

Doping Characteristics of Zinc Oxide Thin Films Deposited by Thermal Chemical Vapour Deposition

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Abstract—Nitrogen (N)-doped ZnO films were deposited on glass substrate by thermal chemical vapour deposition process. Nitrogen gas with different flow rate was used as a dopant source. The effects of varying the carrier gas flow rate to the Zinc Oxide thin film electrical properties were investigated. In this experiment, it is found that NST N-doped ZnO thin film with 60 bubbles/min of nitrogen gas flow rate has optimum electrical properties with high conductivity. The types of metal contact used were Au-Au, Au-Pt, Au-Pd. Au-Au contact with lowest resistivity obtained was observed as the best metal contact.

Keywords: Zinc oxide, Nitrogen-doped Zinc Oxide, Thin films, Nanostructures, Thermal CVD method, metal contacts.

I. INTRODUCTION

Nowadays, the semiconductor materials are widely used in the production of electronic devices. Semiconductor technology refers to the development and innovation of the applications of the semiconductor in various applications, such as blue and ultraviolet (UV) light emitters, solar cell windows, photovoltaic device, gas sensor, and surface acoustic wave device. Most commonly semiconductor used are silicon and germanium. In improving the performance of semiconductor devices, the researcher has developed other semiconductor materials, such as silicon dioxide, SiO₂.

This SiO₂ is widely used due to its high thermal conductivity and low cost process. But, SiO₂ also has weaknesses, which is why the researchers are struggling to invent new types of semiconductor materials that are more suitable for electronic devices. Nanostructured zinc oxide is one of the most famous materials that have gained interest of the researchers to study its properties and characteristics. The nanostructured ZnO has lower resistivity compared to other materials. This

leads to better performance of the electronic devices that used this type of material.

Zinc oxide, which is a wide band gap of 3.37 eV at room temperature, and a large exciton binding energy of 60 meV, is an attractive material because of its application in field effect transistor (FET), light-emitting diode, laser diode, resonator, sensor, and piezoelectric devices [1,2]. Undoped ZnO is usually n-type which is associated with native point defects, either oxygen vacancy or interstitial zinc [3, 4]. Moreover, it was shown that the electrical resistivity of ZnO films could be decreased both by increasing their crystallinity and by doping [18-22]. Obtaining ZnO with p-type conductivity has represented difficulty for many years. Nitrogen, a p-type dopant for ZnSe [5], has been considered as a possible p-type candidate for ZnO [6]. There are some theoretical analysis suggested that nitrogen would be the most efficient element for realizing p-type doping of ZnO [7-9].

There are many techniques that can be used to deposit N-doped ZnO thin films, such as pulsed laser deposition (PLD) [10], metalorganic vapor phase epitaxy (MOVPE) [14], magnetron sputtering [15], sol-gel [16], and spray pyrolysis [11-13,17]. Nitrogen-doped ZnO thin films that demonstrate p-type behaviour by using metalorganic chemical vapour deposition was reported by X. Li [26]. This study will report on the fabrication of nitrogen doped ZnO thin films by Thermal CVD which has special advantages such as large scaling and production.

II. METHODOLOGY

A. Substrate Preparation

Glass plates were used as substrates (2cm x 2cm). These substrates were sputtered with Au

(gold), Pt (platinum), and Pd (palladium) respectively to create different types of metal contact for IV characterization. The thickness of these metal contacts was 60nm.

B. Thin Film Preparation

The deposition method used to create nanostructured ZnO thin films was thermal chemical vapour deposition (CVD). Two types of precursor were used, mixture of ZnO powder and graphite for undoped samples, and zinc acetate powder for doped samples. The mixture of ZnO powder and graphite was due to high melting point of ZnO (1975°C). The existence of graphite helps reduced the melting point of ZnO to 920°C.

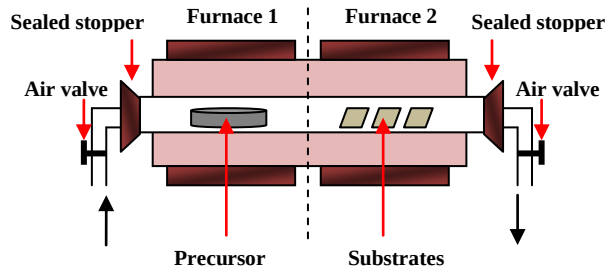


Fig. 1 Illustration of Thermal Chemical Vapour Deposition process.

For Thermal CVD process, there are two furnaces used, as shown Fig. 1, with Furnace 1 for the precursor and Furnace 2 for the substrate. The temperature of precursor furnace was 1000°C, while the temperature of substrate furnace was 500°C. For undoped samples, the carrier gas used was argon (Ag) gas, with the flow rate of 30bubbles/min. As for doped samples, to create N-doped ZnO thin films, the carrier gas used was nitrogen (N₂) gas, with varied flow rate; 30bubbles/min, 40bubbles/min, 50bubbles/min, and 60bubbles/min. Fig. 2 shows the illustration of metal contacts layer of the thin films.

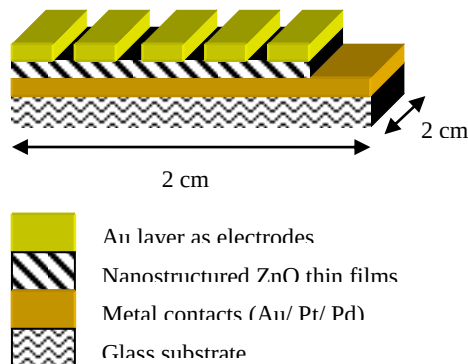


Fig. 2 Illustration configuration layer of nanostructured ZnO thin films.

All of the samples were annealed for 1 hour at 550°C. Then, the samples were sputtered with Au (gold) to create electrodes above the thin films produced. Just then, the IV characterization for all of the samples was done. Fig. 3 shows summary of steps done.

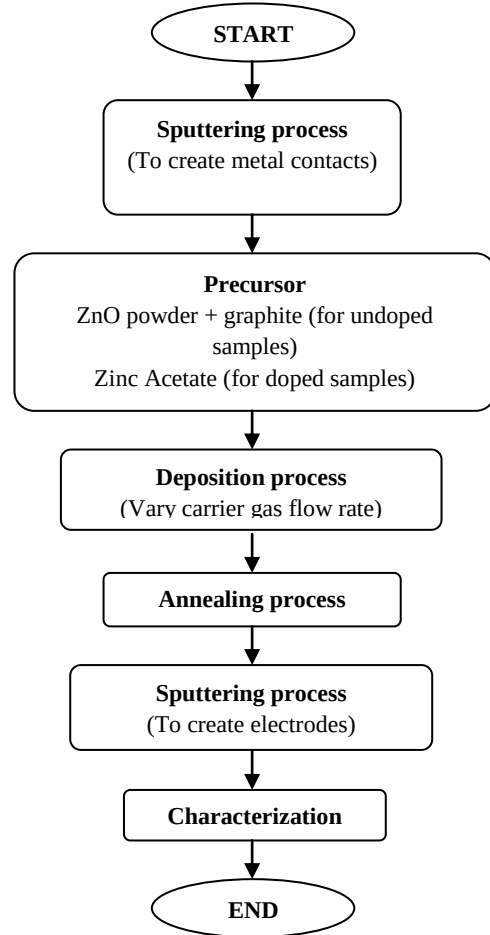
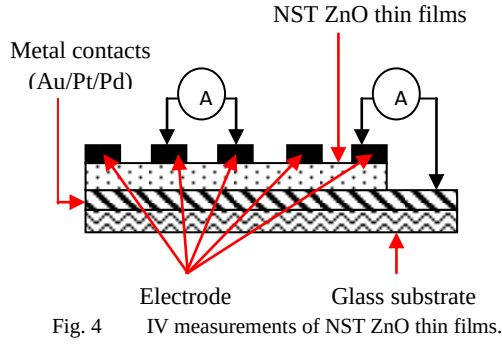


Fig. 3 Flow chart of processes synthesis utilizing on the fabrication.

C. IV MEASUREMENT

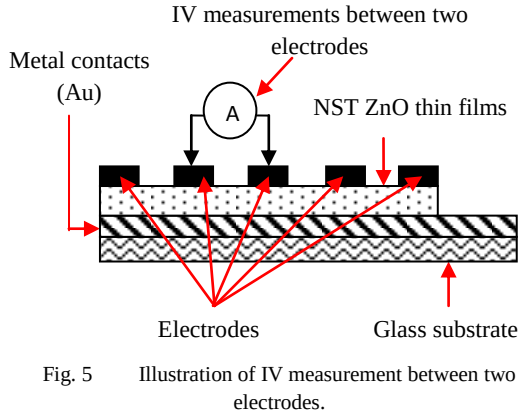
Fig. 4 shows the IV measurements made to obtain the electrical properties of NST ZnO thin films. There are two types of IV measurements made; the conductivity between two electrodes (Au-Au), and also the conductivity between an electrode and metal contact (Au-Au, Au-Pt, Au-Pd). The measurements made between an electrode and a metal contact is to study whether current can flow through the nanostructured ZnO thin films or not. The IV curve, resistivity, and conductivity for both cases will be discussed later in this paper.



III. RESULTS AND DISCUSSIONS

A. Electrical Properties of Au-Au contacts

For this case, the current flow between two electrodes (Au-Au) was measured. The measurement of samples with Au as metal contact was made.



The IV measurement made between the electrodes was to observe whether current can flow with the existence of nitrogen-doped ZnO thin films or not. In order to determine which nitrogen gas flow rate can produces optimum IV characteristics, the comparison of IV characteristics of various flow rates was made and plot in graph shown in Fig. 6. The nitrogen gas, which acts as a dopant source for ZnO thin films deposition, was varied with four different flow rates; 30 bubbles/min, 40 bubbles/min, 50 bubbles/min, and 60 bubbles/min.

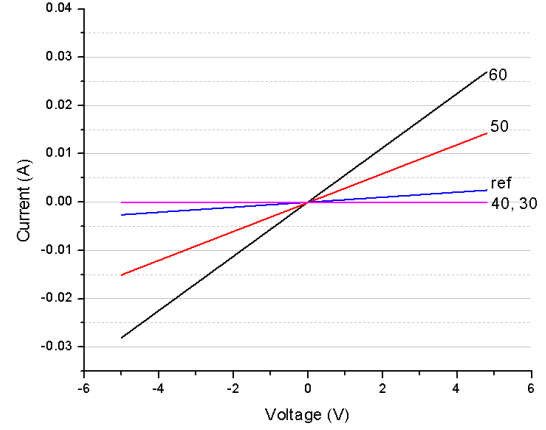


Fig. 6 IV characteristics of NST ZnO thin films produced by varying nitrogen gas flow rate.

Based on the graph in Fig. 6, it can be seen that IV characteristics for nitrogen-doped ZnO thin films are strongly dependent on the amount of the dopant source.—This condition was the same as reported by K. Shtereva [27]. The most optimum IV characteristics obtained was from ZnO thin films with 60 bubbles/min flow rate of nitrogen gas. It also can be seen from the graph that the heavily-doped ZnO thin films produced better current flow compared to the undoped ZnO thin films. This behaviour may be the consequence of the combined effect of the incorporation of nitrogen into the ZnO lattice and of the role on nitrogen on grain growth.

The summary of resistivity and conductivity of NST ZnO thin films with varied nitrogen gas flow rate was depicted in Table 1. As shown in Fig. 7, the resistivity of the thin films decreases as the flow rate of the dopant source increases. ZnO thin films with nitrogen flow rate of 60 bubbles/min shows lowest resistivity, with 0.002983 Ωcm , followed by thin films with flow rate of 50bubbles/min, with 0.0056067 Ωcm . The lowest flow rate of nitrogen gas, 30 bubbles/min shows highest resistivity obtained, 7. 42397 Ωcm . Based on the results, it can be seen that the resistivity decreases with the increase of the nitrogen gas flow rate. K. Shtereva et. al reported that the resistivity decreases with the increase of the nitrogen from 25% to 75% and the further increase of nitrogen in sputtering gas from 75% to 100% leads to the increase of resistivity [27]. The conductivity of the thin films was inversely proportional to its resistivity.

TABLE 1 RESISTIVITY AND CONDUCTIVITY OF NST ZNO THIN FILMS WITH VARIED NITROGEN GAS FLOW RATE

Nitrogen gas flow rate (bubbles/min)	Resistivity, ρ (Ωcm)	Conductivity, σ (S/cm)
0 (undoped)	0.032316	30.944470
30	7.423970	0.134699
40	5.402130	0.185110
50	0.005607	178.358400
60	0.002983	335.242190

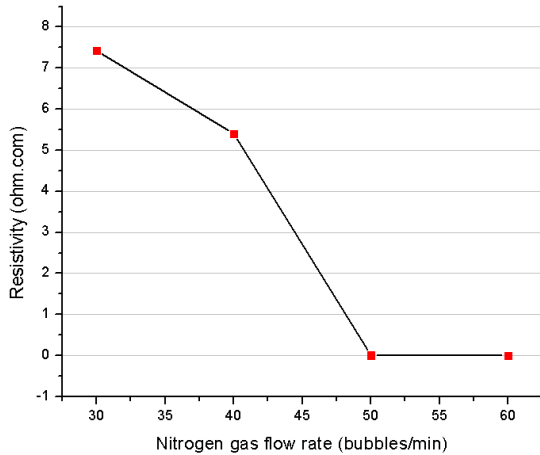


Fig. 7 Resistivity curve resulted from varying the nitrogen gas flow rate

As depicted in Fig. 8, the highest conductivity obtained was 335.24219 S/cm by flow rate of 60 bubbles/min, while the lowest conductivity obtained was 0.134699 S/cm by flow rate of 30 bubbles/min. The conductivity of nitrogen-doped ZnO thin films increases with increased in nitrogen gas flow rate. This different sensitivity may be due to differences in point defect concentration, grain size, or in crystallite or grain boundary composition. As the doping level increases, the grain size increases with decrease in porosity. The presence of air gaps between the grains result in the formation of inhomogeneous dielectric structure, causing the resistivity to be low and the conductivity to be high [23,24]. Therefore the smaller the porosity, the greater the grain size will be and the higher will be the conductivity.

K. Shtereva reported that resistivity of nitrogen doped ZnO were in the range 7×10^2 - $2.8 \times 10^3 \Omega\text{cm}$ while Z.Z Ye et al reported lowest resistivity of $1.2 \times 10^3 \Omega\text{cm}$. [27]. The lowest resistivity obtained, which is $0.002983 \Omega\text{cm}$ confirm the p-type features of our ZnO thin film prepared by Thermal CVD.

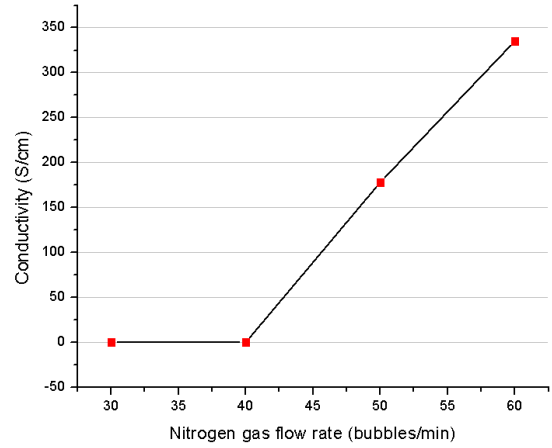


Fig. 8 Conductivity curve resulted from varying the nitrogen gas flow rate.

B. Electrical Properties of Au-Au, Au-Pt, Au-Pd contacts

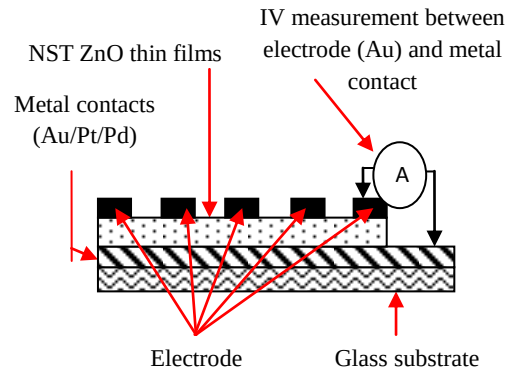


Fig. 9 Illustration of IV measurement between an electrode and metal contact.

As depicted in Fig. 9, the IV measurement between Au electrode and various types of metal contact were made in order to study which metal contact can conduct current effectively. Table 2 shows the summary of resistivity and conductivity for each type of metal contact; Au-Au, Au-Pt, Au-Pd.

TABLE 2 RESISTIVITY AND CONDUCTIVITY OF AU ELECTRODE WITH VARIOUS TYPES OF METAL CONTACT THROUGH N-DOPED ZNO THIN FILM.

Types of metal contact	Resistivity, ρ (Ωcm)	Conductivity, σ (S/cm)
Au	0.005496	181.937490
Pt	0.073378	13.626220
Pd	11.018436	0.090760

As shown in Fig. 10, the resistivity of Au-Au contact shows the lowest resistivity, with value of 0.005496 Ωcm , followed by Au-Pt contact with 0.073378 Ωcm of resistivity and Au-Pd contact shows highest resistivity, which is 11.018436 Ωcm . As the conductivity is inversely proportional with the resistivity, the Au-Au contact has the highest conductivity, which is 181.937490 S/cm compared to the Au-Pt contact and Au-Pd contact which have 13.626220 S/cm and 0.090760 S/cm respectively. This is due to the fact that Au metal has lowest electrical resistivity compared to the other two material, which is 22.14 n Ωm .

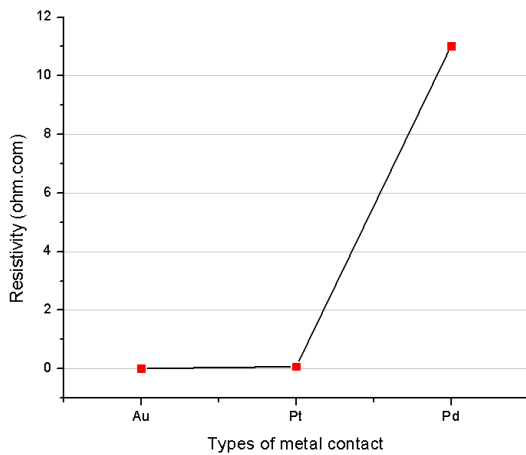


Fig.10 Resistivity curve for different types of metal contact.

Aurum metal is known as the noble metal, where it is a metal that is resistant to corrosion, which makes it to be highly conductive to electricity [25]. Besides that, aurum metal has high concentration of free electrons, which is $5.90 \times 10^{22} \text{ cm}^{-3}$. The higher concentration of free electrons a metal has, the more conductive the metal is. Compared to aurum metal, platinum metal has much higher electrical resistivity, which is 105n Ωm , while palladium metal has 105.4n Ωm . The higher the electrical resistivity of a metal, the less conductive the metal would be. The graph of conductivity of each metal contact is depicted in Fig. 11.

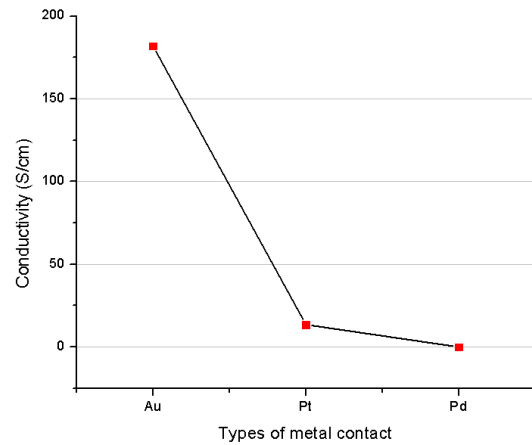


Fig. 11 Conductivity curve for different types of metal contact.

IV. CONCLUSION

The thin film was deposited using Thermal Chemical Vapour Deposition (Thermal CVD) with nitrogen gas dopant source. The flow rate of nitrogen gas was varied from 30 to 60 bubbles/min. NST N-doped ZnO thin film with nitrogen gas flow rate of 60 bubbles/min achieved the lowest resistivity. Under this flow rate the optimum IV characteristics was achieved as compared to the undoped one. By varying the metal contacts, we found that the Au-Au contact has the highest conductivity. For the future research, it is recommended to synthesis nitrogen-doped ZnO thin film with varied annealing temperature to see the changes in IV characteristics. Lastly, the results obtained proved that the flow rate of the dopant source gives effect to the properties of nanostructured nitrogen-doped ZnO thin films.

V. ACKNOWLEDGEMENT

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