sm} \) will increase. However, the electron flux from the metal to the semiconductor remains the same because the barrier \( \Phi_{Bn} \) is not affected. When a reverse bias is applied, the built-in potential barrier height will increase and the electron flux flowing from the semiconductor into the metal will decrease.

\[
J = J_{sm} - J_{ms}
= A'T^2 \exp[-q(\Phi_{Bn} - V_a) / kT] - A'T^2 \exp(-q\Phi_{Bn} / kT)
= A'T^2 \exp(-q\Phi_{Bn} / kT)[\exp(qV_a / kT) - 1]
= J_s[\exp(qV_a / kT) - 1]
\]

(2.5)

where \( J_s = A'T^2 \exp(-q\Phi_{Bn} / kT) \) is the saturation current density and the applied
voltage V is positive for forward bias and negative for reverse bias. By extrapolating
the forward I-V characteristic curve to \( V_a = 0 \), we can find \( J_s \). From \( J_s \), the barrier
height \( \Phi_{Bn} \) can be obtained.

![Diagrams](image)

a) Thermal equilibrium

b) Forward bias
Fig. 2.12: Current transport by the thermionic emission process. [26, 36]

The ITO n-type semiconductor contact simulation was performed. According to some reports, the ITO work function was chosen to be 5eV. There are always some surface states present, a typical value is $3 \times 10^{10} \text{cm}^{-2}$. The parameters for the simulation are summarized in Table 2.2. Fig. 2.13 shows the I-V result of the simulation. As discussed earlier, the current as a function of the applied bias is described by Eq. 2.4. Fig. 2.13 a) is the linear scale I-V curve, which shows when the applied voltage is greater than the built-in potential, the current increases with the applied bias linearly rather than exponentially. This is due to the presence of series resistance. Fig. 2.13 b) has logarithm scale, which shows when the applied bias is small, the current increases exponentially with the applied bias. The reverse biased situation is shown in Fig. 2.13 c), the current is much less (about ten magnitudes lower) than the forward biased situation.
Fig. 2.13: The I-V curve of the simulated ITO n-type silicon contact. a), b) linear and logarithm scale for forward bias. c) Reverse bias.
Table 2.2: Parameters for ITO n-type semiconductor simulation

<table>
<thead>
<tr>
<th>Simulation parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO work function</td>
<td>5eV</td>
</tr>
<tr>
<td>Si sheet resistance</td>
<td>$150\Omega/\square$</td>
</tr>
<tr>
<td>Surface state density</td>
<td>$3 \times 10^{10}\text{cm}^{-2}$</td>
</tr>
<tr>
<td>ITO size</td>
<td>$5\text{um x 6um}$</td>
</tr>
</tbody>
</table>
Chapter 3
Deposition method

Various methods can be used for ITO film deposition. However, different processing usually produces ITO films with significantly different properties. In the following sections, thermal evaporation, spray pyrolysis technique, pulsed laser deposition and screen printing techniques will be briefly introduced. In this study, ITO films were produced by DC magnetron sputtering, so this method will be introduced in detail.

3.1 Thermal evaporation

Thermal evaporation involves vaporizing a solid by heating the material to sufficiently high temperatures and recondensing it on a cooler substrate. The high temperature can be achieved by resistively heating, or by firing an electron or ion beam at the boat containing the material to be evaporated.

Under ideal circumstances, the total evaporated metal is:

$$\overline{M_e} = \int_0^t \int_{A_e} \Gamma_e dA_e dt$$  \hspace{1cm} (3.1)

where $A_e$ is the surface area of the source, $\Gamma_e$ is the evaporation rate, $\overline{M_e}$ is the total evaporated mass and $t$ is time.
In the situation illustrated in Fig. 3.1, the mass received by per area of the wafer is:

\[
\frac{dM_s}{dA_s} = \frac{M_e \cos \theta}{4\pi r^2}
\]  

(3.2)

where \( \theta \) is the incident angle of the evaporated metal, \( r \) is the distance from the evaporation source to the wafer surface, \( A_s \) is the area receiving the incident evaporated species.

For ITO deposition, the typical source is a 95% In - 5% Sn alloy (by weight). The oxidation process happens in the chamber, so oxygen must be incorporated into the chamber to form the ITO film. This process is referred as reactive thermal evaporation and is one of the most widely and successfully used techniques for good quality ITO deposition.

ITO film properties strongly depend on oxygen partial pressure and other parameters. Reports of substrate temperatures being raised from 300°C up to 450°C during evaporation in order to enhance conductivity and transmittance are reported in
the literature. However, due to the difference of the indium and tin vapor pressure, it is very hard to achieve the proper stoichiometry in the film.

### 3.2 Spray pyrolysis

Pyrolysis refers to the thermal decomposition of gaseous species at a hot surface. The major advantage of pyrolysis technique is its relatively fast deposition rate (> 1000 Å/min) and it does not require a vacuum. The ITO spray is obtained from an alcoholic solution of anhydrous indium chloride (InCl₃) and tin chloride (SnCl₄·5H₂O) with nitrogen acting as the carrier gas. The spraying is carried out in a furnace, held at 400°C. Critical parameters include positioning of the substrate and the chemical composition of the spray solution. Ashok, et. al. [29] have reported resistivities of 1x10⁻³Ω-cm for a 4200Å ITO film with transmission greater than 90% at 550 nm while corresponding values obtained by Haitjema [21] are 3x10⁻⁴Ω-cm and 85% respectively. This demonstrates an apparent trade-off between the conductivity and the transmittance of ITO films.

### 3.3 Screen Printing Technique

This technique is suitable for large scale non-device oriented applications where relatively thick layers of ITO are required such as in liquid crystal displays, blackwall contacts and anti-reflection coatings for solar cells. Typically, the deposited thickness varies in the range 10 to 30um and the post deposition crystallization temperature can be as high as 600°C for a period exceeding an hour. The resistivity (> 4x10⁻⁴Ω-cm) of
the ITO film is said to be comparable to those obtained by other deposition techniques. However, its transparency is markedly lower (< 80%).

### 3.4 Pulsed laser deposition

Thin films can also be created by pulsed laser deposition (PLD). The principle of this technique is simple. A solid target in an ultra high vacuum chamber is evaporated by means of short and high-energy laser pulses [16, 30]. In a typical PLD process, a researcher places a target in a vacuum chamber. A pulsed laser beam vaporizes the surface of the target, and the vapor condenses on a substrate. The main components are a laser, optics, and a vacuum system. This technique is conceptually simple, cost-effective and fast, however the typical film field produced by this technique is only a few square centimeters.

### 3.5 Sputtering

The basic idea of sputtering is using accelerated particles to bombard the target and knock the target atoms out. These free atoms then will be deposited onto the substrate. Plasma is basically a low-pressure gas between two electrodes and is widely used for sputtering because it contains charged particles, which are easily directed by electric fields. It also has an atom in electrically excited state, so it is chemically more reactive. To obtain plasma, a voltage is applied on a pair of electrodes. Free electrons can gain energy from the field and then collide with gas particles, eventually cause ionization. This process is known as a direct-current (DC) glow discharge. Fig. 3.2 shows the structure of a DC glow discharge followed by description of the regions.
The cathode is an electrical conductor with a secondary electron emission coefficient that is very important for the operation of the discharge tube. The Aston Dark Space is a thin region located to the right of the cathode. The electric field in this region is strong, so the electrons can be accelerated through this space away from the cathode. Stray initial electrons together with the secondary electrons from the cathode exceed the number of the ions in this region, so this region has a negative space charge. The gas cannot be ionized because the electrons are too low density and/or energy to excite the gas, so it appears dark. The Cathode Glow is the next region to the right of Aston dark space. Here the electrons are energetic enough to excite the neutral atoms they collide with. The cathode glow has a relatively high ion density. The axial length of the cathode glow depends on the type of gas and the pressure. The cathode glow sometimes clings to the cathode and masks the Aston dark space. The Cathode dark space is a relatively dark region to the right of the cathode glow that has moderate electric field, a positive space charge and a relatively high ion density. The
negative Glow is the brightest intensity of the entire discharge. The negative glow has relatively low electric field, which is long compared to the cathode glow, and is the most intense on the cathode side. Electrons that have been accelerated in the cathode region to high speeds produce ionization, and slower electrons that have had inelastic collisions already produce excitations. These slower electrons are responsible for the negative glow. As these electrons slow down, energy for excitation is no longer available and the Faraday dark space begins. The Cathode Region is the entire region from the cathode to the negative glow. Most of the voltage drop across the discharge tube occurs in this region. Most of the power is dissipated in this region. The electrons are accelerated in this region to energies high enough to produce ionization and avalanching in the negative glow, and in the regions to the right of the negative glow. The electron energy is low in Faraday dark space. The electron number density decreases by recombination and diffusion to the walls, the net space charge is very low, and the electric field is small. The Positive Column is a quasi-neutral, small electric field regime. The electric field is just large enough to maintain the degree of ionization at its cathode end. The positive column is a long, uniform glow. The Anode dark space is the space between the positive column and the anode itself. It has negative space charge due to electrons traveling from the positive column to the anode. There is a higher electric field than the positive column. The anode pulls electrons out of the positive column.

A very small portion of the working gas, e.g. argon is ionized in the glow discharge:
The degree of ionization is typically in the range of $10^{-4}$ to $10^{-2}$.

$$e^- + Ar \rightarrow 2e^- + Ar^+ \quad (3.3)$$

**Fig. 3.3: Micro process of sputtering.**

Fig. 3.3 shows the micro process of sputtering. The incident ions hit the target atoms, the affected target atoms will transfer momentum to other target particles, eventually some of the target particles will be knocked out of the target and deposited onto the substrate. Some side products such as photons, X-rays, and secondary electrons are produced as well.

Fig. 3.4 illustrates a DC sputtering system. A pair of parallel metal electrodes is inside the working chamber. Target is put on the cathode and the substrate is put on the anode. The anode is usually grounded and the cathode is connected to the negative terminal of a DC power supply with a typical power of several hundred watts. A working gas, typically argon is introduced to the chamber to serve as the plasma media after the chamber is evacuated. The pressure of the working gas may range from several to a hundred mtorr. An appropriate voltage and power are necessary to
maintain the visible glow discharge, where ionization occurs. A magnetic field may be used to improve the ionization efficiency. Typically the target is bonded to a backing plate, which is made of copper. Indium solder is used to bond target to backing plate.

![DC magnetron sputtering system](image)

**Fig. 3.4: DC magnetron sputtering system. [Regenerated based on ref 31, 32]**

The electric field accelerates the positive ions toward the cathode. Given sufficient energy, they can physically eject or sputter target atoms through momentum transfer when striking on the target. These sputtered target atoms may eventually deposit on the substrate to result in a thin film.

The Sigmund theory provides the specific dependence of deposition rates on energy (related with power) as below:

\[
S = \frac{3\alpha 4M_i M_t E_i}{4\pi^2(M_i + M_t)^2 U_s}
\]  

(3.4)

where \(M_i, M_t\) are mass of incident ion, target metal atom respectively, \(U_s\) is surface bonding energy, \(E_i\) is the energy of incident particles, \(\alpha\) is a parameter which is a
function of the target to ion mass ratio and varies with different sputtering process. From this relationship, we can see that the deposition rate is proportional to the target atom mass.

The Child-langmuir equation shows that the ion flux is proportional to $V^{1.5}$, where $V$ is the applied voltage. Based on this equation, if we increase the voltage, the ion flux will increase and eventually cause the deposition rate to increase [32].

If only argon is used as the working gas, the stoichiometry of the target will be duplicated onto the film. For ITO deposition, there are two major types of targets. One is hot pressed ITO powder. For this target, oxygen may or may not be used and depends on the requirements on the film properties. The other is an indium tin alloy target. For this target, oxygen must be introduced to obtain ITO film. The oxidation process happens during deposition, high oxygen partial pressure will cause a high degree of oxidation. Therefore the partial pressure of oxygen is very important since the properties of the film strongly depend on it.
Chapter 4  

CVC601 Sputterer and initial characterization

Due to its advantages over thermal evaporation, DC magnetron reactive sputtering was chosen as the deposition method. To understand the process, it is essential to understand the tool involved for film deposition.

The tool used is CVC 601 Sputterer. In section 4.1, the configuration of the system will be introduced. In section 4.2, the pumping system and the pumping down process will be discussed. Gas supply and initial characterization of the system are covered by section 4.3.

4.1 The system configuration

Fig. 4.1 is a picture of a CVC 601 sputtering system, which is composed of the control panels and the sputtering chamber. Fig. 4.2 illustrates the system. There are three major parts of the system: 1) vacuum system, 2) gas supplying system, 3) sputtering system.

4.2 Vacuum system

Sputter processing is done in vacuum. There are two major types of pumps: gas transfer pumps and entrapment pumps. Gas transfer pumps remove gas molecules from the pumped volume and convey them into the ambient. Entrapment pumps condense or chemically bind molecules at the walls within the chamber being pumped. In CVC601 sputtering system, both pumps are used.
Fig. 4.1: CVC601 sputterer.

Fig. 4.2: Illustration of CVC601 sputtering
4.2.1 Gas transfer pump

The gas transfer pumps impart the momentum to the gas which is being pushed in such a way that the gas is transferred continuously from the inlet of the pump to the outlet. This is usually done by mechanical moving parts of the pump. So gas transfer pumps are also called kinetic pumps or mechanical pumps. The schematic of a gas transfer pump is shown in Fig. 4.3. The rotating part of the pump accelerates the molecules of the gas and makes the inlet region which is of lower pressure. Therefore, the molecules from the chamber will start moving towards the region of lower static pressure, with the procedure continuously repeating until most of the molecules are taken from the container where we would like to have a vacuum. When the desired
vacuum level is achieved, we isolate the tank by a rough vacuum valve. This valve stops any exchange of gas between the container and the pump.

4.2.2 Cryopump

Gas transfer pumps are not capable of generating low pressure vacuum. Cryopumps rely on the condensation of vapor molecules on surfaces cooled below 120K, so they are gas entrapment pumps. Cryopumps can generate a very clean vacuum in the pressure range of $10^{-3}$ to $10^{-10}$ torr. Cryopumps designed to achieve ultrahigh vacuum have panels that are cooled to 20K. Cryopumps need an initial forepressure of about $10^{-3}$ torr in order to prevent the accumulation of a thick condensate on the cryopanels.

4.3 Gas supply

The sputtering process is discussed in detail in previous chapters. Once the high vacuum is reached, the working gas will be introduced into the chamber.

The gas flow can be read from the flow gauge. The relationship between the pressure and the gas flow should be linear. However, this only holds in some certain range. Fig. 4.4 a) and b) show the relationship between the pressure and the gas flow with the pumps on.

For oxygen, the linearity holds when the gas flow is in between 2-30sccm while for argon flow, the range is in between 30-110sccm. These ranges will be used for design of experiment (DOE).
Fig. 4.4: Gas pressure as functions of gas flow a) oxygen b) argon.
Chapter 5

ITO deposition and processing optimization and film characterization

The actual film deposition was carried out with the system introduced in the previous chapter. The films were deposited onto 2x3 inch glass microslides. The substrates were rotating at 15 RPM. The initial screening investigation was done to find a rough range for the deposition parameters such as the gas flow, the power and the oxygen partial ratio. The determination of annealing conditions was also performed. These are described in section 5.1. Section 5.2 covers the optimization of the deposition process through design of experiment (DOE). Processing was optimized to get high transmission and low resistivity. Deposition rate as a function of the selected experimental parameters was studied. To further optimize the deposition, a second designed experiment was carried out with just the oxygen partial pressure and the power as experimental parameters. This is discussed in section 5.3. The result shows that in the narrowed experimental parameter range, the electrical property and optical property are not sensitive to the experimental parameters. The property variation is just due to noise. The properties of the optimized ITO film, such as surface roughness, refractive index and uniformity across the wafer are presented in sections 5.4 and 5.5.
5.1 Deposition parameter range determination

There are a few parameters that can affect the ITO properties. These parameters are the power distributed onto the target, the gas flow (argon and oxygen), the gap distance between the anode and cathode, the base pressure, annealing temperature, annealing time and the deposition time. It is a tedious task to do DOE with all seven parameters. To simplify the optimization process, the parameter number was reduced. Some initial deposition process showed that the base pressure did not affect the film properties significantly. So the base pressure was held at $10^{-5}$ torr prior to all the sputtering processes. The gap distance between the anode and the cathode is fixed for this system. The power, oxygen and argon flow were picked as deposition variables. A few runs were done prior to the DOE to find out the proper deposition parameter range. The melting point of indium tin target is low, so the power should be less than 200W to avoid target melting. However, if the power is too low, the deposition rate is expected to be low since the deposition rate is strongly related with the power. For the initial runs, the power was picked to be in the range of 100 – 200W. The total gas flow and oxygen ratio were the other two parameters. The ratio of oxygen was chosen to be in the range of 5-15%. In the previous chapter, the relationship between the chamber pressure and gas flow was discussed. For oxygen flow between 2-30sccm, argon flow between 30-100sccm, the linearity between the gas flow and pressure holds. So the total gas flow was selected to be 40 – 100sccm. The annealing temperature and time were held at 350°C and 3 hours.

The results are summarized in Table 5.1. In this range, the sheet resistance can
be less than $100\,\Omega/\square$ and the transmission can be higher than 80%. This value is close to the reported ITO properties. The experiments were not designed according to DOE, so it is difficult to do quantitative analysis. The general trend shows that high power, low oxygen ratio yielded near metallic films, while low power and high oxygen ratio gave highly oxidized films. Through careful DOE, it is possible to improve the film quality. The deposition rate is strongly related with power. Fig. 5.1 illustrates the relationship between them. The relation is almost linear. Using the data of Fig 5.1, one can describe the relationship between the power and deposition rate as:

$$DepRate = 0.0214 \cdot Power - 1.4759 \, \AA/s \quad (5.1)$$

The actual expression of deposition rate is more complicated than Eq. 5.1, however, it is not possible to get it at this point. However, Eq. 5.1 is a good approximation and will be used as reference for further investigation.

**Table 5.1: Initial study for experimental parameter range determination**

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Gas flow (sccm)</th>
<th>Oxygen ratio (%)</th>
<th>Thickness (Å)</th>
<th>Dep rate (Å/s)</th>
<th>Sheet resistance (Ω/□)</th>
<th>Transmission (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>100</td>
<td>5</td>
<td>970</td>
<td>1.62</td>
<td>19</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>10</td>
<td>1054</td>
<td>1.76</td>
<td>38</td>
<td>75</td>
</tr>
<tr>
<td>150</td>
<td>100</td>
<td>15</td>
<td>1041</td>
<td>1.74</td>
<td>240</td>
<td>high*</td>
</tr>
<tr>
<td>200</td>
<td>50</td>
<td>10</td>
<td>1942</td>
<td>3.24</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>50</td>
<td>20</td>
<td>1425</td>
<td>2.38</td>
<td>17</td>
<td>low</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>10</td>
<td>412</td>
<td>0.69</td>
<td>430</td>
<td>high</td>
</tr>
</tbody>
</table>
Annealing is expected to be important and can cure the defects in the film. Some initial study on annealing was carried out to find the annealing conditions. The samples for annealing study were prepared with the following parameters: power 140W, gas flow 70sccm, oxygen ratio 10%. The result shows that when the temperature was less than 150°C, the effect of annealing is negligible. When the temperature was between 150°C and 300°C, the conductivity and transmission increase with temperature because of grain growth and gradual crystallization [41, 42]. When the temperature is above 300°C, no further improvement was observed. The annealing temperature was fixed at 300°C, Fig. 5.2 is the annealing result with different annealing time. To achieve higher conductivity and transmission, longer annealing time is desired. The annealing time was fixed at 20 hours. Note that the transmission in some region is above 100%. A transmission test was performed to see the effect of annealing on glass. The spectrometer was auto-zeroed with just the light
as the background, and then a transmission measurement was performed with the un-annealed glass in the optical path. The glass was then annealed 20 hours and a transmission measurement was performed again. The result is shown in Fig. 5.3, the glass transmission spectrum change was not observed. The annealing process does not change the optical properties of the glass slides.

The transmission exceeds 100% is actually due to the change of ITO index of refraction. The refractive index measurement showed that the index of refraction of the ITO film was 2.08 at 425nm. For a thin film to act as anti-reflective coating (ARC), the target thickness \( t \) is:

\[
 t = \frac{m\lambda}{2n} \quad (5.2)
\]

where \( \lambda \) is the illumination wavelength, \( n \) is the index of the ARC layer material, and \( m \) is integer number [40]. For our case, the film thickness is 100nm, which matches Eq. 5.2 with \( m \) equal to 1. Note that in Fig. 5.3, the transmission increases gradually with the annealing time when the annealing time is less than 7 hours. However, for 20 hours annealing, the transmission spectrum is very different from the previously three curves. This is because ITO refractive index may be graded due to annealing [40]. Longer annealing time may reduce the variation of refractive index with depth.

The final experimental parameter ranges for the DOE are summarized in Table 5.2.
Fig. 5.2: Longer annealing time improves transmission.

Fig. 5.3: The transmission of glass before and after 20 hours annealing. (The two lines overlap on each other)
Table 5.2: The experimental parameters for ITO deposition

<table>
<thead>
<tr>
<th>Experimental parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>100-180W</td>
</tr>
<tr>
<td>Oxygen ratio</td>
<td>5-15%</td>
</tr>
<tr>
<td>Total gas flow</td>
<td>40-100sccm</td>
</tr>
<tr>
<td>Annealing temperature</td>
<td>300°C</td>
</tr>
<tr>
<td>Annealing time</td>
<td>20 hours</td>
</tr>
</tbody>
</table>

5.2 Processing optimization

The initial results in Table 5.1 are not good enough for high quality application, so further optimization needed to be done for the deposition process. An initial experiment (central composite design) was performed to investigate the effect of oxygen ratio, total gas flow and power. The results before annealing are summarized in Table 5.3. The property variation is very significant. Visual inspection showed some films were opaque and some have good transmission (see Fig. 5.4). The sheet resistance varied from $180 - 1.9 \times 10^6 \Omega/\square$. For some of the samples, the sheet resistance is too high to be measured. Transmission is averaged over the visible range (400-800nm). For most of the samples, the transmission is too low to be measured by Perkin Elmer spectrometer.
Table 5.3: Experimental results before annealing

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Oxygen ratio (%)</th>
<th>Power (W)</th>
<th>Gas flow (sccm)</th>
<th>Sheet resistance (Ω/square)</th>
<th>Transmission (%)</th>
<th>Deprate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>100</td>
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<td>.</td>
<td>46.32</td>
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<td>100</td>
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<td>.</td>
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<td>.</td>
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</tr>
<tr>
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<td>70</td>
<td>140</td>
<td>159.34</td>
<td>.82.1</td>
<td>79.2</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>40</td>
<td>180</td>
<td>264.279</td>
<td>.</td>
<td>164.5</td>
</tr>
<tr>
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<td>15</td>
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<td>100</td>
<td>-</td>
<td>.</td>
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</tr>
<tr>
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<td>.</td>
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<td>70</td>
<td>100</td>
<td>-</td>
<td>.</td>
<td>21.8</td>
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<tr>
<td>9</td>
<td>10</td>
<td>70</td>
<td>140</td>
<td>179.717</td>
<td>81.9</td>
<td>87.1</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>100</td>
<td>180</td>
<td>912.695</td>
<td>.</td>
<td>157.4</td>
</tr>
<tr>
<td>11</td>
<td>15</td>
<td>70</td>
<td>140</td>
<td>-</td>
<td>.</td>
<td>24.3</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>70</td>
<td>140</td>
<td>630.064</td>
<td>.</td>
<td>121.5</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>70</td>
<td>180</td>
<td>51908</td>
<td>.</td>
<td>122.2</td>
</tr>
<tr>
<td>14</td>
<td>15</td>
<td>100</td>
<td>100</td>
<td>4602.88</td>
<td>.</td>
<td>13.08</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>100</td>
<td>180</td>
<td>-</td>
<td>.</td>
<td>58.2</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>40</td>
<td>100</td>
<td>2735.5</td>
<td>.</td>
<td>73.8</td>
</tr>
</tbody>
</table>
Before annealing, sample 4 and 9 showed the best results. This happened to be the center points. The average of the sheet resistance is $169.53\,\Omega/\square$ and the transmission is averaged to be 82%. However, the other data are messy and could not be analyzed.

The samples were annealed at $300^\circ C$ for 20 hours. After annealing, the results are summarized in Table 5.4.

It is very interesting that after long time annealing, the difference for transmission are almost eliminated. This is confirmed by analysis of variance (ANOVA). This is probably due to further oxidation during annealing since there is some residual oxygen in the oven and the annealing time is very long.
Table 5.4: Experimental results after 20 hours annealing.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Oxygen ratio (%)</th>
<th>Gas flow (sccm)</th>
<th>Power (W)</th>
<th>Resistivity ($10^{-4}$ Ω-cm)</th>
<th>Deprate (Å/min)</th>
<th>Transmission (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>100</td>
<td>100</td>
<td>4.87</td>
<td>46.32</td>
<td>96.8</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>100</td>
<td>140</td>
<td>10.74</td>
<td>53</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>40</td>
<td>140</td>
<td>3.85</td>
<td>108.8</td>
<td>94.8</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>70</td>
<td>140</td>
<td>5.58</td>
<td>79.2</td>
<td>94.8</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>40</td>
<td>180</td>
<td>8.28</td>
<td>164.5</td>
<td>89.9</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>40</td>
<td>100</td>
<td>8.18</td>
<td>12.7</td>
<td>96.4</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>40</td>
<td>180</td>
<td>3.01</td>
<td>142.875</td>
<td>96.4</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>70</td>
<td>100</td>
<td>12.97</td>
<td>21.8</td>
<td>91.4</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>70</td>
<td>140</td>
<td>4.39</td>
<td>87.1</td>
<td>95.4</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>100</td>
<td>180</td>
<td>9.2</td>
<td>157.4</td>
<td>93.1</td>
</tr>
<tr>
<td>11</td>
<td>15</td>
<td>70</td>
<td>140</td>
<td>9.02</td>
<td>24.3</td>
<td>96.6</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>70</td>
<td>140</td>
<td>5.48</td>
<td>121.5</td>
<td>92.4</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>70</td>
<td>180</td>
<td>3.25</td>
<td>122.2</td>
<td>87.8</td>
</tr>
<tr>
<td>14</td>
<td>15</td>
<td>100</td>
<td>100</td>
<td>46.88</td>
<td>13.08</td>
<td>96.4</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>100</td>
<td>180</td>
<td>15.54</td>
<td>58.2</td>
<td>97.8</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>40</td>
<td>100</td>
<td>3.14</td>
<td>73.8</td>
<td>92.4</td>
</tr>
</tbody>
</table>

After data analysis, the experimental models are generated by JMP IN software for deposition rate and resistivity. Fig. 5.5 a) shows the dependence of the deposition rate on oxygen ratio and power with the gas flow fixed at 70 sccm while Fig 5.5 b) shows the dependence of the deposition rate on oxygen ratio and total gas flow with the power fixed at 140W. These plots show the deposition rate increasing with power.
and decreasing with oxygen ratio and gas flow. Further analysis showed the change of resistivity due to gas flow is small. So for resistivity contour plot, the gas flow was fixed to be 40 sccm since high deposition rate could be achieved with this gas flow value. The plot shows that a power supply about 140W and oxygen ratio between 6%-10% results in lowest resistivity. Those significant factors for the resistivity and the deposition rate are summarized in Table 5.5 and 5.6. Mathematical models are generated based on the scaled estimates of each factor. The ANOVA is shown in Appendix 1. The deposition rate as function of each significant factor is:

\[
Deprate = 80.4 - 31.2(O-10)/5 - 17.5(G-70)/30 + 47.7(P-140)/40 - 13.2[(O-10)/5]*[(G-70)/30]*[(P-140)/40]
\]  
(5.3)

and the resistivity as a function of each significant factor is

\[
resistivity = 6.51 + 5.17(O-10)/5 + 6.08(G-70)/30 - 3.68(P-140)/40 + 6.07[(G-70)/30]*[O-10]/5 - 5.75[(O-10)/5]*[(P-140)/40] - 3.37[(G-70)/30]*[(P-140)/40] + 5.02[(P-140)/40]^2 - 3.17[(O-10)/5]*[(G-70)/30]*[(P-140)/40]
\]  
(5.4)

where O is the oxygen ratio, G is the gas flow, P is the power in physical units. These two functions are only valid in the range specified by Table 5.2. The coefficient of each term, which indicates how the response depends on each significant factor, is same as in Tables 5.5 and 5.6. To illustrate this, we can use the dependence of resistivity on oxygen partial ratio as an example. The scaled estimate is 5x10^-4, this mean if the oxygen ratio is increased from 10 to 15, the resistivity will increase by 5x10^-4Ω-cm.
Fig. 5.5: The contour plot of the deposition rate. a) The dependence of the deposition ratio on power and oxygen ratio. b) The dependence of the deposition ratio on gas flow and oxygen ratio.
Fig. 5.6: The dependence of the resistivity on power and oxygen ratio with gas flow fixed at 40 sccm.

Table 5.5: The significant factors for resistivity

<table>
<thead>
<tr>
<th>Term</th>
<th>Scaled Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.000651</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.0005166</td>
</tr>
<tr>
<td>Gas</td>
<td>0.0006077</td>
</tr>
<tr>
<td>Power</td>
<td>-0.000368</td>
</tr>
<tr>
<td>(Oxygen-10)*(Gas-70)</td>
<td>0.0006072</td>
</tr>
<tr>
<td>(Gas-70)*(Power-140)</td>
<td>-0.000337</td>
</tr>
<tr>
<td>(Oxygen-10)*(Power-140)</td>
<td>-0.000575</td>
</tr>
<tr>
<td>(Power-140)*(Power-140)</td>
<td>0.0005022</td>
</tr>
<tr>
<td>(Gas-70)<em>(Power-140)</em>(Oxygen-10)</td>
<td>-0.000317</td>
</tr>
</tbody>
</table>
Table 5.6: The effect on deposition rate

<table>
<thead>
<tr>
<th>Term</th>
<th>Scaled Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>80.423437</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-31.2365</td>
</tr>
<tr>
<td>Gas</td>
<td>-17.4675</td>
</tr>
<tr>
<td>Power</td>
<td>47.7475</td>
</tr>
<tr>
<td>(Gas-70)<em>(Power-140)</em>(Oxygen-10)</td>
<td>-13.17938</td>
</tr>
</tbody>
</table>

For the deposition rate, the major effect are oxygen ratio and power as it increases with the power and decreases with the oxygen ratio. Lower resistivity is desired for most applications. The ANOVA analysis shows that the lowest resistivity can be obtained with oxygen ratio 8%, gas flow 40sccm and power at 133W. The effect of gas flow on the deposition rate is small compared with the other two parameters, so a gas flow of 40sccm is the optimized parameter for both deposition rate and resistivity. Eight percent oxygen ratio and 133W power can give acceptable deposition rate. So these parameters are finally determined as the best deposition condition.

5.3 Deposition study with narrowed experimental parameter ranges.

The experimental parameters used were very wide. Since this process is noisy, a second DOE was carried out, where the gas flow is fixed at 40sccm, the oxygen ratio varied from 6% to 10%, and the power varied from 120W to 150 W. Again, the central composite design was chosen. ANOVA analysis showed that no experimental
parameters are significant to the resistivities. This is due to the variation, which is comparable to the processing noise in this narrowed parameter ranges.

The deposition rate can be expressed as

$$Deprate = 1.9 - 0.24(O - 8)/2 + 0.43(P - 135)/15 - 0.12[(P - 135)/15]^2 + 0.088[(O - 8)/2]^2 + 0.078[(O - 8)/2][(P - 135)/15]$$

(5.5)

This indicates the deposition rate increases with power and decreases with oxygen ratio.

<table>
<thead>
<tr>
<th>Oxygen ratio (%)</th>
<th>Power (W)</th>
<th>Deposition rate (Å/s)</th>
<th>Resistivity ($10^{-4}$ Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>135</td>
<td>1.76</td>
<td>3.54</td>
</tr>
<tr>
<td>6</td>
<td>135</td>
<td>2.25</td>
<td>6.29</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
<td>2.15</td>
<td>5.14</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>2.47</td>
<td>8.19</td>
</tr>
<tr>
<td>10</td>
<td>120</td>
<td>1.11</td>
<td>5.03</td>
</tr>
<tr>
<td>8</td>
<td>135</td>
<td>1.88</td>
<td>5.96</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>1.74</td>
<td>6.38</td>
</tr>
<tr>
<td>8</td>
<td>135</td>
<td>1.90</td>
<td>6.63</td>
</tr>
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<td>8</td>
<td>150</td>
<td>2.21</td>
<td>6.46</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>1.39</td>
<td>3.20</td>
</tr>
</tbody>
</table>

5.4 Uniformity and surface roughness

The sheet resistance was measured by the CDE Resmap. The sheet resistances of five points were measured on each sample as shown by Fig. 5.7. The samples used for this measurement were 1000Å ITO films deposited on glass slides. Because only
at the center area, good uniformity was achieved (this will be addressed in the following sections), so the five points were taken at the center of the sample.

The surface roughness was analyzed by a profilometer. The averaged surface roughness of five samples was measured to be 7.4Å after annealing. One measurement is shown in Fig. 5.8 as an example.

Due to the inherent shortcomings of 4” target, the film thickness is not uniform across large wafer area. Fig. 5.9 is the measured thickness across the wafer. Only the positions at the center of the wafer have thickness values close to this target value. If an 8” target were used, the thickness should be more uniform across the wafer.

Fig. 5.7: The sheet resistance measurement (Ω/□).
5.5 The optical constants of ITO film

The $n$ and $k$ values of ITO were measured by Woollam Variable Angle Spectroscopic Ellipsometer (VASE). The bare silicon wafer was well cleaned and then deposited with a layer of ITO film. The ellipsometric analysis showed that the optical constants are uniform across the wafer. The refractive index and extinction coefficient of the ITO film were plotted as functions of the illumination wavelength in Figs. 5.10 and 5.11.
Fig. 5.9: The film thickness across the wafer.
Fig. 5.10: The refractive index of the ITO film.

Fig. 5.11: The extinction coefficient of the ITO film

The absorption coefficient $\alpha$ can be calculated from the extinction coefficient $k$ by using

$$\alpha = \frac{4\pi k}{\lambda}$$  \hspace{1cm} (5.5)$$

where $\lambda$ is the illumination wavelength. Fig. 5.12 shows how the absorption coefficient changes with the incident photon energy. This result matches well with Bender’s result (Fig. 2.5).
Fig. 5.12: The absorption coefficient of the ITO film.
Chapter 6

ITO patterning and ITO-semiconductor Schottky contact fabrication

ITO is widely used for opto-electric devices. The patterning methods for ITO film were investigated and a Schottky contact was fabricated. These are discussed in the following sections.

6.1 Patterning ITO film

Typically there are two methods for thin film patterning. These are lift-off and etching.

6.1.1 Lift-off

For a lift-off process, a masking layer is needed during the sputtering process. Photoresist is typically used as the masking layer. The ideal process is illustrated in Fig. 6.1. A layer of photoresist is first spun onto the silicon wafer, then exposed and developed to get the desired pattern. Step 3 is the sputtering process, when an ITO film is deposited over the entire wafer. After the photoresist removal, the desired ITO pattern would be produced onto the wafer. However, during step 3, the photoresist was damaged by oxygen plasma. The resulting photoresist film cannot be removed by acetone. Therefore, photoresist cannot act as an ideal masking material. Other materials, such as aluminum, silicon dioxide and silicon nitride, might be used as the masking layer. However, this will significantly increase the complexity of the process.
So lift-off process was not considered as the first choice of this study. Etching processing was preferred for ITO patterning.

![Diagram of lift-off process]

**Fig. 6.1:** Ideal lift-off process for ITO on silicon substrate

### 6.1.2 Etching

In etching process, the ITO film was first deposited onto the entire wafer without a masking layer, and then a photoresist layer was spun onto the wafer and exposed with desired pattern. The unmasked area of ITO will be etched away. Both wet etch and dry etch are suitable for ITO patterning according to different application [34, 35].
6.1.2.1 Wet chemical etch

Wet chemical etch is widely used in industry for pattern transfer due to its low cost, excellent selectivity and large yield. Usually oxides can react with acids. Therefore a few acids were chosen as etchant candidates.

According to some references, HF can be used as etchant. However, HF is a very dangerous material. Indium and tin ions can contaminate the HF bath. So HF was not investigated as etchant for this study. Wet etch of ITO in hydrochloric acid was performed at different HCl concentrations. As shown in Fig. 6.2, the etch rate increases exponentially as the HCl concentration increases. To achieve controllable etch rate, the volumetric ratio of 50%-80% can be used. A wafer with photoresist pattern was immersed into standard 37% HCl aqueous solution. No significant thickness loss of photoresist was observed. The selectivity of ITO to photoresist is almost infinity. The inherent disadvantage of this process is the etching is isotropic, so the etching will happen not just along the vertical direction, but also horizontally.

![Wet etch of ITO in HCl](image)

**Fig. 6.2: Wet etch of ITO in HCl.**
### 6.1.2.2 Dry etching

Although wet etch is productive, fast, and highly selective, due to its inherent undercutting problem, for dimensions less than one micrometer, wet etch is not preferred. Dry etching was investigated. This process is similar to sputtering, however, no oxidation process is needed. The “target” is a silicon wafer with ITO underneath photoresist pattern. For simplicity, photoresist will act as mask for dry etch study.

A mixture of argon and oxygen (80sccm of Ar and 5sccm of O₂) was first picked as the working gas. It was found that after ten minutes RIE, all the photoresist was etched, no thickness loss of ITO film was observed. This is because the photoresist was burned by oxygen plasma. Then, argon was chosen as the only working gas. With different parameter setup as described in Table 6.1, the etch rate of ITO film decreases when power decreases. However, the photoresist was damaged. The residue is a layer of dark opaque film. Because the film is not transparent, the film thickness cannot be measured by optical method. It is also very hard to remove the film. Further experiment showed that the photoresist was not degraded when the power was less than 90W. To maximize the etch rate and keep the photoresist unaffected, the power was fixed at 90W for dry etch study.

<table>
<thead>
<tr>
<th>Power(W)</th>
<th>Ar (sccm)</th>
<th>pressure (mtorr)</th>
<th>Etch rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>50</td>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>150</td>
<td>50</td>
<td>70</td>
<td>32.5</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>70</td>
<td>18.5</td>
</tr>
</tbody>
</table>
The other parameters are the argon flow and pressure. At certain gas flow, the pressure cannot vary too much. For example, with large gas flow, it was very difficult to maintain low chamber pressure. The pressure was picked to be 90 mtorr. With different argon flow, the etch rate was different. This is shown in Fig. 6.3.

![RIE etch graph](image)

**Fig. 6.3: RIE of ITO film and the photoresist.**

High gas flow causes the etch rate of photoresist to increase and decreases the etch rate of ITO film. Therefore, in this range, 80sccm argon flow is the optimized gas flow. The selectivity of photoresist to ITO is 13.02. For a thin ITO film this process is suitable. If the film were thick, the photoresist needs to be very thick to mask the etching process.

To increase the etch rate and selectivity, other working gases or masking materials may be investigated. A few other working gases, such as the mixture of
Ar₂/CH₄ [37], HBr [38], were reported as the working gas. Other materials such as aluminum and silicon nitride are possible candidates as the masking materials for ITO dry etch. However, the purpose of this study is to investigate the application of ITO film as for transparent electrodes. The typical feature size needed for this application is on the order of a few tens microns to a few millimeters. So wet etch is adequate for this application. For very small features involving ITO film, the dry etching process needs to be further investigated.

6.2 ITO-silicon Schottky contact

Since ITO can be used as transparent electrode in opto-electrical devices, it is important to understand the contact properties between ITO and the silicon substrate. The ITO and n-type silicon contact was first simulated. The rectifying contact with ITO as the conductor and n-type silicon as the semiconductor was fabricated and characterized.

Fig. 6.4 a) illustrates a one-dimensional metal semiconductor. It has been replaced by MS contact fabricated by planar process. A schematic diagram of the planar MS contact is shown in Fig. 6.4 b). The substrate is lightly doped silicon. The doping level is about $10^{15}$ cm$^{-3}$. The cathode is heavily doped to ensure ohmic contact during test. The anode is ITO film. The barrier between the ITO film and the n-type silicon can be identified on an energy band diagram and was discussed in chapter 2.
6.2.1 The Schottky contact fabrication

To fabricate a Schottky contact, a thin layer of ITO film needs to be deposited onto an n type silicon substrate. The interface plays an important role in the electrical property of MS contact, so the process needs to be very clean. The substrate can not be contaminated by any other metal ions. The RCA clean should be the very first step of the processing. A heavily doped region on the substrate is needed to form ohmic contact with the electrode during test. The processing is shown in Fig. 6.5 and can be described as:

Step 1: RCA clean of the substrate and the masking oxide growth. Because the substrate is heavily doped in certain area, a 500nm oxide is needed as the masking layer.

Step 2: Oxide etching and spin on doping. Only a certain area needs to be heavily doped to form ohmic contact with the electrodes during test, so the oxide is etched by buffered hydrofluoric acid, after which, a layer of phosphorous
glass is spun onto the wafer.

Step 3: Annealing and phosphorous glass removal. The wafer is annealed at 1100°C for two hours to diffuse the phosphorous into the substrate and activate the diffused phosphorous. After annealing, the phosphorous glass is removed by wet etching.

Step 4: ITO deposition. A layer of 100 nm ITO film is deposited onto the wafer by DC magnetron sputtering. The film is annealed in nitrogen for 20 hours.

Step 5: ITO patterning. The ITO is patterned by wet etching; the Schottky contact will be formed.

Fig. 6.5: The processing flow for Schottky contact fabrication.
6.2.2 The current voltage characteristic of the Schottky contact

Because the ITO film was annealed in nitrogen at 300°C for 20 hours, indium may diffuse into the substrate and act as p-type dopant. To test this, a layer of 100 nm ITO film was deposited onto an n-type silicon substrate and annealed in nitrogen at 300°C for 20 hours, then etched by hydrochloric acid. After film stripping, the wafer was tested by a wafer typing. It showed that the wafer was still n type. So the annealing process does not change the substrate type. The contact appears to be an abrupt metal-semiconductor contact, namely Schottky contact.

The I-V curve of forward biased ITO and n-type silicon contact is shown in Fig. 6.6. The analysis is similar with the simulated Schottky contact, the current density is

$$J = J_{\text{em}} - J_{\text{nc}}$$

$$= A T^2 \exp(-q\Phi_{Bn} / kT) \left[ \exp(qV / kT) - 1 \right]$$

so

$$I = AA'T^2 \exp(-q\Phi_{Bn} / kT) \left[ \exp(qV / kT) - 1 \right]$$

where A is the area of the MS contact. When the applied bias is less than the Schottky barrier, the series resistance is negligible since most of the potential drops at the contact region. When the applied bias is greater than the Schottky barrier, the potential drop in the contact region is negligible. The behavior of this Schottky contact is dominated by the series resistance. The current increases linearly with the applied voltage rather than exponentially as predicted by Eq. 6.2.
**Fig. 6.6:** The linear scale I-V characteristic curve of a forward biased ITO silicon Schottky contact.

The series resistance can be easily calculated from the linear region.

\[ R_s = \frac{\partial V}{\partial I} \quad (6.3) \]

This is simply the inverse of the slope and it is calculated to be 6.45Ω.

There are two methods to extrapolate the barrier height from the I-V curve. The simple way is just extend the linear region to cross with the voltage axis. This is the built-in potential height. In this case, the barrier height is extrapolated to be 0.96eV. The barrier height of the Schottky contact can also be calculated from the \( I_o \). When \( V > 3kT/q \), equation 6.2 can be simplified as

\[ I = I_o [\exp(qV/kT)] \quad (6.4) \]

From the logarithm scaled I-V curve (Fig. 6.7), by extrapolating the forward I-V
curve to \( V=0 \), we can find \( I_s \). \( I_s \) is found to be \( 2 \times 10^{-12} \) A. Because

\[
I_s = A A^* T^2 \exp\left(-\frac{q \Phi_n}{kT}\right)
\]

so

\[
q \Phi_n = -kT \ln\left(\frac{I_s}{AA^* T^2}\right)
\]

(6.5)

The area of the MS contact is 0.01 cm\(^2\), the effective Richardson constant \( A^* \) of an n-type silicon is 110 AK\(^{-2}\)-cm\(^{-2}\) and the temperature is 295 K. The Schottky barrier height is therefore calculated to be 1.01 eV. This value is very close to the one extrapolated from Fig. 6.6.

![MS contact](image)

**Fig. 6.7: The logarithmic scale I-V characteristic curve of forward biased ITO silicon Schottky contact.**

When a reverse bias is applied, it will increase the built-in potential and make it more difficult for electron to flow from silicon into ITO. Therefore, the reverse current is orders of magnitude small. This behavior can be seen in Fig. 6.8.
Fig. 6.8: I-V curve of ITO-n_silicon contact

The simulated data was presented in chapter 2. The actual device area was 0.01cm², which is much bigger than the simulated contact. Fig 6.9 showed the comparison of the simulated and the actual current density as function of the applied voltage. The difference is quite different. This is due to a few reasons. 1: The simulation accuracy is related to the device dimension, the grid size. If we define the device size to be comparable with the actual device, the grid size will have to increase as well; this will greatly reduce the accuracy. 2: The geometry of the simulated device is different from the actual device. For the simulated device, the anode is deposited at the front side of the wafer while the cathode for measurement is at the backside of the wafer. For the actual device, both the anode and the cathode for test are at the front side of the wafer.
3: The ideality of the Schottky contact is related to the size of the contact [43]. Since the actual device has size much larger than the simulated device, the ideality of these two devices is expected to be different. Overall, the trends of these two curves are same.

![Simulated and actual current density as function of the applied voltage.

**Fig. 6.9:** The simulated and the actual current density as function of the applied voltage.
Chapter 7

Conclusion

7.1 Summary of work performed

An ITO deposition process was successfully developed according to design of experiments principles. With careful post deposition annealing, the electrical and optical properties of the ITO film were characterized. Sheet resistance of $26\,\Omega/\square$ and averaged transmission 90% in the visible wavelength range (400-800nm) were achieved. This film is good for opto-electric device application. The properties of ITO as functions of the deposition parameters, such as the oxygen partial pressure, the power and the pressure were investigated. The dependence of the ITO film properties on these parameters was quantified. With 20 hours annealing, the transmission does not vary significantly with the experimental result. The result shows large processing window for reliable ITO films. With the gas flow fixed at 40sccm, to get ITO film with transmission greater than 90%, the power can vary from 120-150W and the oxygen partial ratio can vary from 6-10%. This is, as the author’s knowledge, the largest processing window reported by literature. The patterning methods, both wet etching and dry etching, were developed to generate desired ITO pattern for device fabrication. The wet etching has a fast etch rate (48nm/min) and great selectivity between the ITO film and the photoresist while dry etching has low etching rate and poor selectivity. Wet etching is suggested for most of the application. The refractive index, real and imaginary, was characterized. A rectifying contact was fabricated with
ITO as the conductor and n-type lightly doped silicon as the semiconductor. The barrier height was calculated to be 0.96V. This high Schottky barrier ensures ITO n-type silicon contact to be rectifying contact.

The 20 hours annealing process results in metallic film which is transparent. After long time annealing, all the films with different deposition parameters show high transmission. This is simply due to further oxidation during the annealing.

These results also showed that with carefully controlled experimental parameters, the as deposited 83-nm ITO films with sheet resistance of 159Ω/□ and 82% transmission over the visible can be obtained by DC reactive sputtering. Further annealing can improve both the resistivity and the transmission. However, for some processing that can only undergo low temperature treatment, the as deposited ITO film may be applied.

### 7.2 Future work

Although ITO films with excellent electrical and optical properties are obtained, this process can be further improved. The uniformity variation resulted from 4-inch target can be solved by using 8-inch target. The dry etch rate is only 1nm/min, the selectivity between the photoresist and the ITO film is 13.02, which needs to be further reduced. These problems may possibly be solved by using different etchant. Ar₂/CH₄ mixture and HBr may be investigated to achieve high etch rate and selectivity. The film properties (optical and electrical) variation between runs still needs to be minimized. The post deposition annealing was carried out in nitrogen.
environment. Since further oxidation after film deposition could significantly improve degree of oxidization, oxygen may be purposely added into the annealing chamber. This may possibly improve transmission and reduce variations. However, this may also increase the resistivity.
REFERENCES


[33] http://acept.la.asu.edu/PiN/rdg/vacuum/vacuum2.html


Appendix

ANOVA analysis for DOE (Table 5.2).

Response Resistivity
Actual by Predicted Plot

![Actual vs Predicted Resistivity Plot]

**Summary of Fit**
- Rsquare: 0.948539
- Rsquare Adj: 0.889726
- Root Mean Square Error: 0.000352
- Mean of Response: 0.000965
- Observations (or Sum Wgts): 16

**Analysis of Variance**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Ratio</th>
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**Lack Of Fit**

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<th>F Ratio</th>
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<td>8.66174e-7</td>
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</table>

Max RSq: 0.9996

**Parameter Estimates**

| Term                     | Estimate | Std Error | t Ratio | Prob>|t| |
|--------------------------|----------|-----------|---------|-------|
| Intercept                | -0.000514| 0.000538  | -0.96   | 0.3713|
| Oxygen                   | 0.0001033| 0.00022   | 4.64    | 0.0024|
| Gas                      | 0.000203 | 0.00004   | 5.46    | 0.0009|
| Power                    | -0.000009| 0.00003   | -3.30   | 0.0130|
| (Oxygen-10)*(Gas-70)     | 0.000004 | 8.291e-7  | 4.88    | 0.0018|
| (Gas-70)*(Power-140)     | -2.81e-7 | 1.036e-7  | -2.71   | 0.0301|
| (Oxygen-10)*(Power-140)  | -0.000003| 6.218e-7  | -4.62   | 0.0024|
| (Power-140)*(Power-140)  | 3.138e-7 | 1.135e-7  | 2.76    | 0.0279|
| (Gas-70)*(Power-140)*(Oxygen-10)| -5.283e-8| 2.073e-8 | -2.65   | 0.0382|
Effect Tests

Source | Nparm | DF | Sum of Squares | F Ratio | Prob > F
--- | --- | --- | --- | --- | ---
Oxygen | 1 | 1 | 0.000000267 | 21.5676 | 0.0024
Gas | 1 | 1 | 0.000000369 | 29.8406 | 0.0009
Power | 1 | 1 | 0.000000135 | 10.9205 | 0.0130
Oxygen*Gas | 1 | 1 | 0.000000295 | 23.8406 | 0.0018
Gas*Power | 1 | 1 | 9.09901e-7 | 7.3534 | 0.0301
Oxygen*Power | 1 | 1 | 0.000000264 | 21.3570 | 0.0024
Power*Power | 1 | 1 | 9.45786e-7 | 7.6432 | 0.0279
Gas*Power*Oxygen | 1 | 1 | 8.03912e-7 | 6.4968 | 0.0382

Scaled Estimates

Continuous factors centered by mean, scaled by range/2

| Term | Scaled Estimate | Std Error | t Ratio | Prob>|t|
| --- | --- | --- | --- | ---
| Intercept | 0.000651 | 0.000144 | 4.53 | 0.0027
| Oxygen | 0.0005166 | 0.000111 | 4.64 | 0.0024
| Gas | 0.0006077 | 0.000111 | 4.66 | 0.0024
| Power | -0.000368 | 0.000111 | 3.30 | 0.0130
| (Oxygen-10)*(Gas-70) | 0.0006072 | 0.000111 | 4.88 | 0.0018
| (Gas-70)*(Power-140) | -0.000337 | 0.000124 | -2.71 | 0.0301
| (Oxygen-10)*(Power-140) | -0.000575 | 0.000124 | 4.62 | 0.0024
| (Power-140)*(Power-140) | 0.0009502 | 0.000182 | 2.76 | 0.0279
| (Gas-70)*(Power-140) | -0.000317 | 0.000124 | -2.55 | 0.0382

Prediction Profiler

\[ \text{resistivity} = 6.51 + 5.17(O - 10)/5 + 6.08(G - 70)/30 - 3.68(P - 140)/40 + 6.07[(G - 70)/30]*[O - 10]/5 - 5.75[(O - 10)/5]*[(P - 140)/40] - 3.37[(G - 70)/30]*[(P - 140)/40] + 5.02[(P - 140)/40] - 3.17[(O - 10)/5]*[(G - 70)/30]*[(P - 140)/40] \]
Response dep rate
Actual by Predicted Plot

Summary of Fit
Rsquare 0.940437
Rsquare Adj 0.918777
Root Mean Square Error 14.5951
Mean of Response 80.42344
Observations (or Sum Wgts) 16

Analysis of Variance
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Lack Of Fit
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Parameter Estimates
| Term                      | Estimate | Std Error | t Ratio | Prob>|t| |
|---------------------------|----------|-----------|---------|------|---|
| Intercept                 | 16.537687| 21.80463  | 0.76    | 0.4641|
| Oxygen                    | -6.2473  | 0.923075  | -6.77   | <.0001|
| Gas                       | -0.58225 | 0.153846  | -3.78   | 0.0030|
| Power                     | 1.193675 | 0.115384  | 10.35   | <.0001|
| (Gas-70)*(Power-140)*(Oxygen-10) | -0.002197 | 0.00086 | -2.55   | 0.0268|

Effect Tests
<table>
<thead>
<tr>
<th>Source</th>
<th>Nparm</th>
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Scaled Estimates

Continuous factors centered by mean, scaled by range/2

| Term                              | Scaled Estimate | Plot Estimate | Std Error | t Ratio | Prob>|t| |
|-----------------------------------|-----------------|---------------|-----------|---------|------|
| Intercept                         | 80.423437       |               | 3.648775  | 22.04   | <.0001 |
| Oxygen                            | -31.2365        |               | 4.615375  | -6.77   | <.0001 |
| Gas                               | -17.4675        |               | 4.615375  | -3.78   | 0.0030 |
| Power                             | 47.7475         |               | 4.615375  | 10.35   | <.0001 |
| (Gas-70)*(Power-140)*(Oxygen-10)  | -13.17938       |               | 5.160146  | -2.55   | 0.0268 |

Prediction Profiler

\[ \text{Deprate} = 80.4 - 31.2(O - 10)/5 - 17.5(G - 70)/30 + 47.7(P - 140)/40 - 13.2[(O - 10)/5]*[(G - 70)/30]*[(P - 140)/40] \]