Fabrication of Si/InGaN Heterojunction Solar Cells by RF Sputtering Method: Improved Electrical and Optical Properties of Indium Gallium Nitride (InGaN) Thin Films
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Fabrication of Si/InGaN Heterojunction Solar Cells by RF Sputtering Method: Improved Electrical and Optical Properties of Indium Gallium Nitride (InGaN) Thin Films

by

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ABSTRACT

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Fabrication of Si/InGaN Heterojunction Solar Cells by RF Sputtering Method: Improved Electrical and Optical Properties of Indium Gallium Nitride (InGaN) Thin Films

Director of Dissertation: Martin E. Kordesch

This dissertation presents a study on the fabrication of Indium Gallium Nitride (InGaN) based heterojunction solar cells using RF magnetron sputtering method. The goal of the study includes improving the electrical, optical and structural properties of InGaN thin films and examining their potential for photovoltaic applications and to reduce the parasitic resistive loses in solar cells.

Reactive radio-frequency (RF) magnetron and Direct Current (DC) sputtering are deposition methods for thin films. The characterization techniques include Hall Effect measurement system for electrical properties, UV-Visible Spectroscopy for optical properties, X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDXS) for structural properties and AM 1.5 G irradiance spectrum to measure current-voltage (IV curves) and photovoltaic measurements.

Copper Oxide thin films and Beryllium Zinc Oxide thin films are fabricated and their properties are examined for their potential to pair with n-InGaN to form a p-n junction. We conclude Silicon (111) wafer has better electrical properties than RF deposited Copper oxide and BeZnO and used as p-type layer. Aluminum (Al) and Indium Tin Oxide (ITO) are used as back and front metallic contacts respectively.
In this study, we present a simple method for optical bandgap tuning of Indium Gallium Nitride (InGaN) thin films by controlling the growth conditions in magnetron RF sputtering. Thin films with different Indium (In) atomic compositions, x = 0.02 to 0.57 are deposited on high temperature aluminosilicate glass and Silicon (111) substrates. Substrate temperature is varied from 35 °C to 450 °C. Total pressure of sputtering gas mixture is kept constant at 12 mTorr but partial pressures of Ar and N\textsubscript{2} are varied. Ar partial pressure to total pressure ratio is varied from 0 to 0.75. Optical bandgap values from 1.4 eV to 3.15 eV, absorption coefficient values of $\sim 10^4$ /cm to $\sim 7 \times 10^5$ /cm and critical film thickness values of 0.04 μm to 4 μm are measured. Resistivity values of 2.6x10$^{-5}$ to 1.68x10$^{-2}$ Ω.cm, mobility values of 0.119 to 1017 cm$^2$/V. s, conductivity values of 0.595 x 10$^3$ to 37.3 x 10$^3$ mho/cm and bulk carrier concentration values -10$^{20}$ to -10$^{22}$/m$^3$ are recorded.

To reduce parasitic loses, Aluminum Nitride (AlN) is used as buffer layer and solvent clean method is used to remove oxide layers. A short circuit current of 80 μA, Voc of 0.24 V, Fill Factor of 0.418 and efficiency of 0.015 % is measured for the solar cells.
DEDICATION

To my parents.

Balachandra Jakkala & Subhadra Jakkala
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CHAPTER 1: INTRODUCTION

What if we had no atmosphere on earth? The average temperature on the Earth's surface would be about -18°C [1]. Earth receives huge amount of radiation from the Sun and energy is radiated into space by the earth, the equilibrium established between these two values results in average temperature on Earth's surface. Atmosphere on the Earth's surface absorbs outgoing radiation and keeps the earth warm. Carbon dioxide absorb strongly in the 13-100 μm wavelength range, other atmospheric gases absorb in 4-7 μm range, outgoing radiation escapes (70%) in 7-13 μm range [2].

Human activities and energy from resources like coal and fossil fuels leads to emission of harmful gases like carbon dioxide, methane, ozone, nitrous oxides and chlorofluorocarbons (CFC's), these gases absorb the outgoing radiation in that 7-13 μm range and prevent the normal escape of outgoing radiation and leads to increase in the temperature of earth, global warming [3]. These conventional resources are not renewable, so, there is a need to look for alternative, renewable and environmental friendly resources of energy. One such alternative is solar energy.

Solar constant: The Sun's power density (i.e. power per unit area normal to its rays) just above the Earth's atmosphere is solar constant and its value is 1366 W/m² [4]. Solar radiation at the Earth's surface varies from the solar radiation incident on the Earth's atmosphere. Cloud cover, air pollution, latitude of a location and the time of the year cause variations in solar radiance at the Earth's surface. This is reduced by around 30% as it passes through atmosphere, giving an insolation of about 1000 W/m² at sea level on a clear day [5]. Average power density received over the whole year is known as annual
mean insolation. Annual mean insolation just above atmosphere is 342 W/m². Average insolation is greatly affected by local climatic conditions, ranging from about 300 W/m² on Sahara Desert to 80 W/m² near poles [6][7]. The amount of energy reaching the surface of the Earth every hour is greater than the amount of energy used by the Earth's population over an entire year. Sun sends $10^{17}$ W towards earth [7]. Most of it falls on the world's oceans, some interrupted by clouds, lot more falls at undesirable places. Yet, even considering all this the Sun is a wonderful resource of energy. Harnessing this energy in an efficient way could solve most of the energy related problems of Human population. Photovoltaics can do the magic of harvesting this energy.

A solar cell turns sunlight into electricity, no fuel, no waste products (!) and no harmful emission of gases. “Photons in and electrons out”. N-type semiconductor is obtained by doping an intrinsic semiconductor with impurity atoms having an excess valence electron. P-type is obtained by doping with acceptor atoms. Amount of positive charge still balances the amount of negative charge. Electrons are majority carriers in n-type material, holes are majority carriers in p-type material.

![Figure 1.1: N-type and p-type semiconductors with carriers.](image)
There are large number of mobile electrons in the n-type material and large number of mobile holes in p-type material. When p-type and n-type materials are joined, high concentration of electrons in n-region makes them diffuse into p-region leaving behind exposed charges on dopant atom sites, positively charged, fixed and unable to move near the interface. Similarly, holes in p-region diffuse into n-region leaving behind negatively charged immobile acceptor ions at the interface. These fixed ions set up an electric field at the junction. This electric field points from the positively charged ions in the n-type material to the negatively charged ions in the p-type material.

The free electrons and holes are influenced by this "built-in" electric field with the electrons being attracted towards the positive dopant ions and the holes being attracted towards the negative acceptor ions at the junction. Thus, the “built-in” electric field causes some of the electrons and holes to flow in the opposite direction to the flow caused by diffusion. These opposing flows eventually reach a stable equilibrium with the number of electrons flowing due to diffusion exactly balancing the number of electrons flowing back due to the electric field. The net flow of electrons across the junction is zero and the net flow of holes across the junction is also zero. This region is also called “depletion region”. The region quickly sweeps out any free carriers, it is depleted of free carriers. Although, there is no net flow of current across the junction there has been an established electric field at the junction and it is this electric field that is the basis of the operation of diodes, transistors and solar cells.

A “built in” potential is formed due to the electric field at the junction. Due to the built in electric field, most majority carriers which reach the junction move back to the
region they originated from. But, few of the majority carriers with high velocities can cross the junction, continue to diffuse away from junction, move a certain distance before it recombines.

This current caused by diffusion of majority carriers across the junction is known as “diffusion current”. Minority carriers that reach the junction swept across the junction by the electric field, this current is called “drift current”. At equilibrium, drift current and diffusion current balance out each other. In terms of band energy diagram shown in Figure 1.2, this equilibrium is attained by balancing the fermi energy levels.

\[ \text{Built-in Field} \]

\[ \text{p-type} \quad E_g \quad \text{n-type} \]

\[ \text{Depletion Region} \]

\[ E_v \quad E_f \quad E_c \]

*Figure 1.2: Energy band diagram of p-n homojunction at equilibrium, Fermi levels.*
Using Poisson’s equation, we can derive built-in potential, electric filed in the junction and the depletion width. If \( x_p \) and \( x_n \) are the edges of depletion region in p-type and n-type side respectively, \( N_A \) and \( N_D \) are acceptor and donor densities respectively, \( n_i \) is the intrinsic carrier concentration, then,

Electric field in the depletion region,

\[
E = \begin{cases} 
\int -\frac{qN_A}{\epsilon} \, dx = -\frac{qN_A}{\epsilon} x + C_1, & \text{for } -x_p \leq x < 0 \\
\int \frac{qN_D}{\epsilon} \, dx = \frac{qN_D}{\epsilon} x + C_2, & \text{for } 0 \leq x < x_n
\end{cases}
\]  \hspace{1cm} (1.1)

Built-in voltage, \( V_{bi} \),

\[
V_{bi} = \frac{kT}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right)
\]  \hspace{1cm} (1.2)

Balance of charge requires,

\[
x_n N_D = x_p N_A
\]  \hspace{1cm} (1.3)

Depending on the relative doping, junction extends unequally into the n and p regions. Junction width is deeper in the lightly doped region of two. When semiconductors of different bandgaps are brought together to form a p-n junction (hetero junction), bandgap discontinuities and difference in electron affinity values of the two semiconductors brings discontinuities as shown in Figure 1.3 in the conduction (\( \Delta E_c \)) and valence (\( \Delta E_v \)) band edges [8] [12]. A p-i-n junction is a junction formed from three regions. An intrinsic or undoped layer is sandwiched between p and n type semiconductors [9]. The intrinsic layer enlarges the drift region and decreases the
junction capacitance [10]. It creates a large potential barrier for majority carriers and fast drift responses for minority carriers as shown in figure 1.4 [11].

\[ \text{Vacuum level} \]

\[ \text{Figure 1.3: P-N heterojunction with conduction and valence band offsets.} \]

The junctions between metal and lightly doped semiconductor exhibit rectifying properties (Schottky barrier) and junction between metal-heavily doped semiconductor exhibit ohmic properties [12]. The difference between the values of metal work function and electron affinity of semiconductor is the barrier height (\( \Phi_b \))[13] [12].
\[ \Phi_b = \Psi_M - \chi_s \]  

(1.4)

Where \( \Psi_M \) is metal work function and \( \chi_s \) is semiconductor’s electron affinity.

Vacuum level

Light generated electron

p-type

\( E_g \)

i-layer

n-type

Light generated hole

Depletion region

Figure 1.4: p-i-n junction band energy diagram with large depletion region

Basic single junction solar cell: A solar cell works based on photovoltaic effect which directly converts Sun light into electricity. It produces both current and voltage to generate electric power. A basic single junction solar cell consists of a p-type, n-type semiconductors sandwiched together to form a p-n junction, front and back metal contacts, anti-reflective coating to reduce the reflection of light from top surface.
The solar cell is connected to the external circuit through metal contacts. When n-type semiconductor material is brought in contact with p-type material, excess electrons in n-type diffuse to the p-side exposing positive ion cores, excess holes in p-type diffuse into n-side exposing negative ion cores, this results an electric field at the junction and a depletion region is formed. A p-n junction acts like a diode and allows current only in one-direction. The energy gap between valence band and conduction band of a semiconductor is known as band gap or band width. Electrons in p-type and holes in n-type regions are minority carriers. Carrier lifetime is average time a carrier can spend in excited state after electron-hole generation before they recombine.

Current generation from light/photons in action: A stream of photons with tiny packets of energy shines on the cell. In strong sunlight, a 6-inch cell receives more than
$10^{19}$ photons per second. Not all the photons are productive, some photons reflect from top surface, front metal contacts and some even from the back contact. Rest of them enters the cell body. Electron-hole pair is created only if the incident photon has energy greater than band gap of the absorbing material. The remaining energy of each photon after absorption will be used as kinetic energy of the generated carriers. However, electrons in p-type and holes in n-type material (minority carriers) are meta-stable and can exist only for a time equal to average minority carrier life time before they recombine. If the carrier recombines then there is no light generated current. The minority carriers should reach p-n junction before they recombine where they are swept across the p-n junction. The most productive photons create electron-hole pairs close to the p-n junction, less productive ones create electron-hole pairs far from the junction. Also, minority carriers cannot cross the semiconductor-metal junction, so they must be collected by p-n junction.

Majority carriers play an important role in semiconductor diode. However, with solar cells it is light generated minority carriers that play a major role. Majority carriers experience a 'hill to climb' while minority carriers see 'a hill to roll down' at the p-n junction. Minority carriers are swept across the p-n junction by the electric field at the junction. A potential barrier at the p-n junction positively encourages the transfer of minority carriers (say a hole, when electron-hole pair is created in n-type semiconductor) while inhibits the transfer of majority carriers (electron). These minority carriers (holes) once cross the junction becomes majority carriers (in p-type), by diffusion they reach the semiconductor-metal junction (back contact). Electron (a majority carrier) that was
created in n-type dissipates its energy at the external load and recombines with a hole at
the back contact completing the circuit.

I-V curve and parameters of a solar cell: Superposition of IV curve of a solar
diode in the dark with the light generated current gives the IV curve of a solar cell [14].
The light shifts IV curve down to fourth quadrant, diode law equation in the first quadrant
becomes [15],

\[ I = I_L - I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \]  

Short-circuit current (I_{sc}) is the largest light generated current drawn from a solar
cell. Area of the solar cell, light intensity, spectrum of incident light, optical loses and
minority carrier life time are some of the factors that I_{sc} depend on [16]. Maximum
voltage available from a solar cell at zero current is open circuit voltage (V_{oc}), it
corresponds to the forward bias voltage of the solar cell junction with I_L [15] [16] [17].

\[ V_{oc} = \frac{nkt}{q} \ln \left( \frac{I_L}{I_0} + 1 \right) \]  

Fill factor is the measure of "squareness" of the IV curve [15], it is the ratio of
maximum power from the solar cell to the product of V_{oc} and I_{sc}. An empirical relation of
fill factor is given by equation (1.7) [18],

\[ FF = \frac{V_{oc} - \ln(V_{oc} + 0.72)}{V_{oc} + 1} \]  

FF is measured from IV curve and is given by eq. (1.8)

\[ FF = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}} \]  

Efficiency of solar cell is given by eq. (1.9) [16] [17] [18]

\[ \eta = \frac{V_{oc}I_{sc}FF}{P_{in}} \]
Why InGaN? Most solar cells are made from silicon. Cheap, amorphous silicon-based solar cells have efficiencies of less than 10 percent, and the efficiencies of even the most advanced single-crystal silicon cells are limited to about 21 percent [7].

1. Indium gallium nitride (InGaN) is a direct band gap semiconductor [19] [20]. Creation of electron-hole pair in an indirect band gap semiconductor like Silicon involves crystal lattice vibrations, wasting lot of the incoming photon energy. Whereas, direct bad gap semiconductors do not involve crystal lattice vibrations and creates charge carriers more efficiently.

2. Band gap of InGaN can be varied from 0.7eV to 3.4eV depending on the Indium/Gallium ratio [21]. This extraordinary range of band gaps in one type of material (alloy) makes it a special semiconductor which can absorb entire visible spectrum from near infrared to deep ultraviolet and every color in between.

3. Absorption coefficient of InGaN is $10^5$/cm which shows high strong light absorption for thin layers.

4. InGaN is n-type semiconductor [22]. Do not require any further doping.

5. It can be grown on a transparent substrate including sapphire, silicon carbide and glass.

6. “Two layers of indium gallium nitride, one tuned to a bandgap of 1.7 eV and the other to 1.1 eV, could attain a theoretical 50 percent maximum efficiency for a “two-layer” multi-junction cell.” [23] Indium gallium nitride solar cells could be made with more than two layers, perhaps a great many layers with only small
differences in their band gaps. Currently, no other material with these band gaps can be grown together.

7. Very high heat capacity and the value vary from 27 J/K mol to 40 J/K mol depending on the composition of Indium and Gallium at 300 K.

8. Group III nitrides are extremely resistant to radiation.

9. For all In/Ga compositions, InGaN retains its semiconductor properties, which is generally not the case with other materials. This tunable band gap allows one to vary the optical and electrical properties that are directly related to how photons are absorbed to generate carriers. If InGaN is doped successfully both p-type and n-type, theoretical efficiencies of ~30% for a single junction and >50% for a multi-junction cell can be made [24].

Current InGaN standings:

1. 20.284% efficient – Simulated value using Microelectronic and photonic structure analysis.

2. 4.5% efficiency has been recorded for p-InGaN/n-Si solar cells grown using MBE and Energetic Neutral Atom Beam Lithography Epitaxy [25].

1.1 References


CHAPTER 2: EXPERIMENTAL METHODS/DETAILS

2.1 Sputtering

2.1.1 Basic Theory

The impingement of energetic ions or atoms upon a solid surface produces a wide variety of effects. The effects of ion bombardment on a material differ substantially from those of electron and photon bombardment because the ion mass is of the same order as the mass of the atoms in the bombarded solid. Consider a head-on, binary, elastic collision between an impinging particle of mass \( m_1 \) and energy \( E_1 \) with a target particle of mass \( m_2 \) which is initially at rest. Conservation of energy and momentum require that the recoil energy of target particle for head-on case is [1],

\[
R = \frac{4 m_1 m_2}{(m_1 + m_2)^2} E_1
\]  

(2.1)

If the impinging particle is a 10-keV electron and the target is a Ni atom of mass 59 atomic mass units then the recoil energy is 0.37 eV which is enough to heat up the Ni atom but not enough to dislodge it from its lattice site. If \( m_1 = m_2 \), then all the energy is transferred to the target atom and gives ions the ability to move atoms around. Recoil energy of few tens of eV is enough to displace a surface atom into the bulk of the solid or dislodge a surface atom into the vapor phase. This dislodging a surface atom by ion bombardment is known as sputtering. Depending on ion beam energy and mass of the ion, when energetic ion strikes the target’s surface, several things can happen. For ion beam energy, less than 5 eV (adsorption or reflection), 5 - 10 eV (surface damage and migration), 10 - 3 keV (Sputtering) and energies greater than 10 keV (Ion implantation) [2]. Physical sputtering is driven by momentum exchange between the ions and atoms in
the target materials, due to collisions. At higher energies, recoil is minimal and incident ion sets off “collision cascades” in the target, when such cascade recoil and reach the target surface with energy greater than the surface binding energy, an atom would be ejected [3]. The energies required for sputtering are much higher than lattice bonding and vibration energies which are the causes of inelastic interactions, therefore sputtering collisions can be considered elastic. Ions will incident on target at different angle so the transferred energy has a cosine term in it [1],

\[ R = \frac{4 \cdot m_1 \cdot m_2}{(m_1 + m_2)^2} \cdot E_1 \cdot \cos^2 \theta \] (2.2)

For normal incidence, primary collision cannot eject an atom, however the secondary collision can. At oblique incidence, primary collisions can result in ejection. Sputter yield is the number of atoms sputtered per incident ion. This value depends on type of target atom, binding energy of target atoms, relative mass of ions and target atoms, incident ion energy and angle of incidence of ions. Sputtered atoms have relatively small energies, typically between 2-7 eV [2].

2.1.2 Sputtering as Physical Vapor Deposition (PVD)

Sputtering is a physical vapor deposition process used for depositing thin films onto a substrate, where particles are ejected from a solid material onto a substrate by bombarding energetic ions in a high vacuum environment. In sputtering, the target material and substrate are placed in a vacuum chamber. Electrically neutral atoms typically inert gas atoms like Argon are introduced into the vacuum chamber at very low pressures. A voltage is applied between the target and substrate which ionizes Argon atoms and create plasma, hot gas-like phase consisting of ions and electrons. Positively
charged Argon ions are accelerated to the target (cathode), these energetic ions bombard the target and ejects target atoms, which travel to the substrate through diffusion process and eventually settle.

Generating plasma: The process begins when a “free” electron near the cathode is accelerated towards the anode and inelastically collides with a neutral gas atom, Argon. These collisions can cause excitation and ionization of Argon atoms. Collisions that cause excitation results in glow discharge. Excited Argon atoms come back to ground state by releasing energy in the form of photon results in plasma glow. So, glow exists where there are lots of electrons to excite Argon atoms. Ionization creates a positively charged ion and an additional electron, these two electrons which can then collide with other neutral gas atoms and ionize them creating a cascade process until the gas breaks down. The breakdown voltage ($V_{bd}$) depends on the pressure in the chamber and the distance between the electrodes given by Paschen’s law [4],

$$V_{bd} \propto \frac{PL}{(b+10gP.L)}$$

(2.3)

Initially, the charge flow is small, as charges multiply there are enough ions and charges for the plasma to be self-sustaining. Condition for self-sustaining plasma [8],

$$L \cdot P > 0.5 \text{(cm. torr)}$$

(2.4)

where, ‘L’ is Electrode spacing and ‘P’ is Chamber pressure. Also, mean free path of an atom in gas ambient is [5],

$$\lambda = \frac{5 \times 10^{-3}}{P \text{(torr)}}$$

(2.5)

Therefore, at too low pressures, very large mean free path results in very few collisions and cannot sustain plasma. At too high pressures, there are so many collisions
that electrons do not have enough time to gather energy between collisions to ionize the atoms. Typical target-substrate spacing is approximately 10 cm. At atmospheric pressure, 760 Torr mean free path of electrons is extremely short, so we need vacuum chamber to generate plasma. Extremely strong electric field can create plasma in the form of arcing instead of steady state glow charge.

2.1.3 DC Sputtering

High DC voltage, 2-5kV is applied between electrodes in a gas environment which would result in ionization [6]. Avalanche breakdown is needed to form plasma. Per Kinetic theory [7], Thermal velocity,

\[ V = \sqrt{\frac{3kT}{m}} \]  

Therefore, velocity of Argon ions is approximately 400 m/sec and that of electrons is $10^4$ m/sec. At high voltages, velocity of Ar with energy 100 eV is 20000 m/sec and that of electron is 600000 m/sec. Plasma is conducting due to electrons and the voltage drop is minimal where electrons are rich. This shows that voltage drop exists at electrodes where electrons lost to the electrode. Therefore, plasma is always positively biased relative to any electrode. The positive bias might accelerate Ar ions to the anode but very small bias voltage (~10V) [8] at anode results in no sputtering of substrate. Total bias at cathode is positive bias and applied voltage leading to sputtering of cathode. Energy of incoming ion is in hundreds of eV, some of its energy goes to the sputtering, some goes to create secondary electron. Most of its energy goes to target heating which is a serious problem. So, high rate sputter processes need efficient cooling techniques to avoid target damage from overheating. Most of the sputtered atoms are neutral, less than
1% of them are ions. Energy of sputtered atom is usually less than 10 eV [8]. Electrons move too fast near cathode and cannot excite Ar atoms which results in no glow. This is called Cathode dark space or sheath.

![Diagram of DC sputtering process](image)

*Figure 2.1: Schematic of DC sputtering process [23].*

But, very close to the target, secondary electrons are created by Ar bombardment of target material, this result in glow called cathode glow region. Electrons are lost to anode and create a dark space called Anode sheath. DC sputtering is great for depositing metallic thin films but not for insulators and semiconductors. High resistivity of the insulator target would require an impossibly high voltage ($10^{12}$ V) for a small current to pass through it [6]. Insulating cathode will cause positive charge build up during Ar$^+$ bombarding, reduces the voltage between electrodes, lack of current will extinguish the plasma and stops the process. This limits DC sputtering to materials of less resistivity.
2.1.4 RF Sputtering

High voltage is applied to energize electron, polarity of applied voltage is switched at a high radio frequency (13.56 MHz) [24]. On the positive cycle, electrons are attracted to the cathode creating a negative bias and on the negative cycle ion bombardment continues. By avoiding a constant negative voltage on the cathode, ion build up is prevented for insulating targets. Electrons neutralize the positive charge buildup on both electrodes. At low frequency (< 100 KHz), both electrons and ions can follow the switching of the voltage (essentially DC plasma) and at high frequency (>1 MHz), heavy ions cannot follow the switching. High mobility of electrons enables them to be more energetic and this mobility disparity between them will make target bias itself more negatively than anode. Ions are accelerated by dark-space voltage (~100 V), however, there are two dark spaces and this should sputter both target and substrate at
different cycles. This can be avoided by making the target with smaller area than substrate [25].

\[
\frac{V_t}{V_s} \propto \left( \frac{A_s}{A_t} \right)^n \quad (2.7)
\]

\( n = 1,2 \). \( V_t \) and \( V_s \) are voltages across target and substrate sheath. \( A_t \) and \( A_s \) are areas of target and substrate. So, larger dark-space voltage develops at electrode with smaller area. RF plasmas tend to fill the chamber as opposed to DC plasmas which are confined to smaller regions. RF sputter systems basically a capacitor with gas as dielectric. Any type of film can be RF sputtered but deposition rates are slow.

*Figure 2.3: Lab built heater*

*Figure 2.4: RF plasma with thermocouple.*
2.1.5 Magnetron Sputtering

Normally once an electron is out it will move towards the anode under the influence of cathode-anode voltage, if we can confine the electrons near the cathode, high density of electrons will increase plasma density thereby increasing the efficiency of sputtering. Addition of a strong magnetic field near the target can cause the traveling electrons to spiral along magnetic flux lines near the target instead of being attracted toward the substrate because of the Lorenz forces.

Figure 2.5: Schematics of Magnetron vs non- magnetron sputtering processes [23]
Another advantage is that the plasma is confined to the region near target without causing any damage to the thin film being formed at substrate. Mean free path of electrons is high, electrons travel longer distance increasing the probability of further ionizing inert gas atoms. It also means that the plasma can be sustained at a lower pressure. This will result in stable plasma and increase the sputter efficiency.

Sputtered atoms are neutrally charged and so are unaffected by the magnetic trap. A series of magnets with alternating polarity are attached to the back side of the target in a circular fashion which create curved magnetic files lines that confine the secondary electrons to them.

Electrons will hope near the target. Radius of cycloid [26],

$$r \sim \frac{1}{B} \sqrt{\frac{2mV_d}{e}}$$  \hspace{1cm} (2.8)

$V_d \sim 100$ V and $B \sim 100$ G. Therefore, radius $r$ for electron is $\sim 0.3$ cm and for $\text{Ar}^+$ ion $r \sim 81$ cm.

Magnetic nature of the target material interferes with the magnetic field generated by sputtering gun, reducing the efficiency. Micro magnets magnetron sputtering design can solve this problem. They create magnetic circuitry in magnetron guns. Magnets with high Curie temperature ensures high operating temperatures [23].

Impedance Matching [27]: For steady state DC, there is no need for impedance matching as there are no oscillations but for RF, impedance matching is critically important. Output voltages and current capabilities of these generators are limited, so they need to work on a load. Most power generators available in the market are specified to transfer power into a 50 Ω load. Generated plasma can act as a rectifier that generates
an average negative voltage at the target. To build up a self-bias voltage, cathode must be capacitively blocked to avoid DC current.

*Figure 2.6: Single target RF sputtering machine in our lab.*

*Figure 2.7: Lab-built heater to deposit samples at higher temperatures (up to 200 °C).*
Figure 2.8: Upgraded RF sputtering machine. Three target system in our lab.

A dedicated blocking capacitor is added to allow RF operation. If the matching network is not properly “tuned”, the power will be reflected to the generator, portion of it will be delivered to the load (plasma chamber).

Combination of good “transmission line” with a proper “matching network” can provide the best transfer of power from generator to plasma.

Transmission line: Coaxial cable, adapters and connectors constitute the transmission line. For a transmission line with no adapters, length is chosen to be quarter wavelengths multiples.

\[ \lambda = \left( \frac{\text{wave speed}}{\text{frequency}} \right) \cdot \text{velocity factor} \]  

(2.9)

During RF, radio frequency is 13.56 MHz, velocity factor depends on cable (7/8” Flex well: 0.93, air :1, RG 218 it is 0.69) which gives lambda 67.5 ft., one quarter is 16.9 ft. Transmission lines of non-quarter wavelength can generate reflected power,
localized heating of RF cable, harmonics present on RF cable due to presence of frequencies other than 13.56 MHz.

Matching Network: The main purpose of matching network is to convert the impedance of the chamber so that, viewing from the transmission line the forward power sees an impedance of 50 Ω. For example, if the body of the periscope is made from flexible pipe and is assumed to rotate at the corners, then the angles of mirrors would also have to move accordingly to allow the viewer see from one end through the other. As with the flexible body of periscope, plasma chamber is very dynamic, so capacitors also dynamically adjust to allow for continuous “tuning” of generators to the load.

2.2 Hall Effect

Electrical properties of conductors and semiconductors can be measured using Hall effect method. The Hall effect occurs when a current carrying material is subjected to a magnetic field perpendicular to the direction of the current [9]. Carriers in the semiconductor (or conductor) experiences a Lorentz force \( F_B \) when magnetic field \( B_z \) is applied perpendicular to its surface. This force push the moving carriers (left-hand rule) to one side of the semiconductor (or conductor), a build-up of these charges generates an electric field \( F_E \) at the sides of the semiconductor and produces a measurable voltage called Hall-Voltage \( V_H \). At a steady state, induced electric force \( F_E \) balances the Lorentz force \( F_B \).
Hall voltage $V_H$ (when a current of $I$, $B_z$ is the magnetic field, $t$ is the thickness of sample, $n$ is the bulk density and $q$ is the elementary charge)

$$V_H = \frac{IB_z}{qnt} \quad (2.10)$$

Hall coefficient ($R_H$) measures the magnitude of Hall effect in the sample is given by,

$$R_H = \frac{E}{IB_z} \quad (2.11)$$

The sheet resistance ($R_S$) of the semiconductor can be conveniently determined by use of the van der Pauw resistivity measurement technique and since $R_s$ involves both mobility and density [11], Hall mobility can be found from the equation;

$$\mu = \frac{V_H}{R_sIB_z} \quad (2.12)$$

$$\rho = R_st \quad (2.13)$$
Figure 2.10: Ecopia HMS-3000 Hall Measurement System used for electrical properties.

Figure 2.11: Magnet set associated with HMS-3000, sample holder is placed in it.

Specifications:

1. Permanent magnets (diameter: 50mm)
2. Magnet Flux density (B), Standard field strength: 0.55 Tesla

3. Pole gap: 26 mm

4. Constant current supply system (320x300x105mm)

5. Current source: HMS-3000 (1 nA – 20 mA)

6. Input impedance: 2x10^7

7. Input voltage range: +/- 12V

2.3 UV-Visible Spectrophotometry

All Chemical compounds absorbs, transmits and reflects electromagnetic radiation over a wavelength range. Spectrophotometry is a quantitative measurement of the absorption, reflection or transmission properties of a material as a function of wavelength [12]. A spectrophotometer is an instrument that measures the number of photons (the intensity of light) absorbed after it passes through sample [13]. The system is a single beam instrument, which means, first run a scan on the reference sample to determine the intensity of the lamp at each wavelength, I₀ (λ) then run the scan with the actual sample to get the spectrum again I (λ). Absorbance is calculated from the ratio of these spectra.

\[ A(\lambda) = \log_{10} \frac{I_0(\lambda)}{I(\lambda)} \]  

(2.14)

The absorption coefficient (α) is related to Absorbance with the Beer-Lambert’s law, if the thickness of the sample is t, then

\[ A = \alpha t \]  

(2.15)

In diode-array spectrophotometer, a deuterium discharge lamp for the full UV and visible range, rather than a deuterium lamp for the UV and a tungsten incandescent lamp
for the visible is used [14]. Under optimum conditions, they can detect as many wavelengths simultaneously as their number of individual diodes, resolution elements or pixels [15]. UV-Vis absorption spectroscopy is one of the frequently used methods to characterize optical properties of thin films. Using optical absorption data, Tauc [16] proposed a method to determine bandgap. Bandgap can be found from the following equation,

\[(\alpha hv)^n = B (hv - E_g)\]  \hspace{1cm} (2.16)

Where, \(\alpha\) is absorption coefficient, \(h\) is Planck’s constant, \(v\) is photon’s frequency, \(E_g\) is the bandgap of the material and \(B\) is proportionality constant.

*Figure 2.12: The UV-Vis spectrophotometer used in our lab.*
In this study, optical properties are measured using Ultraviolet-Visible absorption spectroscopy. HP 8451A diode array spectrophotometer, shown in Figure 2.12 is used to collect absorption spectrum. The lamp in the spectrophotometer discharges full UV and visible range of 190 -820 nm. A reference sample is used to cancel the absorbance spectrum from the substrates, if any. Tauc plots are used to find the bandgap of samples from the acquired absorption spectrum.

2.4 X-Ray Diffraction (XRD)

Crystalline materials are characterized by the orderly periodic arrangements of atoms. The unit cell is the basic repeating unit that defines a crystal [17]. “When an x-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions we will have destructive interference, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However, the atoms in a crystal are arranged in a regular pattern, and in a very few directions we will have constructive interference. The waves will be in phase and there will be well defined x-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of many scattered rays mutually reinforcing one another [18]”

Why XRD? To Measure the average spacing between layers or rows of atoms, to determine the orientation of a single crystal or grain, to find the crystal structure of an unknown material, to measure the size, shape and internal stress of small crystalline regions, if any amorphous material is present in the mixture etc. Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable
to atomic spacing are incident upon a crystalline sample, are scattered in a specular fashion by the atoms in the system, and undergo constructive interference in accordance to Bragg’s law [19]. When X-rays incident on a surface of a substance, an X-ray which reflects from the surface has traveled less distance than an X-ray which reflects from a plane of atoms inside the crystal. The penetrating X-ray travels down, reflects, and travels back at the surface. Separation of the layers (d) and the angle at which the X-ray entered the material (θ) determines the distance traveled. For these two X-rays to be in phase, X-ray that penetrated the material needs to have traveled a whole number of wavelengths while inside the material [19] [20]. This condition is called Bragg’s condition represented by equation (2.17)

\[ 2d \sin \theta = n\lambda \]  

(2.17)

Inter atomic spacing is denoted by d, θ is the scattering angle, λ is the wavelength and n is an integer determined by the order given.

Figure 2.13: Bragg’s law for diffraction (public domain image)

XRD Instrumentation and pattern: A powder X-ray diffractometer consists of an X-ray source (usually an X-ray tube), a sample stage, a detector and a way to vary angle
θ. The X-ray is focused on the sample at some angle θ, while the detector opposite the source reads the intensity of the X-ray it receives at 2θ away from the source path. The incident angle is then increased over time while the detector angle always remains 2θ above the source path. An X-ray diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample. Xrd pattern is different for different phases. Amorphous materials do not produce any sharp peaks. Most diffraction data contain Kα₁ and Kα₂ peak doublets rather than just single peaks. The Kα₁ and Kα₂ peak doublets are further apart at higher angles of 2θ.

![Schematics of theta/2theta X-ray diffraction method](image)

*Figure 2.14: Schematics of theta/2theta X-ray diffraction method [21]*

Apparatus and software used: MiniFlex II Benchtop XRD system is used to characterize the samples. “Standard measurement” software associated with MiniFlex II Benchtop XRD system is used to obtain the spectrum and peaks. International Centre for Diffraction Data (ICDD) software to use and compare the database values.
Experimental Conditions: Tube output voltage of 30kV, Tube output current of 15mA, scanning speed of 5 deg/min is used. Start angle is 5 degrees and stop angle is varied from 80 to 120 degrees depending on the sample.

Figure 2.15: XRD apparatus used in our lab

2.5 Energy-Dispersive X-Ray Spectroscopy (EDX or EDS)

Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). The EDX technique detects x-rays emitted from the sample to characterize its elemental composition. A sample is bombarded by SEM’s high energetic electron beam, the incident beam bounces through the sample creating secondary electrons, it leaves vacancies in the electron shells where the secondary electrons used to be. To stabilize the
atoms, electrons from higher state will drop into the vacancies releasing energy in the form of X-rays. The X-rays emitted from the sample atoms are characteristic in energy and wavelength to not only the element of the parent atom but also the electronic states involved. The EDX detector measures the relative abundance of emitted x-rays and their energy. When an incident x-ray strikes the detector, it creates a charge pulse that is proportional to the energy of the x-ray. Charge pulses are converted to voltage pulses and sent to multichannel analyzer which sorts the pulses by voltage.

Figure 2.16: Schematic diagram of SEM. [22] [Open License]

This allows the SEM to perform elemental analysis in very selected areas and a spectrum can be created using a software. Hitachi S-2460 SEM model shown in Figure 2.17 is used to perform experiments in our lab. It is a 3-lens reduction type, 2-stage
electromagnetic deflection type with 0.1 and 0.2mm objective lens aperture size. It can
have a magnification range from 20 to 20,000x. At 25kV accelerating voltage and
working distance (WD) of 5mm, a 4nm resolution can be obtained using this model.
NORAN system SIX X-ray Microanalysis software has been used. It provides complete
microanalysis acquisition, analysis, reporting and file management. System SIX can
automatically identify and label peaks and quantify data during or after spectral
acquisitions.

Figure 2.17: Hitachi S-2460 SEM/EDX system used in our lab.

2.6 Solar Simulator

A device that provides illumination approximating natural sunlight to perform a
controllable indoor test under laboratory conditions is a solar simulator. AM1.5 is the
standard terrestrial spectra condition used [28]. “AM 1.5”, 1.5 atmospheric thickness
corresponds to a solar zenith angle of 48.2°.
\[ AM = \frac{1}{\cos \theta} \]  

(2.18)

where \( \theta \) is the zenith angle. AM0 (1353 W/m\(^2\)) refers to spectral irradiance just outside the earth’s atmosphere, AM1 (1000 W/m\(^2\)) is when sun is overhead, sea level and on horizontal surface, AM1.5G (963.8 W/m\(^2\)) is on 37° tilted surface facing south at 48.2° zenith angle [29].

**Figure 2.18:** Abet Technologies SunLite TM solar simulator (Model 11002)

Specifications:

1. AM1.5G Sun irradiance.
2. 50x50 mm field uniformity.
3. 100 W Xenon arc lamp.
Keithley 2460 SourceMeter with “kickstart” software is used to measure IV curves.

2.7 References


CHAPTER 3: PRELIMINARY RESULTS

3.1 Suitability of RF Sputtered Copper Oxide Thin Films for Solar Cells

Copper oxide has been studied as one of the alternative semiconductors for Silicon in fabricating solar cells. Bandgap values of Copper oxide are reported to be in the range of 1.5 eV – 2.1 eV [1] [2] [3]. It has been used as active layer in various solar cells. [2][4] We wanted to see if RF sputtered CuO thin films on glass substrates are suitable for Heterojunction solar cells.

Experimental details of CuO fabrication: Four batches of four samples in each batch, a total of 16 samples are fabricated and studied to analyze properties of RF sputtered Copper oxide thin films and their suitability in solar cell application. All electrical and optical values presented are average values. HMS-3000 hall effect measurement system is used to measure electrical properties. UV- Vis Spectrophotometer along with Tauc plots are used to measure optical bandgap and absorption coefficient values in the wavelength 190 – 820 nm.

Thin film deposition:

1. Method: Magnetron RF sputtering
2. Substrate: 18 x 18 mm Corning glass
3. Thickness: 100 – 450 nm
4. Growth rate: 0.1 Å/sec
5. Power: 80 W & 120 W
6. Pressure: 14 mTorr
7. Sputtering gases: Argon and Oxygen with equal partial pressure ratios
8. Growth temperature: Room temperature growth

Figure 3.1: A two-inch copper target used in RF sputtering to deposit copper oxide.

Metal contact deposition to CuO:

1. Method: DC sputtering
2. Metal contacts: Aluminum (Al)
3. Thickness: 100 nm
4. Growth rate: 0.3 Å/sec
5. Current: 20 mA
6. Sputtering gas: Argon
7. Growth temperature: Room T
8. Growth Pressure: 10 mTorr (Average value)
Figure 3.2: A four-inch Al target used in DC sputtering to deposit metal contacts.

Figure 3.3: CuO thin films on glass substrate with Al metal contacts at the corners.
Table 3.1

*Electrical properties of copper oxide*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Copper oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk concentration (/cm$^3$)</td>
<td>$9.72 \times 10^{22}$</td>
</tr>
<tr>
<td>Sheet concentration (/cm$^2$)</td>
<td>$9.72 \times 10^{17}$</td>
</tr>
<tr>
<td>Mobility (cm$^2$/V.s)</td>
<td>$1.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>Conductivity (/Ω. Cm)</td>
<td>24.9</td>
</tr>
<tr>
<td>Resistivity (Ω.cm)</td>
<td>$4.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>Hall coefficient (cm$^3$/C)</td>
<td>$+ 6.42 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

*Figure 3.4: Absorption coefficient values of copper oxide films.*
Figure 3.5: Bandgap calculation: Tauc plots for CuO thin films of different thickness.

From Figure 3.5, Copper oxide films grown are direct bandgap semiconductors, average bandgap values of 1.54, 1.85 and 1.9 eV are measured, which are in good agreement with values reported by Chauhan [1]. Increase in thickness of the film decreases the bandgap value [5] [6]. High Absorption coefficient of $10^5$/cm (Figure 3.4) makes it a good absorbing layer in solar cell.

From Table 3.1, a positive Hall coefficient proves CuO is a p-type semiconductor. 0.0016 cm$^2$/V.s of mobility and 24.9 /Ω.cm of conductivity values are extremely low. In Solar cell applications, extremely low mobility and conductivity values make light
generated carriers to recombine quickly before they reach p-n junction. RF sputtered Copper oxide thin films grown in this study are optically good quality but electrically very poor. In conclusion, these films are not suitable to use as active layers in solar cell fabrication.

3.2 Suitability of RF Sputtered Beryllium Zinc Oxide (BeZnO) Thin Films for Solar Cells


Experiment: Thin films of BeZnO (25–500 nm) thick were grown onto crystalline Si (100) and glass substrates at temperature $T < 52 \, ^\circ\text{C}$ by reactive radio frequency (RF) magnetron sputtering of a metallic Zn target (99.999% purity) and a metallic Be (99.999% purity) as a dopant in an Ar (99.999% purity)/O₂ atmosphere. To maintain the homogeneity and stoichiometry of the films, the system is evacuated to a base pressure in the range $4–6 \times 10^{-7} \, \text{Torr}$ while the deposition pressure during the film growth was kept at $8 \times 10^{-3} \, \text{Torr}$. The RF sputtering power throughout the growth was maintained at 140 W with average reflected power 4–11 W. The content of Be in the films varied by changing the number of the Be pieces on the Zn target keeping the sputtering conditions fixed. The electrical properties of a-ZnO/glass and a-BeₓZnᵧO/glass thin films were determined by Van der Pauw Hall (VDPH) measurements, where the Hall voltage can be measured to determine the exact carrier conductivity type [7]. The results of the VDPH measurements are given in Table 3.2.
Figure 3.6: A two-inch Zn target with four Be pieces used in RF sputtering method

Four samples are measured in our experiment, where sample #1 is an undoped amorphous ZnO thin film and the rest of samples are Be doped ZnO thin films with a varied Be concentration. From the experimental results listed in Table 3.2, the resistivity increases with increasing Be concentration. Therefore, the a-BeₓZn₁₋ₓO films show an insulating nature with a resistivity of 7.05 × 10⁴ Ω cm for sample #4 while the resistivity of a-ZnO film (without doping) exhibits the lowest value of 0.35 Ω cm. Additionally, the electron concentration decreases as the Be concentration increases to reach a minimum value of 2.77 × 10¹² cm⁻³ for sample #4. Furthermore, the contribution of Be dopants is to reduce the electron mobility of a-ZnO films (46.43 cm²/Vs).
Table 3.2

*Electrical properties of BeZnO films with different Be concentrations*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample #1</th>
<th>Sample #2</th>
<th>Sample #3</th>
<th>Sample #4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Be</td>
<td>1 Be piece</td>
<td>2 Be pieces</td>
<td>4 Be pieces</td>
</tr>
<tr>
<td>Bulk conc. (/cm$^3$)</td>
<td>-3.847x10$^{17}$</td>
<td>-9.33x10$^{15}$</td>
<td>2.99x10$^{15}$</td>
<td>2.77x10$^{12}$</td>
</tr>
<tr>
<td>Sheet conc. (/cm$^2$)</td>
<td>-3.847x10$^{12}$</td>
<td>-9.33x10$^{10}$</td>
<td>2.99x10$^{9}$</td>
<td>2.77x10$^{7}$</td>
</tr>
<tr>
<td>Mobility (cm$^2$/V. s)</td>
<td>46.43</td>
<td>36.55</td>
<td>11.30</td>
<td>31.9</td>
</tr>
<tr>
<td>Condu. (/Ω.cm)</td>
<td>2.86</td>
<td>0.054</td>
<td>5.4x10$^{-3}$</td>
<td>1.42x10$^{-5}$</td>
</tr>
<tr>
<td>Resistivity (Ω.cm)</td>
<td>0.35</td>
<td>18.30</td>
<td>185.20</td>
<td>7.05x10$^{4}$</td>
</tr>
<tr>
<td>Hall coefficient A-C</td>
<td>-5.17x10$^{1}$</td>
<td>-6.30x10$^{2}$</td>
<td>-4.09x10$^{3}$</td>
<td>2.21x10$^{6}$</td>
</tr>
<tr>
<td>Hall coefficient B-D</td>
<td>-1.931x10$^{1}$</td>
<td>-7.08x10$^{2}$</td>
<td>8.27x10$^{3}$</td>
<td>2.29x10$^{6}$</td>
</tr>
</tbody>
</table>

However, to the best of our knowledge, there are currently no systematic reports on the electrical properties of amorphous ZnO and BeZnO thin films. In addition, the effect of the Be doping on the electrical characteristics of amorphous ZnO has not been investigated much [7][8]. Hence, it is worth discussing and comparing the electrical characteristics measured in this work within the context of other available literature on the subject, to accurately model, design, and analyze the films to be used in optoelectronic devices. The electrical properties such as carrier density, mobility, and resistivity of crystalline ZnO film were determined to be $4.66 \times 10^{17}$ cm$^{-3}$, 41 cmV$^{-1}$/s and 0.326 cm Ω, respectively by D. Ye et al. [8].

From Table 3.2, Undoped ZnO is n-type semiconductor with decent electrical characteristics. As the Be doping increases the films loose n-type conductivity and turn
into p-type semiconductors. BeZnO doped with four Be pieces is a p-type semiconductor but it has extremely high resistivity and low conductivity values. Moreover, the carrier concentration is very low. In Conclusion, RF sputtered BeZnO thin films are not suitable for solar cell application as p-type semiconductors.

3.3 Successfull Fabrication of Test Solar Cells: Si/InGaN Heterojunction

Results from sections 3.1 and 3.1 confirms RF sputtered Copper oxide and BeZnO are not suitbale p-type semiconductors to fabricate solar cells. In this section, first, we present fabrication of RF sputtered Indium Gallium Nitride (InGaN) thin films and their suitability for solar cells. Next, this section also discuss the method and results of successful fabrication of single junction solar cells. Silicon/InGaN heterojunction solar cells are fabricated.

Experimental details of InGaN thin film growth (Testing stage):

1. Method: Magnetron RF sputtering

2. Substrate: 18 x 18 mm Corning glass

3. Thickness: 220 nm

4. Growth rate: 0.2 Å/sec

5. Power: 100 W

6. Pressure: 12 mTorr


8. Growth temperature: Room temperature growth
Figure 3.7: A two-inch In/Ga target used to deposit InGaN films during testing stage.

Metal contact deposition to InGaN:

1. Method: DC sputtering
2. Metal contacts: Aluminum (Al)
3. Thickness: 100 nm
4. Growth rate: 0.3 Å/sec
5. Current: 20 mA
6. Sputtering gas: Argon
7. Growth temperature: Room T
8. Growth Pressure: 10 mTorr (Average value)
Figure 3.8: DC sputtering; Depositing Al metal contacts on the corners of InGaN films.

Table 3.3

*Electrical properties of InGaN thin films*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>InGaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk concentration (/cm³)</td>
<td>-7.36 x 10^{20}</td>
</tr>
<tr>
<td>Sheet concentration (/cm²)</td>
<td>-7.36 x 10^{15}</td>
</tr>
<tr>
<td>Mobility (cm²/V.s)</td>
<td>0.612</td>
</tr>
<tr>
<td>Conductivity (/Ω. Cm)</td>
<td>72.2</td>
</tr>
<tr>
<td>Resistivity (Ω.cm)</td>
<td>1.38 x 10^{-2}</td>
</tr>
<tr>
<td>Hall coefficient (cm³/C)</td>
<td>-8.47x 10^{-3}</td>
</tr>
<tr>
<td>Semiconductor type</td>
<td>N-type</td>
</tr>
</tbody>
</table>
HMS-3000 hall effect measurement system is used to measure electrical properties. UV-Vis Spectrophotometer along with Tauc plots are used to measure optical bandgap and absorption coefficient values in the wavelength 190 – 820 nm.

![Graph showing bandgap value of InGaN (test film).](image)

*Figure 3.9: Bandgap value of InGaN (test film).*

InGaN test films grown by RF sputtering are n-type semiconductors with good carrier concentration values. Conductivity of InGaN test films is three times higher than conductivity of Copper Oxide films. Mobility is 600 times higher Bandgap value is found to be approximately 2.2 eV.

Atomic composition of In to Ga is found to be 74:26 (see EDX analysis). These values of test films suggest RF sputtered InGaN films are suitable for solar cell application but quality of films need to be improved. InGaN films of varying Indium and
Gallium composition are fabricated by changing the growth conditions. Si/InGaN heterojunction solar cells (Test solar cells): After successful fabrication of test films and improving the quality of films thereafter, these methods are used to deposit InGaN films in fabricating first basic solar cell.

Individual layers: outline.

1. P-type: Polycrystalline Commercial Silicon
2. N-type: Indium Gallium Nitride (InGaN)
3. Front Contact: Indium Tin Oxide (ITO)
4. Back contact: Aluminum

Deciding on metal contacts: A solar cell requires two metal contacts. Two metal-semiconductor junctions need to be formed. A front metal contact and back metal contact to receive the light generated carriers and pass it on to the external load.

Choosing a proper metal contact depend on the work function \( (\varphi) \) of metal and electron affinity \( (\chi) \) of semiconductor. Work function of Aluminum is \( 4.28 \text{ eV} \) and electron affinity of Silicon is \( 4.01 \text{ eV} \) [9] [10].

Aluminum is also p-type dopant to Silicon; any annealing would aid conduction through tunneling. Amick et. Al [11], Mandelkorn et. Al [12] and Eguren et. Al [13] reported successful use of Aluminum contacts to p-type silicon using sputtering method.

To allow maximum sunlight possible into the solar cell, Indium Tin Oxide (ITO), a transparent conductive oxide is used as front contact. Experimental steps of fabrication are given below.
Step 1: Depositing Aluminum metal back contacts: Aluminum metal contacts are deposited on commercial 165 µm thick p-type Si (111) using DC sputtering method. Thickness of contact is about 30 nm. Growth pressure is 10 mTorr with Ar as sputtering gas. Growth rate is about 0.3 Å/sec.

Step 2: Vacuum heating: Silicon surface is contaminated with oxide layer due to atmospheric exposure. Si sample with Al back contact is annealed at 450 °C for about 15 minutes under vacuum. This makes the Al metal penetrate the oxide layer to contact silicon and make better electrical contact. This also aid conduction through tunneling.

Step 3: Depositing InGaN and ITO: The sample is next transferred to RF sputtering machine to deposit InGaN thin film. Similar experimental details described in the beginning of this section for InGaN growth is followed here. Thickness of sample is 250 nm. Sputtering machine was upgraded to a two-target system. Once the desired thickness is reached, ITO is deposited on top of InGaN, a 300-nm thick ITO layer is deposited. Ar (10 mTorr) and Oxygen (2 mTorr) are used during ITO deposition. During the transfer from DC to RF, an extra substrate is placed along with the ‘Al coated Si’ sample to study the deposited InGaN layer exclusively.

Step 4: Cutting the edges: Edges of the cell is also coated with ITO during deposition. Therefore, edges need to be cut carefully to remove the shorting.
Table 3.4

Comparing RF sputtered InGaN with commercial p-silicon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Commercial silicon</th>
<th>InGaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk concentration (/cm³)</td>
<td>$2.74 \times 10^{19}$</td>
<td>$-2.45 \times 10^{21}$</td>
</tr>
<tr>
<td>Sheet concentration (/cm²)</td>
<td>$2.74 \times 10^{14}$</td>
<td>$-2.45 \times 10^{16}$</td>
</tr>
<tr>
<td>Mobility (cm²/V.s)</td>
<td>$2.99 \times 10^{2}$</td>
<td>$2.462 \times 10^{0}$</td>
</tr>
<tr>
<td>Conductivity (/Ω.cm)</td>
<td>$1.31 \times 10^{3}$</td>
<td>$9.663 \times 10^{2}$</td>
</tr>
<tr>
<td>Resistivity (Ω.cm)</td>
<td>$7.64 \times 10^{-4}$</td>
<td>$1.035 \times 10^{-3}$</td>
</tr>
<tr>
<td>Average Hall-coefficient</td>
<td>$2.21 \times 10^{-1}$</td>
<td>$-2.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>Semiconductor type</td>
<td>P-type</td>
<td>N-type</td>
</tr>
</tbody>
</table>

Figure 3.10: Bandgap of ITO measured using UV-vis spectrophotometer.
Bandgap of ITO films (Figure 3.10) deposited by RF sputtering method is found to be close to 3.7 eV which shows that the deposited film is transparent to visible spectrum. Activation spectrum (Figure 3.11) obtained from monochromator analysis of solar cell show peaks around 2.16 eV and 1.6 eV which shows the photovoltage is from InGaN and Si, not from the ITO.

IV curves and efficiency measurement: Current and voltage values from light generated carriers are measured both in laboratory conditions and under the sun. A lab built IV measurement system shown in Figure 3.12 is used in the laboratory under a 300 W bulb that has a spectrum in the 400 – 870 nm wavelength range. Cells are placed approximately 10 cm from the bulb. Open-circuit voltage measurements under sun were taken from December 13, 2013 to December 17, 2013 every day around 2:30 pm at the same spot outside Clippinger laboratories in Athens, OH.
A maximum open-circuit voltage of 148 mV for batch 1 and 240 mV for batch 2 are measured both under sun and laboratory conditions (with in experimental error). A short-circuit current of 13.8 µA and 16.6 µA for batch 1 and batch 2 samples are measured respectively.

Input Power: A 300 W bulb at 10 cm has the power density of 0.238 W/cm². Batch 1 solar cell under investigation has an area of 0.6 cm². This cell receives an input power of 0.140 W. Batch 2 sample has a surface area of 1.5 cm² which will receive an input power of 0.357 W.
Figure 3.13: IV curve and PV curve of Si/InGaN test solar cell. Batch 1.

Figure 3.14: IV and PV curve for Si/InGaN test solar cell. Batch 2
Table 3.5

*Efficiency and FF values of Si/InGaN test solar cells*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Batch 1</th>
<th>Batch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>((V_{oc}, I_{sc}))</td>
<td>(148, 13.6) (mV, µA)</td>
<td>(240, 16.4) (mV, µA)</td>
</tr>
<tr>
<td>((V_{max}, I_{max}))</td>
<td>(81, 6) (mV, µA)</td>
<td>(133, 9.2) (mV, µA)</td>
</tr>
<tr>
<td>(P_{in} \ (W))</td>
<td>0.140</td>
<td>0.357</td>
</tr>
<tr>
<td>Fill Factor (FF)</td>
<td>0.241</td>
<td>0.306</td>
</tr>
<tr>
<td>Efficiency ((\eta))</td>
<td>0.0004</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

Discussion of results: From Figures 3.13 and 3.14, IV curves are far from Ideal IV curves. The “knee” in the IV curves are either missing or extremely insignificant. Early bending or deviation of curves from the “knee” of Ideal curve shows the presence of parasitic resistances (shunt and series). Downward shift of “knee” indicates low shunt resistance and leftward shift of “knee” indicates high series resistance.

1. Our graphs indicate the presence of both low shunt resistance and high series resistance in the cells. Low shunt resistance is due to manufacturing defects and create an alternate path for light generated current and reduces the voltage from the solar cell. InGaN films fabricated for test cells are amorphous in nature and contain defects.

2. High series resistance is due to the poor movement of light generated carriers through the p-n junction, metal-semiconductor junctions. I believe vacuum heating technique in step 2 of fabrication process has not given positive results and presence of oxide layer must be insulating the carrier flow from p-type
semiconductor to Aluminum back contact. Also, p-n junction created between Si and InGaN films might not be swift enough for the minority carriers to cross the junction.

These problems can be addressed by

1. Increasing the quality of InGaN films during sputtering process. Change in growth conditions changes the quality of thin films.

2. Following proper cleaning techniques of silicon wafer. RCA etch or Solvent clean methods can be used.

3. Adding intrinsic layer (buffer layer) converts p-n junction into p-i-n junction with larger junction width.

3.4 InGaN Thin Films Grown by RF Sputtering for HIT Solar Cells


Introduction: Indium gallium nitride (InGaN), a group III-V compound semiconductor material has received a great deal of attention in the recent years. The direct band gap of $\text{In}_x\text{Ga}_{(1-x)}\text{N}$ can be varied from 0.7eV($x=1$) to 3.4eV ($x=0$) depending on the Indium/Gallium ratio [14]. Materials with this wide range of band gap, if used properly, can absorb the entire visible solar spectrum from near infrared to deep ultraviolet and every color in between. Large difference in inter atomic spacing between InN and GaN, difference in enthalpy formations and high vapor pressure of InN compared to that of GaN are some of the problems that affect the quality of InGaN films.
[15]. However, these problems can be minimized by changing the parameters of growth conditions such as growth temperature, gas flow ratio, growth rate and growth pressure. Growth conditions can significantly affect the optical, electrical and structural properties of InGaN films [15] [16].

A slight change in the growth parameters can affect the quality and properties of InGaN thin films in a large way. So, it is important to understand the growth kinetics which eventually may develop the fabrication techniques for higher quality InGaN thin films. This work concentrates on growing InGaN thin films using RF magnetron sputtering method by changing the growth conditions such as growth temperature and nitrogen flow ratio to understand the change in optical (band gap), electrical and structural properties of these thin films.

Experiment: InGaN thin films were grown on high temperature aluminosilicate glass and silicon (111) substrates by RF magnetron sputtering method. Argon(Ar) and Nitrogen (N$_2$) are used as Inert and reactive gases respectively in the sputtering process. A constant RF plasma power of 100W and a total pressure of 12 mTorr or 1.599 Pa is maintained for all samples grown irrespective of growth temperature.

Parameters we changed for the current study are substrate temperature and nitrogen gas flow ratio. Samples are made at 35 °C, 150 °C and 200 °C substrate temperatures. N$_2$ concentration in (N$_2$+Ar) was varied from 0.25 to 1.0 for low temperature samples and 0.3 to 0.8 for high temperature samples. A two-inch diameter 50-50 (by atomic percent) "home-built" In/Ga material is used as target. Thickness of all samples tried to kept at approximately 100 nm. Aluminum metal contacts are deposited at
the four corners of thin films using DC sputtering method. Thickness of the metal
contacts varied from ~40nm to ~80nm. Hall-effect measurements were performed to
assess the electrical properties of the samples using HMS-3000 hall-effect measurement
system, optical measurements (bandgap) were carried out using UV spectrophotometer
and Tauc plots, Energy-dispersive X-ray spectroscopy(EDX) was performed to do the
composition analysis and X-ray diffraction (XRD) measurements to check the change in
amorphous nature.

Data: A total of 24 samples were fabricated at low temperatures and six samples
were fabricated at high temperatures. All the values in the tables and graphs are average
values with error analysis.

Optical properties: InGaN is a direct band gap semiconductor [14]. Band gap
measurements were performed using UV spectrophotometer. It collects absorbance(α)
values of the samples for each wavelength of light passes through it. Band gap of the
sample can be found from Tauc plot which is drawn between Energy(E) of the light and
(αE)². Table 3.6 and Figure 3.15 shows the values of band gaps with change in N2
concentration.
Figure 3.15: N2 concentration Vs Band gap at 200 °C(left) and 35 °C (right)

Table 3.6

<table>
<thead>
<tr>
<th>N2 concentration in (Ar+N2)</th>
<th>Bandgap (eV) (35 °C)</th>
<th>Bandgap (eV) (200 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>1.05</td>
<td>--</td>
</tr>
<tr>
<td>0.34</td>
<td>1.2</td>
<td>1.07</td>
</tr>
<tr>
<td>0.5</td>
<td>1.6</td>
<td>--</td>
</tr>
<tr>
<td>0.67</td>
<td>1.85</td>
<td>2.0</td>
</tr>
<tr>
<td>0.8</td>
<td>2.0</td>
<td>2.4</td>
</tr>
<tr>
<td>1.0</td>
<td>2.1</td>
<td>--</td>
</tr>
</tbody>
</table>
It can be observed from the Figures 3.15, 3.16 and the Table 3.6 that increase in the \( \text{N}_2 \) concentration increases the band gap of the InGaN thin films. The errors are within the limit. To confirm the band gap values, we did composition analysis using EDX method. Table 3.7 shows the change in atomic percentages of Indium and Gallium with \( \text{N}_2 \) gas flow ratio. Figure 3.17 is one of the images to show the EDX compositions of Indium and Gallium.
Table 3.7

Percentages of In and Ga with N₂ ratio

<table>
<thead>
<tr>
<th>N₂ %</th>
<th>0.34</th>
<th>0.67</th>
<th>0.84</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium %</td>
<td>24.0</td>
<td>20.11</td>
<td>14.0</td>
</tr>
<tr>
<td>Gallium %</td>
<td>15.2</td>
<td>20.63</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Figure 3.17: EDX analysis of InGaN sample.

From Table 3.7 and Figure 3.17, it is evident that Indium composition decreases with increase in N₂ concentration in (Ar + N₂) gas mixture. Both EDX analysis and spectrophotometer values strongly agree with each other. Hall-effect measurements were performed to understand the electrical properties. We measured mobility, resistivity, conductivity, carrier concentration values of all samples. These values play a significant role in improving the short circuit current value of the photovoltaic materials and so it is
important to understand and improve them. Resistivity is measured in Ohm.m units and mobility is measured in Cm²/V.s.

Figure 3.18: Temperature dependence of resistivity & mobility values.

From Figure 3.18 & 3.19, we can observe that as the resistivity decreases, conductivity increases, mobility increases with increase in temperature. This is a good sign as a good quality thin film should always have low resistivity, high carrier mobility and conductivity values. The average hall coefficient values of all the samples remain negative which shows n-type nature.
Figure 3.19: Temperature dependence of conductivity (mho/m) and carrier concentration.

Table 3.8

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average Hall co-efficient (m³/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>-1.99 E-3</td>
</tr>
<tr>
<td>150</td>
<td>-1.39 E-2</td>
</tr>
<tr>
<td>200</td>
<td>-3.15 E-3</td>
</tr>
</tbody>
</table>

XRD measurements: Samples deposited on silicon substrates are used for XRD and EDX analysis. From Figure 3.20, we can observe that at low temperature InGaN thin film does not show any peaks which means it is amorphous. At 150 °C, we can observe
high intensity peaks at \( \sim 31^\circ \) angle and as the temperature increased intensity of the peak increased at the same angle. This shows that samples grown at high temperature show polycrystalline and crystalline nature [16]. This also support the improvements in electrical properties.

![XRD measurements](image)

Figure 3.20: XRD measurements of samples deposited at different temperatures.

Results: All samples are n-type semiconductors. As growth temperature increased from 35 \(^\circ\)C to 200 \(^\circ\)C, resistivity of thin films decreased by 1200 times, conductivity increased by 2000 times, mobility increased by 5 times. This can be attributed to the fact that crystalline nature of the samples was increased and reduced defects. When a 50-50
In/Ga target was used, band gap of InGaN thin films increased with increase in N\textsubscript{2} flow ratio in (Ar+N\textsubscript{2}) mixture, this is because of increase in the Gallium atomic percentage in InGaN. Increase in Ar flow ratio increases Indium atomic percentage.

3.5 References


CHAPTER 4: RESULTS - ELECTRICAL PROPERTIES OF INGAN THIN FILMS.


4.1 Introduction

Among the ternary compounds of III-nitride semiconductors, InGaN has received a great deal of attention in the recent years. Its uniqueness becomes apparent when you vary the Indium (In) to Gallium (Ga) atomic ratio in the compound material. For all In/Ga compositions, InGaN retains its semiconductor properties, which is generally not the case with any other material. [2] This tunable property allows one vary the optical and electrical properties that are useful in fabrication of photovoltaics and light emitters. Growth conditions can significantly affect the properties of thin films and slight change in growth parameters can affect the quality and properties in a large way. [1] So, it is important to understand the growth kinetics which eventually may develop the fabrication techniques for higher quality InGaN thin films.[3] Bond length of InN is 2.15Å and that of GaN is 1.94 Å [24], this difference in interatomic spacing between InN and GaN results in solid phase miscibility gap and the relatively high vapor pressure of InN (~10^4 atm at 850 °C) [26] compared to the vapor pressure of GaN (~1 atm at 850 °C) [26] leads to low indium incorporation in the InGaN alloy.[1][4] The difference in formation enthalpies for InN (-19.3 kJ/mol ) [19] and GaN (-157.7 kJ/mol) [25] causes a
strong indium surface segregation on the growth front. [1][5] These problems, however, can be minimized by optimizing the growth parameters.

Per E.L Piner, [6] as the growth temperature is reduced from 850 °C to 500 °C, desorption of the indium from the surface is substantially reduced. Indium droplets, phase separation and composition inhomogeneity are observed in the InGaN thin films with a high indium composition, and these leads to lower quality material which could be attributed to the low surface mobility of adatoms. [9] [10] Large V/III ratios were found to be able to suppress the indium segregation during growth of InGaN. [7][8] During MBE and MOCVD growth of InGaN, when the substrate temperature is increased, indium incorporation decreases [11] [12], however, when the temperature and N₂ flux are maintained constant, indium incorporation is found to be increased at low metal flux. When both In and Ga fluxes are increased, the additional Ga atoms will compete to go into the bulk, most of the additional Ga atoms will go into the bulk and displace the indium atoms, eventually indium incorporation decreases. [1] [11]

This study investigates the growth by RF sputtering. Electrical properties of InGaN thin films are investigated relatively less compared to their optical and structural properties, especially which are grown by RF sputtering method. High resistivities in the range of 10⁹ - 10¹¹ Ohm.cm were measured grown below 620 °C and their resistivities dropped drastically to the range of 10⁻² - 10⁻¹ Ohm.cm for growth temperatures above 620 °C [4]. During plasma-enhanced MBE process, at lower temperatures, samples grown at 400 °C showed strong increase in carrier concentration with increasing InN composition, whereas for the unheated substrates this value appeared to be insensitive. [13] Mobility
increased as growth temperature increased. Resistivity of the samples decreased with In content while mobility and carrier density were found to be increased with In content. [14]

In this study, Van der Pauw technique and Hall Effect were used to measure the electrical properties of the thin films. Hall coefficient is a parameter that measures the magnitude of Hall Effect in the sample. Hall coefficient;

\[ R_H = \frac{E}{jB} \]  

(4.1)

Where, E, J and B are magnitudes of Electric field, current density and magnetic field respectively. Hall voltage is the potential difference across the semiconductor that is produced by the Hall field. This is the voltage exactly enough to compensate for the deflection of charge carriers by the magnetic field, so that the net current perpendicular to applied voltage is zero. [15] Hall voltage;

\[ V_H = \frac{jB}{qnd} \]  

(4.2)

I is the current, d is the thickness of the sample, q is elementary charge and n is the charge density. Hall mobility;

\[ \mu = \frac{V_H}{IBRS} \]  

(4.3)

Rs is the sheet resistance. Resistivity;

\[ \rho = \frac{1}{qn\mu} \]  

(4.4)

4.2 Experiment

InGaN thin films were grown on high temperature aluminosilicate glass and Silicon (111) substrates by RF magnetron sputtering method. Argon (Ar) and Nitrogen
(N\textsubscript{2}) are used as Inert and reactive gases respectively in the sputtering process. A constant RF plasma power of 100W and a constant total pressure of 12 mTorr or 1.599 Pa is maintained for all samples grown irrespective of growth temperature. Parameters changed in this study are growth temperature and partial pressures of N\textsubscript{2} and Ar. Samples are made at 35 °C, 150 °C, 250 °C, 300 °C 350 °C, 400 °C and 450 °C temperatures. Ratio of Ar partial pressure to total pressure, x, in (N\textsubscript{2}+Ar) gas mixture is increased from 0 to 0.75 while varying the N\textsubscript{2} partial pressure ratio by (1-x) to keep the total pressure constant.

A two-inch diameter 50-50 (by atomic percent) "home-built" In/Ga material is used as target. Thickness of all samples are approximately 100 nm and deposited on 18mm x 18mm substrates. The growth of InGaN thin films on the substrates is by On-axis RF magnetron sputtering method. Substrates are placed centered vertically above target at 10 cm. Deposition rates of these thin films can be found in Table 4.1. The thicknesses of the deposited InGaN films have been kept approximately same for all the films within the error. Changing the growth conditions changed the deposition rate but we maintained the thickness of all samples to be the same by varying the deposition time. Aluminum metal contacts are deposited at the four corners of thin films using DC sputtering method. Total area of the four metal contacts at the corners of each sample kept less than 1/8 th of the total area of the sample. A lab built heater is used to grow the samples at higher temperatures. Four samples are fabricated at every growth temperature and every partial pressure ratio. All the values in the tables and graphs are average values with error analysis. In this study, electrical properties of the films are measured using Van
der Pauw Ecopia HMS-3000 measurement system. Aluminum metal contacts are tested for Ohmic contact quality using I-V curves. A standard magnetic flux density of 0.55 Tesla is used during the Hall measurements. Samples are fabricated at different growth temperatures but all electrical measurements are performed at room temperature.

Table 4.1

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Room T</td>
<td>1.6</td>
<td>3.0</td>
<td>5.5</td>
<td>6.1</td>
</tr>
<tr>
<td>250 °C</td>
<td>0.9</td>
<td>1.2</td>
<td>2.71</td>
<td>3.3</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.7</td>
<td>0.68</td>
<td>1.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

4.3 Results and Discussion

Hall- coefficient: This value determines the magnitude of Hall Effect in the samples. It has units of Ω.m/Tesla, contrast to resistivity which has units of Ω.m. Semiconductor’s conductivity type can be determined using hall coefficient value. Semiconductors of p-type have positive hall coefficient and n-type semiconductors have negative hall coefficient.

From Table 4.2, it is evident that Hall coefficient values of all samples are negative. It shows that all RF sputtered InGaN thin films are n-type semiconductors irrespective of substrate growth temperature and partial pressure ratio. This n-type conductivity of InGaN thin films can be attributed to the existence of triplet of donor sites appear because of nitrogen vacancy, donor depth and band gap. [16] Unlike in AlN, anti-
site compensation is not significant in InN and GaN due to the large atomic size differences between metal and nitrogen. [16]

Table 4.2

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Room T</td>
<td>-2.00x10⁻³</td>
<td>-3.25x10⁻³</td>
<td>-6.87x10⁻⁴</td>
<td>2.01x10⁻³</td>
</tr>
<tr>
<td>150 °C</td>
<td>-1.67x10⁻³</td>
<td>-1.96x10⁻³</td>
<td>-2.81x10⁻⁴</td>
<td>N/A*</td>
</tr>
<tr>
<td>250 °C</td>
<td>-1.63 x10⁻³</td>
<td>-6.10x10⁻⁴</td>
<td>-5.27x10⁻⁴</td>
<td>-4.95x10⁻²</td>
</tr>
<tr>
<td>300 °C</td>
<td>-2.03 x10⁻³</td>
<td>-8.80x10⁻⁴</td>
<td>-5.71x10⁻⁴</td>
<td>N/A*</td>
</tr>
<tr>
<td>350 °C</td>
<td>N/A*</td>
<td>-1.79x10⁻³</td>
<td>-8.79x10⁻⁴</td>
<td>-8.15x10⁻²</td>
</tr>
<tr>
<td>400 °C</td>
<td>-2.49x10⁻³</td>
<td>-4.17x10⁻³</td>
<td>-2.24x10⁻³</td>
<td>N/A*</td>
</tr>
<tr>
<td>450 °C</td>
<td>-1.17x10⁻⁴</td>
<td>-1.88x10⁻³</td>
<td>-1.23x10⁻³</td>
<td>-5.07x10⁻⁰⁰</td>
</tr>
</tbody>
</table>

*N/A – Samples at these growth conditions were not fabricated.

Resistivity: Figure 4.1 and Figure 4.2 shows the variation of resistivity with growth temperature at different N₂ and Ar partial pressure ratios. From Figure 4.2, resistivity of the samples that are grown at equal partial pressures of Ar and N₂ (Ar: N₂ :: 6:6) is found to be weakly dependent on the growth temperature, though there is a small increment in the range of 300 °C to 350 °C growth temperature. For samples grown with
only N\textsubscript{2} as the sputtering gas, resistivity drops significantly for samples grown in the range of 35 \degree C to 350 \degree C and steeply increases for samples grown above 350 \degree C.

Thermal decomposition of InN happens at 400 \degree C substrate temperature in magnetron sputtering. [17] Our resistivity results are a good indication of this decomposition and in agreement with resistivity results from Tansley [17]

![Graph showing resistivity vs growth temperature](image)

*Figure 4.1:* Resistivity Vs growth temperature, only N\textsubscript{2} as sputtering gas.

Figure 4.3 shows the variation of resistivity with the Argon partial pressure variation in the sputtering gas mixture. From the EDX analysis (Table 4.3) we found that increase in Ar in gas mixture increases Indium content in InGaN thin films. Error in In. at. \% values found are less than 2\%. From the graph, for samples grown at room
temperature, resistivity decreases steeply with increase of Indium content in InGaN thin films.

Figure 4.2: Resistivity at varying Ar and N$_2$ partial pressures, total pressure constant.

Figure 4.3: Resistivity with Ar partial pressure ratio at three different temperatures.
Table 4.3

**EDX analysis: In. at. % with Ar partial pressure at different substrate temperatures**

<table>
<thead>
<tr>
<th>Ar ratio</th>
<th>In at. % (RT)</th>
<th>In at. % (250 °C)</th>
<th>In at. % (350 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.39</td>
<td>5.08</td>
<td>1.03</td>
</tr>
<tr>
<td>0.25</td>
<td>41.35</td>
<td>16.7</td>
<td>10.12</td>
</tr>
<tr>
<td>0.5</td>
<td>51.76</td>
<td>39.11</td>
<td>25.53</td>
</tr>
<tr>
<td>0.75</td>
<td>52.29</td>
<td>44.15</td>
<td>37.11</td>
</tr>
</tbody>
</table>

In this study, we report extremely low resistivity values well below 400 °C growth temperatures using RF magnetron sputtering. For low Ar partial pressure in the sputtering gas mixture, x < 0.5, resistivity is in the range of 1.6x10⁻⁴ to 1.7x10⁻² Ω.cm and for high Ar, x > 0.5, it is varied from 2.6x10⁻⁵ to 2.4x10⁻³ Ω.cm.

Among all the samples, the highest average resistivity is found to be 1.68x10⁻² Ω.cm for samples grown at room temperature with only N₂ as sputtering gas. Lowest average resistivity is found to be 2.6x10⁻⁵ Ω.cm for samples grown at 300 °C at x = 0.75 in the sputtering gas mixture.

Mobility: According to T.L. Tansley [17] [22] Mobility in thin films related to effective mass of the carrier and scattering time by,

\[
\mu = \frac{q \tau}{m^*}
\]  

(4.5)

Effective electron mass of electron in InN, *m_e is 0.055m_o [21] and in GaN, it is 0.20m_o at room temperature where m_o is the true mass of the electron. [20] Therefore, mobility of the films increases with increase in Indium content. However, InN tends to degenerate and at higher carrier concentration, electron mobility values decrease due to
ionized impurity scattering [23] [14]. From figure 4.4, for Ar partial pressure ratio, $x = 0.25$ (Ar: N$_2$:4:8) and $x= 0.5$ (Ar: N$_2$: 6:6) in the sputtering gas mixture, average mobility value of the films grown at 350 °C has highest value and decreases for films grown above and below 350 °C growth temperature. For $x = 0$ (only N$_2$) and $x= 0.75$ (Ar: N$_2$: 8:4) average mobility values constantly increases when growth temperature increases.

Figure 4.4 shows that mobility of InGaN thin films showed improvement as the growth temperature is increased and dropped significantly when the growth temperature is above 350 °C. This pattern is like the results presented by Beierlein. [13] The presence of density defects could be the reason for low mobility values at low and very high temperatures. At low temperatures ionized impurity scattering dominates and at very high temperatures polar mode phonon scattering dominates and the actual mobility reaches its peak at an intermediate temperature. [23] [22] From the figure 4.4 we can see that 350 °C is that intermediate temperature for InGaN thin films grown by RF sputtering.

In this study, we found that lowest mobility value is 0.119 cm$^2$/V. s for InGaN samples grown at room temperature with no Ar in the gas mixture (high GaN molar fraction). Highest mobility is 45.2 cm$^2$/V. s for samples grown at 350 °C when $x = 0.25$ (moderate InN molar fraction). C.P. Foley [18] reported 30 cm$^2$/V. s mobility value for InGaN films grown by RF magnetron sputtering.
Figure 4.4: Mobility variation with $T$ at different partial pressure ratios.

From figure 4.5, conductivity of InGaN thin films are highest for the samples grown in the range of 300 °C – 350 °C growth temperature and steeply falls for samples grown above 350 °C. It can be noticed that for a specific growth temperature, conductivity values are higher for samples grown in high Ar concentration (high In content). Lowest values of conductivity are recorded for samples grown without Ar in the sputtering gas mixture (lower In content). Similar arguments and reasons made in resistivity and mobility part of this article will be applicable for conductivity too. Highest conductivity is $37.3 \times 10^3$ mho/cm is recorded for samples grown at 350 °C when Ar concentration, $x=0.75$, in the sputtering gas mixture. Lowest conductivity is $0.595 \times 10^3$
mho/cm is recorded for samples grown at room temperature with no Ar in the sputtering gas mixture.

Figure 4.5: Conductivity variation with growth temperature at different gas flow ratio.

In this study, we found that electron carrier concentration of all InGaN films are in the range of $10^{20} - 10^{22}$ /m$^3$. For Ar partial pressure ratio, $x = 0$, 0.25 and 0.75 samples grown at 400 °C showed higher carrier concentration values. Samples grown at 400 °C when $x = 0.75$ (high In content) have highest carrier concentration value, $1.11 \times 10^{22}$ /m$^3$. For room temperature growth, carrier concentration in films appeared to be insensitive to the variations of Ar and N$_2$ partial pressure ratios. These findings agree with the study reported by Beirlein. [13]
4.4 Conclusion

With no additional doping, all InGaN samples fabricated are n-type semiconductors irrespective of growth temperature and gas flow ratios. Resistivity values of these InGaN semiconductors grown at different substrate temperatures but measured at room temperature follow the similar pattern of temperature dependence of semiconductors grown at room temperature.

Resistivity of the samples decreases with the Indium concentration. Resistivity values are decreased in the order of $10^3$ by increasing the growth temperature to 300 °C and by increasing the Ar concentration in sputtering gas mixture (high In content).
Mobility values of InGaN thin films were increased by 452 times and conductivity values are improved by 63 times by increasing the growth temperature to 350 °C and by increasing the Indium content to a moderate level. We can conclude that electrical properties of InGaN thin films grown by RF sputtering machine can be improved by changing the substrate growth temperatures and by varying partial pressures of Argon and Nitrogen in the sputtering gas mixture. These improved InGaN thin films can be used as n-layer in fabrication of photovoltaics.

4.5 References


830–2

197–203

[26] Bradshaw M L 2009 Epitaxial growth of InN on (0001) sapphire PhD Thesis
(Arizona State University) AAI3357255
CHAPTER 5: RESULTS - BAND GAP TUNING AND OPTICAL PROPERTIES OF INGAN THIN FILMS

The contents of Chapter 5 are published in Materials Research Express journal with the title “Bandgap tuning and spectroscopy analysis of In\(_x\)Ga\(_{1-x}\)N thin films grown by RF sputtering method” Mater. Res. Express (2016), 103079.R2 (IOP publishing).

5.1 Introduction

Indium Gallium Nitride (InGaN) is a group III-V direct bandgap semiconductor [1]. Unlike in indirect bandgap semiconductors like Silicon, creation of electron hole pairs in direct bandgap semiconductor do not involve crystal lattice vibrations and creates charge carriers more efficiently. By varying the Indium at. % and Gallium at. % in the InGaN alloy its bandgap can be varied from 0.7 to 3.4 eV [1]. This range of bandgaps in one type of material makes it special in that can absorb entire visible spectrum from near infrared to ultraviolet. For all In/Ga compositions, InGaN retains its semiconductor properties. Radiative recombination is one of the key characteristics to consider in direct band gap semiconductors that are used in light emitting diodes and some photovoltaic devices. Rate of recombination depends strongly on the bandgap of the material and its temperature dependence. Changing the growth parameters can significantly change the quality and properties of the InGaN semiconductor. Accurate knowledge of bandgap as a function of alloy composition is required to tailor the optical emission and absorption characteristics of novel optoelectronic devices and photovoltaics [2]. In multi junction solar cells, light can be efficiently absorbed between active layers by stacking
semiconductors of varying bandgaps, therefore knowledge of bandgap tuning will be helpful.

Deposition rate, substrate temperature, Indium molar fraction and thickness of the film can influence optical properties of InGaN [2]. Indium incorporation increases by decreasing the growth temperature [3]. At higher deposition rates, incorporation of Indium becomes higher [2]. Pereira et al. [4] reported that increase in Indium at. % in InGaN films decreases bandgap. Absorption coefficient and penetration depth are crucial in determining the critical thickness of thin films for absorption over a specific wavelength range. Measuring the absorption coefficient for various energies gives information about bandgaps of the material [5]. High absorption coefficient values yield strong absorption for relatively thin films [1]. Singh [6] reported $10^4 – 10^5$/cm absorption coefficient value for InGaN films grown by MBE and reported that InGaN films with higher Indium at. % have higher absorption coefficient. David [7] reported $\sim 10^5$/cm absorption coefficient for InGaN films in 400-450 nm wavelength range.

InGaN thin films grown by MOCVD and MBE methods are extensively studied but less known about films grown by RF sputtering method. In this study, we not only investigate optical properties of InGaN thin films grown by RF sputtering method but also present a novel bandgap tuning method for films by controlling growth conditions like substrate temperature and partial pressure ratios of sputtering gases.

UV-Vis absorption spectroscopy is one of the frequently used methods to characterize optical properties of thin films. Using optical absorption data, Tauc [8]
proposed a method to determine bandgap. Bandgap can be found from the following equation,

\[(\alpha h \nu)^n = A (h \nu - E_g)\]  \hspace{1cm} (5.1)

Where, \(\alpha\) is absorption coefficient, \(h\) is Planck’s constant, \(\nu\) is photon’s frequency, \(E_g\) is the bandgap of the material and \(A\) is proportionality constant. For direct allowed transitions, \(n = 2\). Basic procedure for Tauc analysis is to acquire optical absorption data for the sample that spans a range of energies [9]. InGaN is direct band gap, so \(n = 2\), \((\alpha h \nu)^2\) is plotted against incident energy, absorption becomes stronger and shows a region of linearity near bandgap value, this linear region is extrapolated to the X-axis intercept to find the bandgap value [9].

Absorption coefficient;

\[\alpha = 4\pi k/\lambda\]  \hspace{1cm} (5.2)

It indicates how easily light can penetrate the material [10]: p.128. Absorption depth is the inverse of absorption coefficient and determines the depth the light (photon) penetrates a semiconductor before being absorbed [11]. High absorption coefficient indicates most of the light is absorbed near the semiconductor surface. Absorption depth is an important parameter to determine the thickness of a semiconductor film in photovoltaic applications.

5.2 Experiment

InGaN thin films are grown on high temperature aluminosilicate glass and Silicon (111) substrates by RF magnetron sputtering. Under same conditions, thin films are deposited both on aluminosilicate glass substrates and Silicon substrates simultaneously.
Films grown on glass substrates are used for UV-Vis Spectroscopy analysis. During EDX analysis, to avoid charging effects that can arise from glass substrates, films grown on Silicon substrate are used. Argon (Ar) and Nitrogen (N\textsubscript{2}) are used as inert and reactive gases respectively in the sputtering process. RF Magnetron sputtering is powered by a capacitively coupled 13.56 MHz RF generator with a matching network. Electrons in the plasma at this frequency are extremely “hot” and have an energy of 2-7 eV at 100W power [27].

Temperature of an electron with energy of 2 eV is \( \sim 23000 \) K compared to neutral particles which have 0.025 eV (293 K). N\textsubscript{2} dissociates/ionize in RF plasma and is reactive under these conditions. A constant RF plasma power of 100W and a constant total pressure of 12 mTorr or 1.599 Pa is maintained for all samples grown irrespective of growth temperature. Parameters changed in this study are growth temperature and partial pressures of N\textsubscript{2} and Ar.

Samples are made at 35 °C, 250 °C, 300 °C, 350 °C, 400 °C and 450 °C temperatures. Ratio of Ar partial pressure to total pressure, \( y \), in (N\textsubscript{2}+Ar) gas mixture is increased from 0 to 0.75 while varying the N\textsubscript{2} partial pressure ratio by (1\(-y\)) to keep the total pressure constant. The metal target is water cooled, so that the vapor pressures of Indium and Gallium are extremely low and insignificant compared to Ar and N\textsubscript{2} partial pressures (\( \sim 4 \) to 12 mTorr).

Vapor pressure of Gallium at 619 °C is \( 10^{-5} \) mTorr and vapor pressure of Indium at 487 °C is \( 10^{-5} \) mTorr [28]. In and Ga vapor pressure values are even lower at the substrate temperatures considered in this study, < 450 °C. A two-inch diameter 50-50 (by
atomic percent)"home-built" In/Ga material is used as target. Target used is a eutectic alloy. The target is placed vertically below the substrates is stable in the liquid state. Chemical reaction of metal and Nitrogen takes place in the plasma and InGaN condenses on the substrate. Thickness of all samples are kept approximately 100 nm and deposited on 18mm x 18mm substrates. The growth of InGaN thin films on the substrates is by on-axis RF magnetron sputtering method. Substrates are placed centered vertically above target at 10 cm.

Deposition rates of these thin films can be found in Table 5.1. The thicknesses of the deposited InGaN films have been kept approximately same for all the films within the error. Changing the growth conditions changed the deposition rate but we maintained the thickness of all samples to be the same by varying the deposition time. A lab built heater is used to grow samples at higher temperatures. Four samples are fabricated at every growth temperature and every partial pressure ratio. All the values in the tables and graphs are average values with error analysis.

In this study, optical properties are measured using Ultraviolet-Visible absorption spectroscopy. HP 8451A diode array spectrophotometer is used to collect absorption spectrum. The lamp in the spectrophotometer discharges full UV and visible range of 190-820 nm. A reference sample is used to cancel the absorbance spectrum from the substrates, if any. Tauc plots are used to find the bandgap of samples from the acquired absorption spectrum.
Table 5.1

Deposition rate (Å/min) at different temperatures and partial pressure ratios

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Ar: N₂::6:6</th>
<th>Ar: N₂: 4:8</th>
<th>Only N₂</th>
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<tbody>
<tr>
<td>35 °C</td>
<td>5.5</td>
<td>3.0</td>
<td>1.6</td>
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<tr>
<td>250 °C</td>
<td>2.71</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>300 °C</td>
<td>2.24</td>
<td>1.05</td>
<td>--</td>
</tr>
<tr>
<td>350 °C</td>
<td>1.1</td>
<td>0.68</td>
<td>0.7</td>
</tr>
<tr>
<td>400 °C</td>
<td>0.82</td>
<td>1.10</td>
<td>--</td>
</tr>
<tr>
<td>450 °C</td>
<td>0.84</td>
<td>1.2</td>
<td>0.78</td>
</tr>
</tbody>
</table>

5.3 Results and Discussion

5.3.1 Atomic Composition Variation with Partial Pressure Ratio

Sputter rate of a surface layer due to Ar ion bombardment is proportional to the ratio of molar weight and density of the material [12]. Sputter rate;

\[ R = \frac{M}{e r N_A} \cdot S \cdot j_p \]  \hspace{1cm} (5.3)

Where, M is molar weight, r is density of material, e is electron charge, Nₐ is Avogadro number, S is sputter yield and j_p is ion current density. Molar weights of Indium and Gallium are 114.8 g/mol and 69.72 g/mol respectively [13]. Density of Indium and Gallium are 7.29 g/cc and 5.91 g/cc respectively [14]. Substituting M, r, e and Nₐ values for Indium and Gallium, we get

\[ R_{In} = 1.3 \cdot R_{Ga} \cdot S \cdot j_p \]  \hspace{1cm} (5.4)
Table 5.2

*Sputter yield (S) of In and Ga at different Ar\(^+\) incident energies and angles, by Shea [15]*

<table>
<thead>
<tr>
<th>Ar(^+) Energy</th>
<th>500 eV</th>
<th>1 keV</th>
<th>2 keV</th>
<th>5 keV</th>
<th>10 keV</th>
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<tr>
<td></td>
<td>0°</td>
<td>45°</td>
<td>0°</td>
<td>45°</td>
<td>0°</td>
</tr>
<tr>
<td>Indium</td>
<td>2.13</td>
<td>3.14</td>
<td>3.08</td>
<td>4.56</td>
<td>4.16</td>
</tr>
<tr>
<td>Gallium</td>
<td>1.57</td>
<td>2.44</td>
<td>2.29</td>
<td>3.56</td>
<td>3.08</td>
</tr>
</tbody>
</table>

From Table 5.2, for every Ar\(^+\) ion incident energy and incidence angle, Ar sputtering yield (S) for Indium is greater than Gallium and therefore, Ar Sputter rate for Indium (R\(_{\text{In}}\)) is greater than Gallium (R\(_{\text{Ga}}\)) at a constant primary ion current density. Table 3.3.2 values are reported by Shea et al. [15] and National Physics Laboratory. During “only N\(_2\)” test, energy transfer function during elastic collision between target atom(Ga/In) and projectile ion (N\(^+\) or N\(_2^+\)) is given by

\[
\gamma = \frac{4M_1M_2}{(M_1+M_2)^2}
\]  (5.5)

Atomic masses of Indium and Gallium is 114.8 u and 69.7 u. Atomic mass of Nitrogen is 14 u. [29] From the above equation \(\gamma\) for Gallium is higher than Indium which implies sputter yield for Gallium is higher than Indium during Nitrogen ion bombardment.
Figure 5.1: Indium atomic % variation with change in Ar ratio in the sputtering gas

From figure 5.1, at all growth temperatures, it has been observed that increase in Argon ratio in the sputtering gas during deposition increased the Indium atomic percentage in the InGaN thin films. This is due to higher sputter rate of Indium compared to Gallium during Ar ion bombardment. EDX analysis is used to find atomic composition in these InGaN thin films. Bandgap engineering for sputtered-deposited thin films is reported by Little [30] and Chen et al [31]. InGaN chemical composition is verified in our previous work through XRD analysis, reported in [32] and [33].
Table 5.3

*EDX analysis at different temperatures and partial pressure ratios*

<table>
<thead>
<tr>
<th>Ar ratio</th>
<th>In. at% (RT)</th>
<th>In. at% (250 °C)</th>
<th>In at. % (350 °C)</th>
<th>In at. % (450 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.39</td>
<td>5.08</td>
<td>1.03</td>
<td>1.26</td>
</tr>
<tr>
<td>0.25</td>
<td>41.35</td>
<td>16.70</td>
<td>8.12</td>
<td>11.69</td>
</tr>
<tr>
<td>0.5</td>
<td>57.16</td>
<td>39.11</td>
<td>25.53, 18.12 (400°C)</td>
<td>21.28</td>
</tr>
</tbody>
</table>

5.3.2 Bandgap Variation with Indium at. %

In this study, we are reporting the bandgap values of InGaN thin films with In at. %, x, for 1 < x < 60. We report highest bandgap, $E_g = 3.15$ for x = 1.03% and lowest bandgap, $E_g = 1.4$ for x = 57.16%. From figure 5.2, we can see that bandgap of InGaN thin films is decreasing with increase of Indium at. %. Similar pattern is reported for InGaN thin films grown by MOCVD by Pereira et al. [4] and in InGaN thin films grown by MBE method by O’Donnell et al. [16]

The reason for this pattern in figure 5.2 is attributed to the difference in interatomic spacing between InN and GaN. Increased interatomic spacing reduces the potential seen by the electrons in the material, thereby reducing the bandgap, high interatomic spacing is low band gap [8]. Bond length of InN is 2.15 Å and that of GaN is 1.94 Å [17].
From figure 5.1 and figure 5.2, we can conclude that bandgap of InGaN thin films can be controlled by varying the Ar partial pressure in the sputtering gas mixture. Keeping total pressure constant, increase in Ar partial pressure in the (Ar+N$_2$) sputtering gas mixture increases Indium content and thereby decreases the bandgap of InGaN thin films deposited using RF magnetron sputtering method.

5.3.3 Bandgap Tuning with Substrate Temperature

Figure 5.3 shows the variation of energy bandgap with growth temperature at varying Ar and N$_2$ partial pressure ratios keeping total pressure constant. From figure 5.3, bandgap energy of InGaN films grown at different partial pressures is found to be increasing with increase in substrate temperature.
The increase in bandgap with temperature is due to the low Indium incorporation in the InGaN thin films at higher substrate temperatures. Indium incorporation increases with decrease in substrate temperature [3]. This is verified from EDX analysis. The values of Indium at. % in the films grown at different substrate temperatures are presented in Table 5.3. Similar relation of Indium incorporation with temperature is reported for InGaN thin films grown by MOCVD by Heng-Ching Lin [18], Van der Stricht [19] and for InGaN films grown by LPMOVPE by Lee [20].

In figure 5.3, a slight decrement in the bandgap value is observed at 400 °C for films grown at equal Ar and N₂ partial pressure ratios and at 350 °C for films grown at...
other partial pressure ratios in this study. Beierlein [21] reported that InGaN samples grown at 400 °C showed a strong increase in InN composition across the entire alloy range [2]. Our results agree with this and can be verified from Table 5.3 and figure 5.3. Variation of bandgap with substrate temperature in figure 5.3 can also be explained by sputtering growth rate. Incorporation of Indium becomes higher at higher growth rates [2]. Growth rate of InGaN thin films grown by sputtering in our study are presented in Table 5.1.

5.3.4 Spectroscopic Analysis

![Figure 5.4: α Vs λ of InGaN thin films grown at different partial pressures.](image-url)
Figure 5.4 is for the samples grown at room temperature. These samples are compared to Silicon values reported by Green M.A et. al. In figure 5.4, the absorption spectra of InGaN films grown at room temperature and at different Ar partial pressure ratios, y = 0 (Only N₂), 0.25 (Ar: N₂::4:8), 0.5 (Ar: N₂::6:6) and 0.75 (Ar: N₂::8:4) are shown. The absorption spectra of Silicon reported by Green M.A [22] is also shown to compare with our films. The spectra are taken in the wavelength range of 250 to 820 nm. The data is graphed on a log scale. It is clear from figure 5.4 that all InGaN samples under consideration have high absorption coefficients (α) within the investigated range (250 – 820 nm) and the absorption extends beyond visible spectrum (390 – 700 nm).

Absorption coefficient values decrease with increase in wavelength. Highest absorption coefficient value, α ~ 7 x10⁵/cm is measured for InGaN films grown at y = 0.25 Ar partial pressure ratio. A similar value, α ~ 10⁵/cm is reported by Wierer [23] for InGaN films grown by MOCVD method. For samples grown at Ar partial pressures, y = 0.5, 0.75 and y = 0, α is slightly lower but still above 10⁵/cm.

Within the investigated range, at longer wavelengths alpha values remain above 10⁴/cm for all InGaN samples. This strong absorption coefficient values are attributed to the fact that InGaN is a direct bandgap semiconductor [2]. From figure 5.4, alpha value of Silicon decreases sharply with wavelength and drops down to 707/cm at 820 nm [22] which is significantly less than InGaN absorption values. This is because Si is an indirect bandgap semiconductor and involves phonon or lattice vibrations in electron band-to-band transition [22].
In figure 5.5, absorption spectra of InGaN films grown at the same Ar and N₂ partial pressure (Ar: N₂::6:6) but at different substrate temperatures are shown. Figure 5.5 is in log scale. In this study, at short wavelength range (280 – 400 nm), high alpha values, \( \alpha \sim 1.3 \times 10^5 /\text{cm} \), \( \alpha \sim 1.1 \times 10^5 /\text{cm} \) and \( \alpha \sim 1.0 \times 10^5 /\text{cm} \) are measured for samples grown at room temperature, 250 °C, 350 °C and 450 °C respectively. At longer wavelengths, alpha values, \( \alpha \sim 3 \times 10^4 /\text{cm} \) (room temperature) and \( \sim 2 \times 10^3 /\text{cm} \) (350 °C) are measured. Difference between alpha values of these samples at shorter wavelengths is small but there is large difference at longer wavelengths when the growth temperature is increased. Trainor [24] reported absorption coefficient of InN in the range of \( 10^4 - 10^5 \) /cm for 350 – 820 nm wavelength spectrum. Ambacher [25] reported absorption
coefficient of GaN in the range of $10^2 – 10^4$ /cm for 350 -820 nm wavelength spectra which are lower than InN values. From figure 5.5, absorption coefficient decreased with increase in growth temperature. The reason for this pattern is due to change in the atomic composition of the samples with substrate temperature. For InGaN samples under this study, when the substrate temperature is increased, Indium at. % is decreased. So, at higher temperatures, absorption spectra of these samples shift away from InN spectra to the values like GaN spectra. A similar relation of absorption coefficient versus substrate temperature is reported by Sharma [26]. Indium at. % values are presented in and can be verified from Table 5.3.

Figure 5.6: Absorption depth Vs $\lambda$, samples grown at different substrate temperatures and sputtering gas partial pressure ratio: (Ar: N$_2$: 6:6)
Figure 5.6: Variation of absorption depth values with wavelength for InGaN films grown at different substrate temperatures. Under investigated range, for shorter wavelengths (280 - 400 nm), an absorption depth ($\delta$) of $\sim 0.04$ $\mu$m is measured for InGaN films grown at all three growth temperatures under consideration. For longer wavelengths (750 – 820 nm), the values are measured to be $\sim 0.3$ $\mu$m (room temperature), $\sim 0.5$ $\mu$m (250 °C) and $\sim 4$ $\mu$m (350 °C). For longer wavelengths absorption depth is ten times more when growth temperature is increased to 350 °C for samples under consideration.

Figure 5.7 shows variation of absorption depth values with wavelength for InGaN films grown at different sputtering gas partial pressure ratios but keeping growth
temperature same. For shorter wavelength range (280-400 nm), absorption depth values, \( \delta \sim 0.01 \mu m, \delta \sim 0.05 \mu m \) and \( \delta \sim 0.05 \mu m \) are measured for films grown at \( y = 0.25, 0.5 \) and 0.0 Ar partial pressure ratios respectively. For longer wavelengths, these values remain to be less than \( \sim 0.2 \mu m \).

For Silicon, on the other hand, per the values reported by Green M.A [22], for longer wavelengths (750-800 nm), \( \delta \sim 14 \mu m \). This value is approximately 100 times more than InGaN values. As \( \delta = 1/\alpha \), similar arguments and explanations made in absorption coefficient parts will be applicable for absorption depth patterns in both figure 6.6 and figure 5.7. These low absorption depth values for InGaN films grown at different sputtering gas partial pressure ratios and substrate temperature measured in this study shows InGaN films are good candidates for thin films.

5.4 Conclusion

Composition of Indium and Gallium in InGaN films can be tailored successfully by controlling the partial pressure ratios of Argon and Nitrogen in RF sputtering method. Increase in Ar partial pressure ratio in the sputtering gas mixture increases Indium at. % in InGaN alloy and therefore decreases the bandgap of deposited films. Bandgap is increased when substrate temperature is increased to 350 - 400 ºC. InGaN thin films with bandgaps from 1.4 eV to 3.15 eV are fabricated by controlling growth pressure and growth temperature. High absorption coefficient values \( \sim 7 \times 10^5 /\text{cm} \) show that most of the light is strongly absorbed at the surface of the film. Low penetration depth values of \( \sim 0.04 \mu m \) show that thickness of these films is small. In conclusion, InGaN films grown by
RF sputtering method are good candidates for thin film fabrication and with the wide range of bandgaps they can be used as active layers in photovoltaics.

5.5 References


CHAPTER 6: IMPROVED SI/INGAN HETEROJUNCTION SOLAR CELLS WITH ALN BUFFER LAYER

In section 3.3, results of test solar cells indicate presence of shunt and series resistances with in the cells that limited the maximum power output from the solar cell. This section presents the improved methods and fabrication of InGaN solar cells and addresses the problems caused during test solar cells.

Low Shunt resistance caused by manufacturing defects is not desirable in a solar cell, it reduces $I_{\text{max}}$ value by providing alternate paths to the current. High series resistance caused by poor movement of light generated carriers through the p-n and metal-semiconductor junctions is not desirable either. It doesn’t change the $I_{\text{sc}}$ and $V_{\text{oc}}$ values but greatly lowers $V_{\text{max}}$ and Fill factor value and thereby lowering the $P_{\text{max}}$ and $\eta$ values.

6.1 Shunt Resistance: To Reduce Manufacturing Defects

Upgraded our RF sputtering machine from a single target to three-target machine. This makes in situ deposition of three layers and reduces the atmospheric time exposure to newly formed layers while changing the targets. We also changed growth parameters of thin film deposition. Lab-built heating device: Thin films discussed in section 3.4 used a heating bulb to deposit films at higher temperature but the bulb is limited by its voltage and cannot give higher than 200 °C substrate temperature. So, we built a simple electrical heating device that used a tantalum wire. Tantalum is extremely corrosion resistant and has high absorption rate for residual gases in vacuum systems. A Type K (Chromel –
Alumel) thermocouple that can measure temperatures up to 1350 °C is used to measure the substrate temperature.

Figure 6.1: Upgraded three target sputtering machine in our lab.

Figure 6.2: Lab-built heater/substrate holder to deposit films at higher temperature.
Result: Section 3.4, Chapters 4 & 5 present all the details and results of improved InGaN films in their electrical, optical and structural properties after changing the growth conditions and following this method.

6.2 Series Resistance: To Increase Light Generated Carrier Mobility Across All Junctions

Improving metal-semiconductor junction: In section 3.3, we discussed vacuum heating method to make better contacts between Aluminum back contact and p-type silicon. This method did not yield good results. It made the metallic contact between Al and p-Si better but vacuum heating at higher temperatures resulted in forming extra oxide layer on the free surface of p-type of silicon after removing it from the oven and exposing to atmosphere.

Formation of extra oxide layer has been verified from the Rutherford Back Scattering Experiment (see figures 6.4 and 6.5). So, we used “solvent clean” method to remove the oxide layer.
Figure 6.4: O₂ peak from RBS experiment for unheated sample on silicon surface.

Figure 6.5: Oxygen peak from RBS technique for vacuum heated Si sample.
“Solvent Clean”

1. Ten minutes in Acetone bath at warm temperature (<55 °C)
2. 5 min in Methanol
3. DI water rinse
4. N₂ blow on the sample

Improving p-n junction: Lattice mismatch and difference in thermal expansion coefficient leads to cracking and high defect density between the two layers [1] [2]. Strain is still the major issue for the established growth on Si (111) [3]. To improve the quality of p-n junction, we deposited Aluminum Nitride buffer layer in between p-Si and n-InGaN. Aluminum nitride (AlN) buffer layer is found to decrease the stress sufficiently to avoid crack formation [2]. Dislocation density is significantly decreases at the top surface and optical quality is considerably increased with AlN buffer layer [4]. We added a AlN buffer layer between p-Si and n-InGaN and this improved the quality of InGaN films for their electrical, optical and structural properties. During Ar: N₂: 8:4 partial pressure ratio growth, addition of AlN buffer layer increased mobility of carriers by 23 times and conductivity of carriers by 425 times at 250 °C substrate temperatures. Adding AlN buffer layer and increasing substrate temperature to 350 °C from 250 °C increased mobility by 175 times and conductivity by 515 times compared to InGaN films deposited at 250 °C without buffer layer. This improvement is because AlN buffer reduced cracks in InGaN layers and reduced defect density. From chapter 4, electrical properties of InGaN films are increased by changing the growth conditions. Now, addition of AlN buffer layer further improved the electrical properties of InGaN films.
Table 6.1

*Electrical properties of InGaN with and without AlN buffer layers*

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk conc./cm³</td>
<td>-2.08 x 10^{20}</td>
<td>-4.18 x 10^{19}</td>
<td>-2.2 x 10^{19}</td>
<td>-4.12 x 10^{20}</td>
<td>-6.59 x 10^{19}</td>
</tr>
<tr>
<td>Sheet conc./cm²</td>
<td>-2.08 x 10^{15}</td>
<td>-4.18 x 10^{14}</td>
<td>-2.2 x 10^{14}</td>
<td>-4.12 x 10^{15}</td>
<td>-6.59 x 10^{14}</td>
</tr>
<tr>
<td>Mobility (cm²/V.s)</td>
<td>0.409</td>
<td>3.62</td>
<td>5.793</td>
<td>131.4</td>
<td>1017</td>
</tr>
<tr>
<td>Resistivity (Ω.cm)</td>
<td>7.32 x 10^{-2}</td>
<td>4.1 x 10^{-2}</td>
<td>4.8 x 10^{-2}</td>
<td>1.127 x 10^{-4}</td>
<td>9.312 x 10^{-5}</td>
</tr>
<tr>
<td>Conductivity (Ω.cm)</td>
<td>13.66</td>
<td>24.39</td>
<td>20.833</td>
<td>8873.11</td>
<td>10738.83</td>
</tr>
<tr>
<td>Hall Coeff. (cm³/C)</td>
<td>-3.0 x 10^{-2}</td>
<td>-1.49 x 10^{-1}</td>
<td>-2.79 x 10^{-1}</td>
<td>-3.28 x 10^{-2}</td>
<td>-9.46 x 10^{-2}</td>
</tr>
<tr>
<td>Type</td>
<td>N-type</td>
<td>N-type</td>
<td>N-type</td>
<td>N-type</td>
<td>N-type</td>
</tr>
</tbody>
</table>
Figure 6.6: Bandgap of InGaN with and without AlN buffer layer.

From figure 6.6, addition of buffer layer did not change the bandgap of the InGaN film and no significant change in absorption coefficient values.

6.3 Experimental Steps of Fabrication

Step 1: Removing Oxide layer on p-Si: To remove insulating oxide layer p-Si, we used “solvent clean” method. First, we cut the p-Si wafer to desired size. The p-Si wafer is placed in beaker filled with Acetone. This Acetone beaker is placed on a hot plate (see figure 6.7) which is kept around 50 °C for 10 min. Acetone bath temperature is also measured using Infrared thermometer. After 10 min, the samples are transferred to another beaker containing methanol. After another 5 min, blow the surface of the sample with N2.
Step 2: Depositing Aluminum back contact to p-Si. This step is very much like step 1 of fabrication method discussed in section 3.4.

Figure 6.7: Hot plate usage to remove oxide layer on p-Si using acetone bath.

Step 3: Transferring the sample from DC and load it in RF. We keep the sample in substrate holder/heater shown in figure 6.2. We connect substrate holder to a voltage source to deposit thin films at higher substrate temperature, a thermocouple (figure 6.8) is also connected to substrate holder to measure the substrate temperature. Caution should be maintained when increasing the voltage, any sudden increase in voltage could ruin the tantalum wire. We increased voltage in very small steps. At 2% of V step intervals every 30 minutes, it usually takes us 90 minutes to reach 250 °C (6% of V) and 160 minutes to reach 350 °C (11% of V).
Step 4: Deposition of AlN buffer layer at desired growth pressure and temperature.

Step 5: Depositing InGaN at a desired Ar and N₂ ratio and temperature.

Step 6: Depositing ITO as front metal contact at desired Ar and Oxygen partial pressure ratio. All ITO films are deposited at room temperature irrespective of AlN and InGaN substrate temperature.

Step 7: Cutting out the edges as discussed in section 3.4. Two solar cells are fabricated at different growth conditions. I name them Solar cell 2.0 and Solar cell 2.1.

6.4 Experimental Details

Abet Technologies’ Model 11002 SunLiteTM Solar Simulator is used to analyze these samples. It is a AM1.5G solar simulator, power density from the simulator is 100 mW/cm². Cells are kept at 23 cm. Area of each cell is 0.5 cm².
Table 6.2

*Experimental details for solar cell 2.0*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al (back contact)</th>
<th>AlN (buffer layer)</th>
<th>InGaN</th>
<th>ITO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>DC</td>
<td>RF</td>
<td>RF</td>
<td>RF</td>
</tr>
<tr>
<td>Chamber gases</td>
<td>Argon</td>
<td>Nitrogen</td>
<td>Ar: N₂:6:6</td>
<td>Ar: O₂:10:2</td>
</tr>
<tr>
<td>Pressure</td>
<td>10 mTorr</td>
<td>12 mTorr</td>
<td>12 mTorr</td>
<td>12 mTorr</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room T</td>
<td>250 °C</td>
<td>250 °C</td>
<td>Room T</td>
</tr>
<tr>
<td>RF power</td>
<td>20 mA current</td>
<td>100 W</td>
<td>100 W</td>
<td>100 W</td>
</tr>
<tr>
<td>Growth rate</td>
<td>0.3 Å/sec</td>
<td>0.2 Å/sec</td>
<td>0.1 Å/sec</td>
<td>0.2 Å/sec</td>
</tr>
<tr>
<td>Thickness</td>
<td>40 nm</td>
<td>280 nm</td>
<td>140 nm</td>
<td>250 nm</td>
</tr>
</tbody>
</table>
Table 6.3

*Experimental details for solar cell 2.1*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al (back contact)</th>
<th>AlN (buffer)</th>
<th>InGaN</th>
<th>ITO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>DC</td>
<td>RF</td>
<td>RF</td>
<td>RF</td>
</tr>
<tr>
<td>Chamber gases</td>
<td>Argon</td>
<td>Nitrogen</td>
<td>Ar: N\textsubscript{2}:8:4</td>
<td>Ar: O\textsubscript{2}:8:4</td>
</tr>
<tr>
<td>Pressure</td>
<td>10 mTorr</td>
<td>12 mTorr</td>
<td>12 mTorr</td>
<td>12 mTorr</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>Room T</td>
<td>350 °C</td>
<td>350 °C</td>
<td>Room T</td>
</tr>
<tr>
<td>RF power</td>
<td>20 mA current</td>
<td>100 W</td>
<td>100 W</td>
<td>100 W</td>
</tr>
<tr>
<td>Growth rate</td>
<td>0.3 Å/sec</td>
<td>0.2 Å/sec</td>
<td>0.2 Å/sec</td>
<td>0.2 Å/sec</td>
</tr>
<tr>
<td>Thickness</td>
<td>40 nm</td>
<td>310 nm</td>
<td>180 nm</td>
<td>250 nm</td>
</tr>
</tbody>
</table>
Figure 6.9: IV curve for solar cell 2.0.

Figure 6.10: IV curve for solar cell 2.1
Figure 6.11: PV curve for solar cell 2.0

Figure 6.12: IV curve for solar cell 2.1
6.5 Results and Discussion

Table 6.4

*Efficiency and FF values of Si/AlN/InGaN solar cells*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Solar cell 2.0</th>
<th>Solar cell 2.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(V_{oc}, I_{sc})$</td>
<td>$(188 \text{ mV, } 48 \ \mu\text{A})$</td>
<td>$(240 \text{ mV, } 80 \ \mu\text{A})$</td>
</tr>
<tr>
<td>$(V_{max}, I_{max})$</td>
<td>$(102 \text{ mV, } 37 \ \mu\text{A})$</td>
<td>$(122 \text{ mV, } 63 \ \mu\text{A})$</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>$50 \times 10^{-3} \text{W}$</td>
<td>$50 \times 10^{-3} \text{W}$</td>
</tr>
<tr>
<td>Fill Factor</td>
<td>0.418</td>
<td>0.400</td>
</tr>
<tr>
<td>Efficiency</td>
<td>0.00755</td>
<td>0.01537</td>
</tr>
<tr>
<td>Ideality factor</td>
<td>2.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 6.5

*Comparision of solar cells 2.0 and 2.1 with test cells discussed in 3.3*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test cells</th>
<th>Solar cell 2.0 &amp; 2.1</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voc</td>
<td>148 &amp; 240 mV</td>
<td>188 &amp; 240 mV</td>
<td>No significant change</td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>13 &amp; 16 $\mu$A</td>
<td>48 &amp; 80 $\mu$A</td>
<td>500 % increase</td>
</tr>
<tr>
<td>Fill Factor</td>
<td>0.241 &amp; 0.306</td>
<td>0.418 &amp; 0.400</td>
<td>10 -15 % increase</td>
</tr>
<tr>
<td>Efficiency</td>
<td>0.0004 &amp; 0.0003</td>
<td>0.007 &amp; 0.015</td>
<td>3800% more efficient</td>
</tr>
</tbody>
</table>

1. From Table 6.4, Fill Factor values are 0.418 and 0.400, ideality factor (n) values are 2.5 and 3.5 for solar cell 2.0 and solar cell 2.1 respectively. Short-circuit
current of 80 µA is measured for cell 2.1 which is several time more than what we found in test cells. Efficiency of 0.015 is calculated.

2. FF and ideality factor determines the recombination effects, parasitic resistances in the cell. FF values are around 40 %, it indicates presence of parasitic resistive loses.

3. Unlike in test cells, figures 6.10 and 6.11 show a clear “knee” in the IV curve in the range of 60 – 100 mV range at Isc values. This indicate better shunt resistance characteristics, it indicate improvement in the quality of thin films and this improvement can be verified from the values in Table 6.1.

4. Figures 6.10 and 6.11 also show left shift of “knee” and slope at Voc. This accounts for presence of large series resistance in the cell. Series resistance indicate poor movement of light generated carriers across the junctions or lack of carriers crossing the p-n junction and metal-semiconductor junction. Ideality factor, n > 2 indicates the recombination of carriers both in neutral region and space charge region of the solar cell [5]. Non-ohmic and reverse biased rectifying metal-semiconductor contact also leads to higher ideality factor[6]. This show that “solvent clean” method did not remove the oxide layer completely on p-si wafer, addition of buffer layer improved mobility, resistivity and conductivity values in InGaN films (see Table 6.1) but it did not improve the low carrier life time.

5. From the absorption coefficient values (Chapter 5) and electrical propeties of thin films we can say the active part of the cell performs well but enough light
generated carriers are not reaching the metal contacts and contribute to the final voltage and current values.

6.6 References


CHAPTER 7: CONCLUSION

7.1 Quality of InGaN Thin Films

Quality of films, electrical properties and optical properties of InGaN thin films grown by RF sputtering machine can be improved by changing the substrate growth temperatures and by varying partial pressures of Argon and Nitrogen in the sputtering gas mixture. Resistivity values are decreased in the order of $10^3$, mobility values of InGaN thin films were increased by 8546 times and Conductivity values are improved by 63 times by changing growth conditions and adding AlN buffer layer. Composition of Indium and Gallium in InGaN films can be tailored successfully by controlling the partial pressure ratios of Argon and Nitrogen in RF sputtering method. InGaN thin films with bandgaps from 1.4 eV to 3.15 eV are fabricated by controlling growth pressure and growth temperature.

7.2 Quality of Si/InGaN Heterojunction Solar Cells

Short-circuit current of 80 µA, open circuit voltage of 0.24 V, FF of 0.418 is measured for cell 2.1. Efficiency of 0.015 is calculated. Electrical properties of some of the InGaN thin films fabricated in this study are better than commercial silicon wafer considered in this study. But solar cells fabricated have very poor efficiency values. This is due to high recombination of light generated carriers, poor metal-semiconductor contact (MS) and pn junctions. In conclusion, this study proved electrically high quality InGaN thin films can be fabricated using RF sputtering method.
7.3 Future Direction

If recombination losses are reduced and proper MS contact is established, InGaN thin films can be a great asset to Photovoltaic research and solar cell Industry.

To improve Metal-Semiconductor junction

Step 1. Solvent clean is replaced with RCA etch to remove oxide layer

Step 2. Deposit Aluminum metal contact

Step 3. Vacuum heat the sample to improve ohmic nature

Step 4. Second RCA etch to remove oxide layer formed after vacuum heating

To improve p-n junction

1. Find optimal thickness of AlN buffer layer

2. Improve carrier life time in InGaN films.
APPENDIX: XRD & EDX ANALYSIS

XRD graphs for InGaN films:

Sample D5
InGaN thin film/silicate glass
Room Temperature
Pressure: 12 mTorr (Ar:N$_2$:4:8)

Silicate glass
Intensity (arb. units)

Sample D1
InGaN thin film/silicate glass
substrate temperature 250 °C
Pressure: 12 mTorr (Ar:N$_2$:4:8)
InGaN thin film/silicate glass
substrate temperature 300 °C
Pressure: 12 mTorr (Ar:N₂::4:8)

Substrate temperature : 250 °C
Pressure: 12 mTorr (only N₂)
Substrate temperature: 400 °C
Pressure: (Ar:N₂ :: 6:6)

Substrate temperature: 400 °C
Pressure: (Ar:N₂ :: 8:4)
EDX graphs

1. EDX analysis for each sample was performed at four different magnifications, 100 µm, 10 µm, 1 µm and 500 nm. Values presented in Table. 3 of the manuscript are average values of these four magnifications. For reader’s convenience, we are presenting one EDX graph of each sample at a magnification closest to the average value.

2. In all the graphs, peak value observed at 1.7 – 1.8 keV is from the silicon substrate. The focus of this EDX analysis is not on the substrate.

A. Pressure: 12 mTorr (Only N₂)

![Graph 1: Substrate Temperature: Room T; Pressure: 12mTorr (Only N₂); Indium atomic percent: 33.91%](image)
Graph 2: Substrate Temperature: 250°C; Pressure: 12mTorr (Only N₂); Indium atomic percent: 5.78%

Graph 3: Substrate Temperature: 350°C; Pressure: 12mTorr (Only N₂); Indium atomic percent: 1.18%
Graph 4: Substrate Temperature: 450°C; Pressure: 12mTorr (Only N₂); Indium atomic percent: 1.26%

B. Pressure 12 mTorr (Ar: N₂: 4:8)

Graph 5: Substrate Temperature: Room T; Pressure: 12mTorr (Ar: N₂: 4:8); Indium atomic percent: 41.26%
Graph 6: Substrate Temperature: 350 °C; Pressure: 12mTorr (Ar: N₂: 4:8); In atomic percent: 8.26%

Graph 7: Substrate Temperature: 450 °C; Pressure: 12mTorr (Ar: N₂: 4:8); In atomic percent: 11.69%
C. Pressure 12 mTorr (Ar: N₂: 6:6)

Graph 8: Substrate Temperature: room T; Pressure: 12mTorr (Ar: N₂: 6:6); In atomic percent: 57.72%

Graph 9: Substrate Temperature: 250 °C; Pressure: 12mTorr (Ar: N₂: 6:6); In atomic percent: 39.30%
Graph 10: Substrate Temperature: 350 °C; Pressure: 12mTorr (Ar:N₂:: 6:6); In at percent: 24.29%

Graph 11: Substrate Temperature: 400 °C; Pressure: 12mTorr (Ar:N₂:: 6:6); In. at. percent: 18.49%
Graph 12: Substrate Temperature: 450°C; Pressure: 12mTorr (Ar:N₂:6:6); In. at. percent: 21.92%