

Research Article

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Deposition of Zn-containing films using atmospheric pressure plasma jet

Abstract: The purpose of this work was to deposit Zn-containing films on Si substrates using the commercial atmospheric pressure plasma jet “kINPen’09.” In preliminary experiments Zn-containing films were deposited on the silicon substrates immersed in water solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt. The surface composition of deposited films was analyzed by the XPS (X-ray photoelectron spectroscopy) technique while the bulk composition was studied by means of XRD (X-ray diffraction) measurements. The film thickness was measured by a profilometer. We have determined that the concentration of the zinc nitrate solution as well as changes in the deposition time resulted in a large fluctuation of the deposited film thickness. However, the successful deposition of the Zn-containing films on the Si substrate was definitely confirmed.

Keywords: Atmospheric pressure plasma jet, film deposition, zinc

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1 Introduction

At present, the atmospheric pressure plasma jet (APPJ) as a source of non-equilibrium low-temperature plasma, attracted attention due to its wide potential for interesting applications such as surface modification, bacterial inactivation, thin-film deposition, maskless etching,

etc. [1-9]. The use of APPJ for thin film deposition is very attractive as the reactor chamber can reach very large sizes [10,11]. Deposition of different films such as SiO_2 [12-16], TiO_2 [17] and ZnO using other thin films techniques [18-20] on various substrates were already reported.

The conductive transparent oxide ZnO as thin film has attracted high attention for its low cost, non-toxicity as well as stability. As to the electric properties, the un-doped ZnO thin films are n-type due to intrinsic defects. To increase the stability and conductivity of ZnO films group-III elements, alternative dopants such as Al, Ga, and In were used.

A number of methods was reported that can be used for deposition of ZnO-based thin films on several substrates such as RF magnetron sputtering [21], ion plating [22], pulse laser deposition [23,24], and metalorganic chemical vapor deposition [25]. Among those techniques also stands the procedure using the APPJs. This technique has many advantages, such as low cost, high processing speed and good suitability for large-scale applications mainly because it does not require an expensive vacuum system.

For the deposition of Zn-containing films, the zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has been usually used as a precursor [26-28]. The reason for choosing this salt is its low price and its capacity while heated to form zinc oxide, nitrogen dioxide and oxygen. Next, the Zn-containing films can play an important role in the development of new materials for the next generation of green device applications, displays or in plasma-assisted catalysis [29].

As mentioned before, a chance for deposition of Zn-containing films was already reported. But to our best knowledge in all reported experiments dealing with the Zn, film depositions were obtained only by precursors and additives in the gas phase. However, so far, nobody tested to deposit of these films onto substrate directly from solutions. This method has many advantages. First of all, temperature sensitive materials could be treated in such a way. Different chemical compounds could be deposited on various substrates to achieve the desirable properties. Moreover, this technique is low-cost and easy to handle.

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2 Experimental procedure

2.1 Plasma source

For our experiments, the atmospheric pressure plasma jet “kINPen 09” which generates cold plasma was used. This APPJ was selected as it is one of the industrially available plasma sources that allow obtaining non-equilibrium atmospheric plasma. The principal scheme of the plasma source is shown in Fig. 1. A pin-type electrode of 1 mm in diameter is coupled with a high-frequency (HF) voltage (1.1 MHz, 2 - 6 kV_{pp}) generator and is mounted into the capillary made of quartz (1.6 mm inner diameter). The ignition of plasma takes place at the top of the centered electrode and propagates outside the nozzle. The length of the plasma jet depends on the RF power and was 10 mm for the working power of 7 W. The diameter of the plasma jet was about 1 mm. The temperature of the plasma could range from 30°C to 150°C depending on the gas flow rate, distance from the nozzle and working power of the device. The detailed description and technical details of the atmospheric pressure plasma jet “kINPen 09” can be found under another reference [30].

For our work, argon gas was selected as a working gas. The working gas flow rate was set to 2 L min⁻¹ in all experiments. The plasma deposition was realized under normal laboratory environment conditions (20°C, 40% relative humidity).

2.2 Deposition process

The zinc nitrate hexahydrate salt ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; supplied by Sigma Aldrich) was dissolved in distilled water and was used as a source of Zn. The purity of salt was 98%. The concentrations of the solutions were prepared ranging from 0.01 M to 0.5 M. The silicon pieces 1.5×2 cm were used as samples which were not treated before the deposition.

The deposition procedure was as follows. A silicon substrate was put into a Petri dish with 45 mL of solution. The sample was fixed by glass pieces which prevented it from moving. The sample was immersed into the Petri dish which was filled with a 5 mm layer solution that covered the sample. The nozzle from the quartz tube was located above the sample. The distance between the nozzle and the solution level was 3 or 7 mm. In all the experiments, the 3 mm gap was used which appeared to be an optimal distance for the deposition. To perform the deposition, the plasma was ignited and generated during selected time

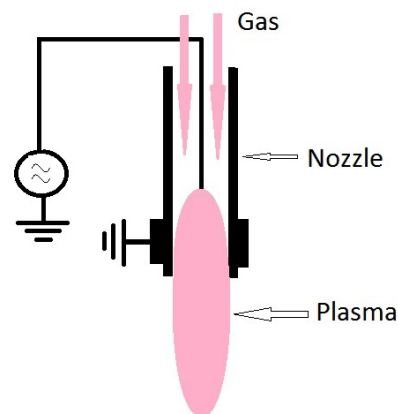


Figure 1: Atmospheric pressure plasma jet (APPJ); INP Greifswald, Germany) - schematic set-up.

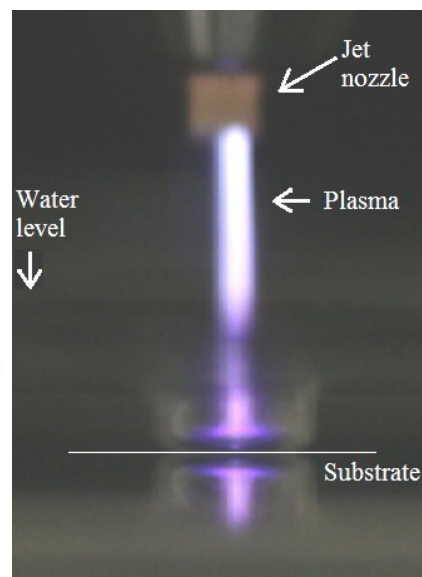


Figure 2: Photograph during film deposition by the APPJ in contact with liquid.

periods. After the treatment, the samples were removed and air dried for 10 minutes. At least 3 samples for each deposition condition were prepared and analyzed.

A principal scheme as well as a photograph of the experiment of Zn-containing film deposition is shown in Fig. 2.

A special procedure was used to prepare films for XRD analyzes. It was conducted to achieve enough thickness of the film. A sample was put into the 45 mL of 0.5 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution and treated with a plasma. The gas flow was 2 slm. The deposition time of one point was 2 minutes. In general, 70 points were deposited making a large rectangular deposited area. The distance between the nozzle of the jet and the water level was 7 mm.

2.3 Film characterization

The thickness of the films was evaluated using a Dektak 8000 profilometer (Veeco). To test film stability the samples were washed in an ultrasonic bath for 15 minutes and then remeasured by the profilometer. Measuring the thickness of the film several profile lines of each film were measured to obtain the average value.

Samples were characterized by X-ray diffractometry (XRD, normal Bragg-Brentano geometry) regarding crystallographic and chemical phases and preferential orientations. XRD was performed on a Seifert “XRD 3000” θ - θ diffractometer equipped with a Goebel mirror. Cu K_α radiation (40 kV, 40 mA) was used.

The XPS measurements were conducted using the ESCALAB 250Xi (ThermoFisher Scientific). The system was equipped with a 500 mm Rowland circle monochromator with microfocused Al K_α X-Ray source. An X-ray beam with 200 W power (650 microns spot size) was used. The survey spectra were acquired with a pass energy of 50 eV and a resolution of 1 eV. The high resolution scans of Zn, N and C were acquired with a pass energy of 20 eV and a resolution of 0.1 eV. An electron flood gun was used to compensate the charges on the surface. Spectra were referenced to the hydrocarbon type C 1s component set at a binding energy of 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software.

3 Results and discussion

Preliminary experiments have shown that a white coloured film can be achieved after about 30 s of treatment.

The deposited film resembled a round spot. The inner diameter had values reaching approximately the diameter of the plasma jet. The diameter of the whole film was approximately twice its size. The inner diameter of the deposited layer was increasing with increasing distance between the substrate and the plasma nozzle.

The variation of the initial concentration of the solvent ranged from 0.01 M to 0.1 M and the deposition time led to the deposition of films with different film thickness. With increasing deposition time and concentration of the solution, the thickness increased as shown in Fig. 3. For the lowest used concentration of 0.01 M and the smallest treatment time of 60 s, the film with the average thickness of around 220 nm was achieved. Increasing the treatment time to 300 s, we were able to achieve film thickness of around 1800 nm. The obtained results showed roughly a linear dependence of thickness vs. treatment time.

A similar behaviour was observed for the films prepared with higher concentrations. The maximum thickness of the film achieved was 9 μm for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.1 M solution and a treatment time of 5 minutes.

In order to test the stability of the film, some samples were washed and then measured again. The results showed that after the wash, the average film thickness decreased. The higher decreases in film thickness were achieved for thicker films. In general, about one half of the film's thickness was washed out. However, the results of the film thickness after the wash showed the same dependence as before.

After affecting the substrate by the plasma during the film deposition, the adhesion of the film was good. Even after washing, the lower parts of the film still exhibited good adhesion properties. We can assume that some amount of the deposited film was removed because of poor adhesion. As far as surface of the film is rough and has peaks of the deposited material we can assume that there are also some pinholes in the volume of the film. After the water treatment in the ultrasonic bath, some part of the deposited material was removed.

In order to compare the effect of plasma on the film formation and film properties, reference samples were prepared. A droplet of solution was put onto the substrate surface and then dried in the ambient air and in the furnace (100°C for 30 minutes). It was observed that after drying, there was a film on the substrate, but the adhesion of it was very weak (the film could be easily removed

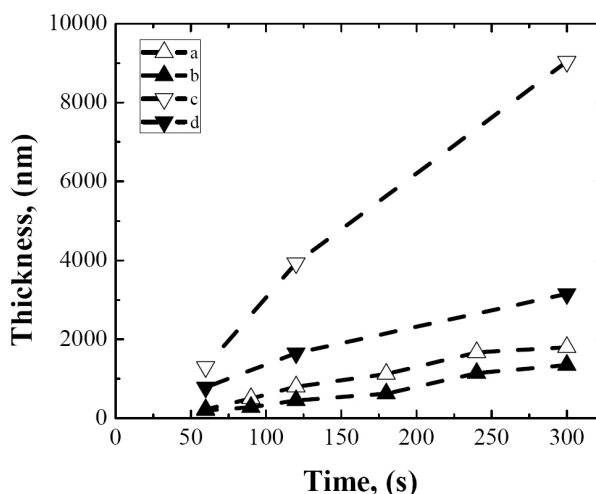


Figure 3: Thickness of deposited films. a) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.01 M solution, b) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.01 M solution after washing, c) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.1 M solution, d) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.1 M solution after washing. Working power – 7 W, distance between the nozzle and solution level – 3 mm.

using one's finger). So we can conclude that the plasma treatment played the major role in the deposition of the Zn-containing film from the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution and the adhesion properties of the films.

The typical profile of the deposited film is presented in Fig. 4. The surface of the film is quite rough. The average thickness (z) for the given parameters (substrate treated 60 seconds in 0.01 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution) is about 300 nm, but the film thickness shows a scattering of values in the range of 200 nm from the average value. The mean diameter values (x) of deposited films are around 2 mm.

The XRD measurements were used to determine the chemical composition of the deposited films. It was found that two crystalline phases were present: $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$ [31] and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ [32] in the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. The results are shown in Fig. 5.

The structure of deposited Zn films with different treatment time was also studied by Irzh [27]. It was shown that for a shorter treatment time, the $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$ films were formed, and for an extended treatment time the films were transformed into pure zinc oxide which with further treatment were transformed into metallic zinc. In the experimental setup [27] a longer treatment time resulted in a higher temperature because the sample holder was not intentionally cooled. It was noticed that the chamber temperature after the deposition was immediately around 250°C. Usually ZnO is obtained using high temperatures of about 500-800°C. In this case, we used plasma with a characteristic temperature of about 50°C (controlled by the thermometer). Also, the water cooling should be taken into account. We assume that the energy of the plasma was sufficient only for dissociating the zinc nitrate in the water and the deposition of ions onto the surface.

In regard to the sample preparation, several dots of the deposited film were used. It can be assumed that in the areas where the dots were overlapping, the film got more energy, and a film structure was changed from $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ to $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$. It can also be assumed that because of a longer treatment time, the amount of H_2O , NO_3 and OH decreased because of evaporation (thermal decomposition).

A XPS analysis was performed to understand the chemical changes that correspond to the deposition of the zinc film. The survey spectrum of a deposited zinc film is shown in Fig. 6. The peaks at 285 eV, 400 eV, 531 eV and 1022 eV correspond to C 1s, N 1s, O 1s and Zn 2p, respectively. The concentration of these elements is summarized in Table 1. Several Auger peaks of Zn (450 - 700 eV), C and O are also present. As it can be visibly noted, a significant amount of carbon exists on the surface of the prepared films. We assume that this is due to the contamination of

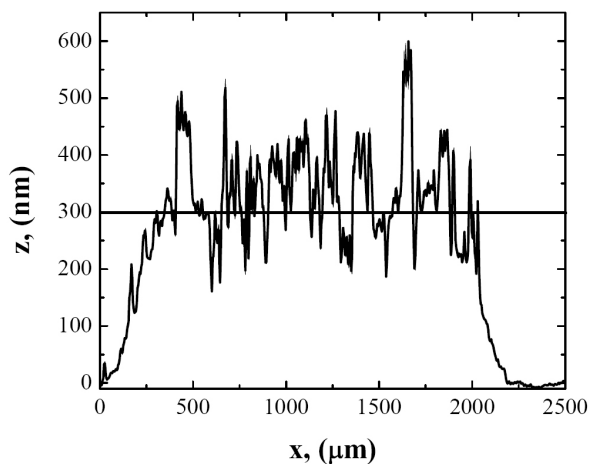


Figure 4: Typical profile of a deposited film. Substrate was treated 60 seconds in 0.01 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. Working power – 7 W, distance between the nozzle and solution level – 3 mm.

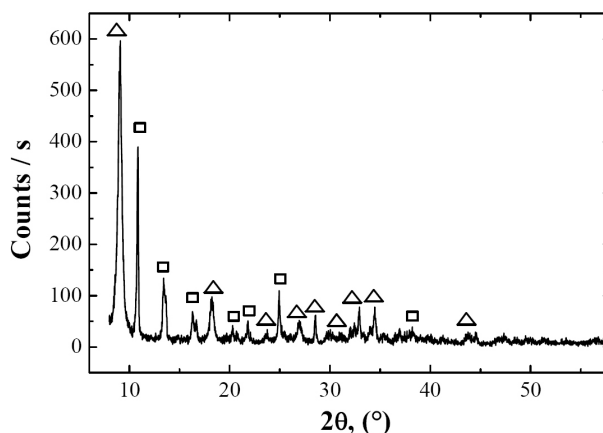


Figure 5: The X-ray pattern of a sample prepared in 45 mL of 0.5 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, Δ $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$, \square $\text{Zn}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})$. Working power – 7 W, distance between the nozzle and solution level – 7 mm.

the film from the surrounding environment. The surface of the films is rough and it is possible that carbon adhered between the peaks of the deposited material.

In order to reveal the chemical nature of the deposited zinc containing film, a deconvolution analysis of Zn 2p, N 1s and C 1s was performed as shown in Fig. 7-9. The Zinc showed that the peak was deconvoluted into 3 components. See Fig. 7. The components at binding energies of 1021.4 eV, 1022.3 eV and 1023.2 eV were attributed to the metal Zn, ZnO and $\text{Zn}(\text{OH})_2$, respectively [33]. The deconvolution analysis revealed three components at binding energies 396.9 eV, 403.6 eV and 407.4, which correspond to N^3 , NO_2^- and NO_3^- , respectively for nitrogen [34] (Fig. 8). Any components which could be attributed to Zn-N bonds (at energy range of 397.5-3985 eV) were not observed. In order to confirm our presumption regarding

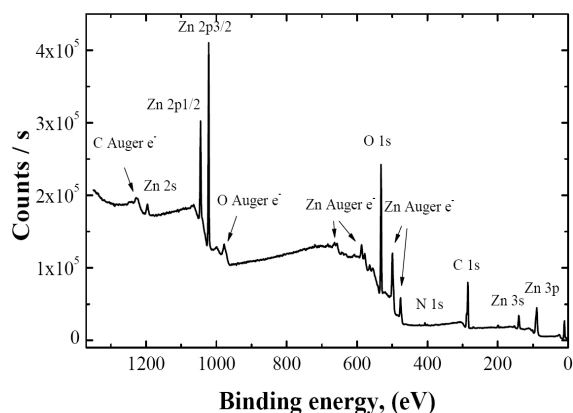


Figure 6: XPS survey spectra of a sample treated in the 0.5 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution for treatment time of 5 minutes. Working power – 7 W, distance between the nozzle and solution level – 3 mm.

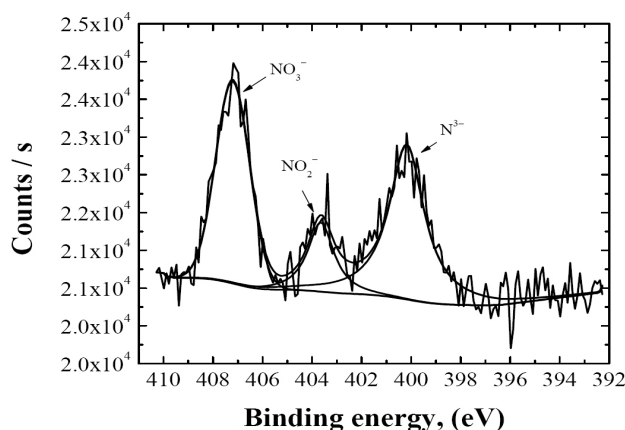


Figure 8: Deconvoluted XPS N 1s peak.

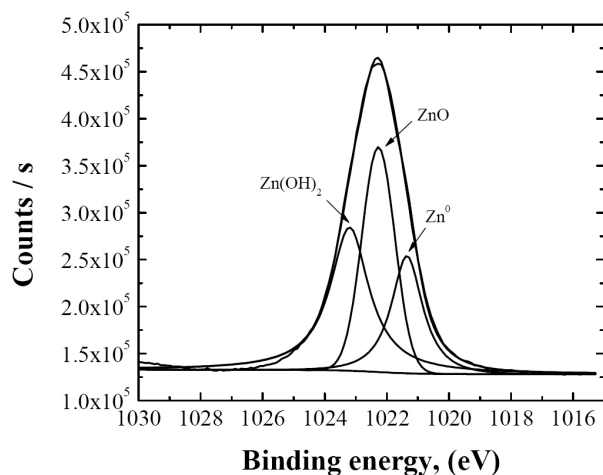


Figure 7: Deconvoluted XPS Zn 2p peak.

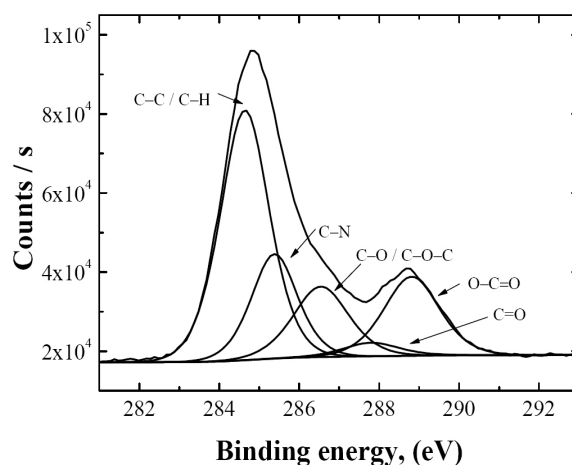


Figure 9: Deconvoluted XPS C 1s peak.

Table 1: Concentration of elements in the deposited films obtained by XPS measurements.

Element	Atomic concentration (%)
O	38
C	46
Zn	14
N	2

the presence of the carbon in Zn films, the high resolution scans of carbon were measured. The C 1s peak that was observed fit with 5 principal components: C-C/C-H (binding energy at 284.7 eV), C-N (285.4), C-O /C-O-C (286.5), C=O (287.8) and O-C=O (288.8) as it is shown in Fig. 9. These results confirmed the feasibility to prepare the zinc film from a liquid solution using the atmospheric pressure plasma jet “kINPen’09”.

4 Conclusions

The atmospheric pressure plasma jet “kINPen’09” was successfully used to test the possibilities of the Zn-containing film deposition on a Si surface from liquids. The plasma deposition was done from a water solution of zinc nitrate hexahydrate salt. Varying the plasma deposition parameters (the distance between the nozzle and the substrate, concentration of the solution and treatment time) it was possible to control the process. The deposited layers were characterized by the XPS and XRD techniques. The formation of new chemical compounds as well as their crystallographic phases with a Zn/N ratio different from $\text{Zn}(\text{NO}_3)_2$ was proved. The results achieved confirm that it is possible to deposit the Zn-containing film of different thickness from the solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt onto the Si substrate. The maximum

average film thickness was about 9 μm for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.1 M solution with a treatment time of 5 min. Films as thin as 220 nm were obtained after 60 s of treatment in the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.01 M solution. The stability of the obtained films was tested as well. It is evident that after the wash, about one half of the deposited film remained on the surface.

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