

Change of conductivity of ZnO films by an annealing

**Oleksiy V.Penkov, Vadim Yu. Plaksin, Rakib Mansur, Min Gook Ko,
Heon-Ju Lee ¹**

¹Department of Energy Engineering, Cheju National University, Jeju-si
Korea, penkov@cheju.ac.kr

The experiment on annealing of ZnO films was performed. Films were deposited by DC Arc plasmatron. The influence of the annealing temperature on the film structure and conductivity were studied. It was shown that annealing at 550°C improves the crystalline structure of the ZnO film and decreases the films resistivity.

Keywords: plasmatron, zno, annealing

1. INTRODUCTION

Transparent conductive zinc oxide (ZnO) has been extensively studied in recent several years because it is non-poisonous, abundant and cheap material with interesting properties. ZnO films have different applications like transparent conductive layers in solar cells, protective coatings and so on. Industrial applications of the ZnO films require of development of cheap, effective and scalable technology. Typically ZnO films have been deposited by various techniques such as RF sputtering, pyrolysis and metal-organic CVD [1-3]. Most of these techniques don't completely satisfy the industrial requirements.

In our previous publications [4] the new perspective ZnO deposition technology based DC Arc Plasmatron was described. This technology has several advantages (low cost, high deposition rate, low substrate temperature). Films deposited using this technology has can be used only as protective or insulation coatings because of very high resistance. Applying of plasmatron technology in the microelectronics or solar cell production requires the improvement of electrical

properties of the films. This can be doping or post-deposition treatment such as annealing, or their combination.

In our work we studied effect of the annealing on the structure and properties of ZnO films deposited by DC arc plasmatron.

2. EXPERIMENTAL DETAILS

ZnO films were deposited using an axial-type DC plasmatron [4,5]. The schematic view of the experimental setup is shown on the Fig. 1. The plasmatron consists of the cathode (tungsten) and the nozzle-type, water-cooled anode. Anode orifice is connected to the activation chamber. An inert gas, argon, is supplied through an anode channel to protect the cathode and the anode. High voltage, high frequency AC is applied across the cathode and the anode to initiate the breakdown in the inter electrode gap, and then a continuous DC voltage maintains the ignited arc.

Oxygen is supplied to argon-arc region (to the activation chamber), where it interacts with the plasma and activates. After this, the plasma flows through the intermediate cap into the reaction chamber.

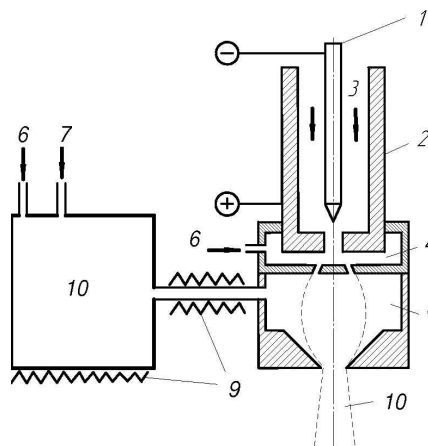


Figure 1: The schematic diagram of the axial plasmatron: 1 – cathode; 2 – anode; 3 – argon supply; 4 – activation chamber; 6 – oxygen supply; 7 – water supply; 8 – zinc precursor tank; 9 – heater; 10 – resulting plasma flow.

The zinc precursor ($\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$) was contained in the temperature controlled tank and was kept at 100°C. Since using of monohydrate form of the zinc acetylacetonate gives better results, the water was injected into the tank to prevent dehydration during heating. The micro-dose pump was used for injection of the water. The water flow rate was 0.3 sccm. The $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$ gas carried with oxygen through the heated pipe into the reaction chamber.

The ZnO films were deposited under following conditions: the plasmatron current 50 A, voltage – 15 V (power about 750 W), argon flow rate - 1500 sccm, oxygen flow rate through the activation chamber - 100 sccm, oxygen through the precursor tank – 100 sccm. The structure of the films was studied by x-ray diffractometry and SEM. Resistivity was controlled by 4-probe technique.

Annealing was performed in the automatic controlled oven at the atmospheric pressure. Duration of annealing was 1 hour.

3. RESULTS AND DISCUSSION

The ZnO film was deposited on silicon substrate by the plasmatron at the room temperature. Deposition time was 15 minutes. SEM image of cross-section of the as-deposited film is shown on the fig. 2. We can see that the film has good dense structure without caves and bubbles. Thickness of the film is about 1200 nm.

XRD shows that the as-deposited film has an amorphous structure, because there are no diffraction peaks on the X-Ray diffraction patterns [4]. It was expected since high-speed deposition on cold substrate in nonequilibrium conditions usually leads to the formation of low ordered (or amorphous) structure. During experiment the substrate temperature didn't excide 70°C. The deposition rate of 80 nm/min was achieved.

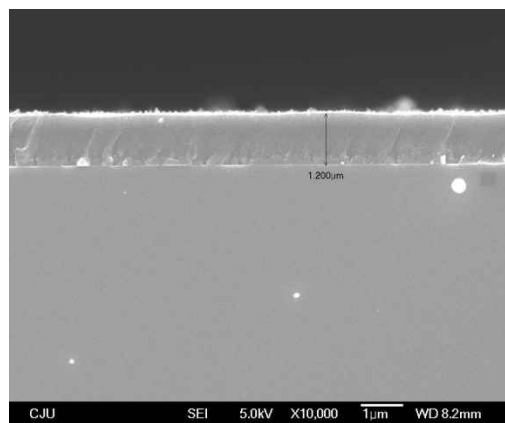


Figure 2: SEM image of the as-deposited ZnO film on silicon substrate.

Because of the amorphous structure and, probably, large amount of the structural defects, the electrical transport in the film is strongly complicated. This leads to high resistivity of the film – the measured value of the resistivity at the as-deposited state was about $2.2 \cdot 10^6 \Omega/\text{cm}$.

After deposition, series of annealing in the wide range of temperatures was done. The aim of the annealing was improving of the structure of the ZnO film.

SEM didn't show any significant changes of the film after annealing. But the crystalline structure of the film was dramatically changed at the annealing temperature more than 500°C. The crystallisation occurs in the temperature range between 450 and 500°C, and the diffraction patterns of the annealed films have a peak at $2\theta=34.4^\circ$. This peak is associated with the (002) crystallographic plane of hexagonal phase ZnO. Increasing of the annealing temperature leads to increasing of diffraction peak's intensity due to re-crystallisation and increasing of the grain size in the film.

Increasing of the annealing temperature leads to decreasing of the film resistivity (fig. 3). In the range from room temperature to 400°C this change is relative small, but effect of the temperature dramatically increase then the annealing temperature became higher than 500°C. These changes correspond to crystallisation process in the film.

After annealing at 550°C the resistance decreases to 30 Ω/cm .

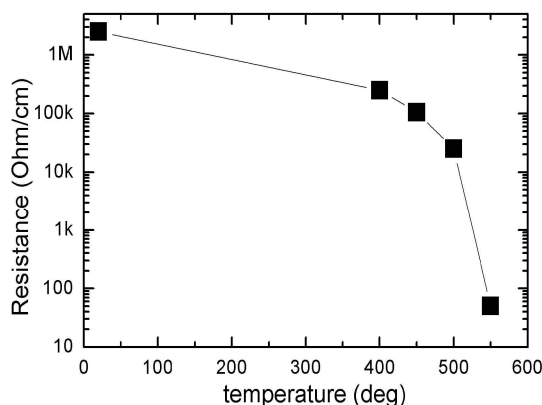


Figure 3: ZnO film resistance vs. annealing temperature.

4. CONCLUSION

The experiment on annealing of ZnO films deposited by DC Arc plasmatron was

performed. It was shown that films deposited at the atmospheric pressure are insulators due to amorphous structure.

Further annealing at the 500-500°C leads to improving of the crystalline structure of the ZnO films and decreasing of their resistivity.

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