The dry process of ZnO film deposition by atmospheric pressure plasma

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Abstract. An atmospheric pressure plasma system has been developed to prepare zinc oxide (ZnO) thin film on the silicon substrate. The precursor of dry powder of Zinc acetylacetonate hydrate was directly sublimated as vapor and carried by Argon into the downstream of Nitrogen plasma jet. The films deposition process was carried out at low temperature and the substrate temperature was not over 300 °C. The examinations of thin film sample by X-ray diffraction (XRD) showed the major peak at 34° was the hexagonal wurtzite structure of ZnO. The surface morphologies and thickness of the films were evaluated by scanning electron microscopy (SEM). The mean square surface roughness of the ZnO film was only 4.063 nm and a smooth surface of ZnO thin film was obtained.

1. Introduction
Over the past few years, several methods were employed for the deposition of ZnO thin film on different substrates, including spray pyrolysis [1-3], sol–gel technique [4, 5], chemical vapor deposition [6, 7], pulsed laser deposition [8], sputtering [9], laser ablation [10] and chemical bath deposition [11]. Sputtering is preferred among these techniques due to its relative high deposition rates, good film properties and process stability [12]. However these processes must be conducted under vacuum in batch process chambers and complicated costly.

Recently, several alternative processes operated at atmospheric pressure were developed. Various types of electrical discharge can be used to generate non-thermal plasmas at atmospheric pressure: dielectric barrier discharge (glow discharge), corona discharge, RF discharge, microwave discharge and arc discharge at atmospheric pressure. Few of studies were restricted as toxic liquid or ZnCl₂ precursor [13-18].

This paper presented the simple process under atmospheric pressure for the deposition of ZnO thin films on silicon wafer. Dry powder Zinc acetylacetonate hydrate was used as the precursor carrying by Argon and sprayed into downstream of the Nitrogen plasma jet to deposit thin film. The temperature of the substrate was not over 300 °C. The power and frequency were maintained at 500 W and 25 kHz, respectively. XRD Rigaku 2200 was used to characterize the diffraction patterns of ZnO thin films. Major peak at 34° of the hexagonal wurtzite structure ZnO were clearly observed. Surface morphology and thickness of the film was evaluated by scanning electron microscopy (SEM) JEOL JSM-6500F.

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2. Experimental Details
The ZnO films were deposited on 5×5 cm silicon wafer by atmospheric pressure plasma jet (APPJ) of CVD system. The schematic of the setup was shown in figure 1. N₂ gas was selected as the main gas to produce plasma and passes through the cannular region between two diodes with 2.5 slm. In this process, dry powder water Zinc acetylacetonate hydrate (Zn (C₅H₇O₂)₂) was used as the Zinc precursor and was put into oil bath for the vaporization using heating oven. The vapour of the Zinc precursor mixed with gas Argon with 900 sccm flow rate were carried to the downstream of the nitrogen plasma jet and sprayed to perform thin film deposition. Oxygen was used as to control the oxygen contents of ZnO films and flow rate was fixed at 30 sccm. The frequency and power of power suppliers were fixed at 25 kHz and 500 W, respectively. The parameters in the process were listed in Table 1.

Rigaku2200X X-ray was used to characterize as-deposited films. The crystallinity was examined by X-ray diffractometry analysis. Thickness and surface morphology of the films were evaluated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively.

![Atmospheric Pressure Plasma Jet](image)

**Figure 1.** Atmospheric Pressure Plasma Jet.

| Parameters used in the deposition process of ZnO film. |
|---------------------------------------------------------|
| Substrate | Silicon wafer, P-type |
| Substrate temperature | 350 °C |
| Source | Zinc acetylacetonate hydrate, 98 % |
| Source Temperature | 150 °C |
| Main gas (N₂) | 2.5 slm |
| Ar carrier gas flow rate | 900 sccm |
| O₂ carrier gas flow rate | 30 sccm |
| Gap | 20 mm |
| Sweep speed | 4 mm/s⁻¹ |
| Deposition time | 5 min |

3. Results and Discussions
The crystal structure of the ZnO film deposited by this APPJ was first examined by Rigaku2200X XRD, and figure 2 showed the diffraction pattern. Three major peaks corresponding to 32 °, 34 ° and 36 ° were significant present. The strong peak observed at 34 ° can be attribute to the (002) plane of the hexagonal wurtzite structure ZnO [19].
Figure 2. The XRD pattern of the ZnO deposited film by using the APPJ.

Figure 3 showed the SEM morphologies for ZnO film. The cross section SEM image for the deposited ZnO thin film in figure 4 showed a well defined compact and uniform. EDS analyzed to identify the Zn element on silicon substrate shown in figure 5. The deposition rate 150 nm/s was demonstrated in figure 6.

AFM 3D and 2D images of the ZnO film of 1×1 μm² sample were shown in figure 7 and 8 respectively. The mean square surface roughness for a 1×1 μm² square section of the ZnO film was only 4.063 nm. The surface morphology of the Zno film in this proposed process was smooth.
4. Conclusions
Thin films of ZnO were successfully deposited on silicon substrates by atmospheric pressure plasma jet in vapor phase using a dry powder Zn precursor. The X-ray diffraction pattern confirmed that the growth of hexagonal ZnO was formed. Thus, this present process provided a potential simple, inexpensive technique to grow ZnO film at a high growth rate with approximate 0.5 μm h⁻¹.

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