Effect of annealing on electrical properties of plasmatron deposited ZnO films

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1. Introduction

Transparent conductive zinc oxide (ZnO) has been extensively studied in recent several years because they have very interesting properties. Besides this, zinc oxide is non-poisonous, abundant and cheap material. ZnO films are employed in different applications like transparent conductive layers in solar cells, protective coatings and so on. Wide industrial application of the ZnO films requires of development of cheap, effective and scalable technology. Typically used technology like RF sputtering, pyrolysis and metal-organic CVD [1-3] 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). Currently, 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 achieved by optimization of deposition parameters, using of doping, or by post-deposition treatment such as annealing, or by combination of mentioned.

It was shown that proposed technology can be used for the deposition of pure ZnO film with good electrical and optical properties. Proposed technology has several disadvantages which can be overcome in the near-term outlook.

2. Experimental details

ZnO films were deposited using an axial-type DC plasmatron [4]. In this paper, liquid ZnO precursor consists of zinc acetylacetonate and ethanol was used, so plasmatron was. The discharge part had no changes, but the rest of the details were seriously modified. The discharge part had no changes, but the rest of the details were seriously modified accordingly.

Compare to basic configuration [4], an injection system for transportation of the easy evaporated solution to the high-temperature reaction chamber was added. On the side wall of the reaction chamber the water cooled copper injector is mounted. To decrease heating by plasma gas and hot body of the reaction chamber, the injector is covered with ceramic. The injector has 4mm diameter inclined channel for transportation of the solvent to the center of the reaction chamber. For retention of the solvent in the reaction chamber, its bottom is closed by brass cap with large amount of small (1 mm) randomly distributed holes and a metal sponge.

The solution is supplied into the reaction chamber by a micro-dose pump. The solvent drops from the injector to the bottom of the reaction chamber, evaporates, because the bottom has high temperature due to heating by plasma flow, and products of the reaction are transported by the gas flow through the to the substrate.

Exit nozzle has conical shape and mounted by thread. This allows easy regulating of the distance between the plasmatron and the substrate. In our experiments, the typical distance was 10 mm.

Substrate is mounted on the heater so its temperature can be varied up to 600°C.

The ZnO films were deposited on silicon substrates under the following conditions: a plasmatron current of 50-100 A, a voltage of 12-15 V, an argon flow rate of 1 - 2 l/min, an oxygen flow rate through the activation chamber of 2 l/min, solution flow of 0.3 – 1 sccm, and a deposition time of 20 min.

Post deposition annealing was done in the hydrogen atmosphere.

The crystalline structure of films was analyzed by X-Ray diffraction using Rigaku DMAX 2200 device with Cu-K_a radiation source. The thickness was measured with Gaertner L1160 ellipsometer.

3. Results

The ZnO film was deposited by the plasmatron at the room temperature and atmospheric pressure. In spite of absence of an external heating, the real substrate temperature was in the range of 120-150 °C because the plasmatron produces the flow of hot particles and heats the substrate. Dependences of substrate temperature and deposition rate versus argon flow rate are linear. Increasing of the argon flow leads to more effective heat transfer from discharge area to the substrate. Increase of the plasmatron current produces more energy and gives the same result. Increasing of both parameters leads to high deposition rate due to more effective decomposition of the zinc precursor. From other hand, the substrate temperature will be increased also. The desired balance between substrate temperature and deposition rate may be achieved from properties of substrate's material.

X-ray diffraction for the film exhibits no diffraction peaks. This fact means that the plasmatron deposition at the atmospheric pressure and without external heating of the substrate leads to growth of amorphous films.

Formation of the amorphous structure during atmospheric pressure deposition can be explained in the following way: high-speed deposition on a cold substrate in non-equilibrium conditions leads to the growth of a low-ordered structure. At atmospheric pressure, the thermal energy of the particles delivered on the substrate is very low due to heat transfer to the ambient atmosphere and the energy of the particles is not enough for arrangement of the structure by surface diffusion.

XPS analysis of the ZnO film surface is shown relative high amount of impurities on the films surface – 15 at.% of carbon and 2 at.% of copper. Using the alcohol solution of the zinc acetylacetonate leads to increasing of the carbon content compare to using of the ZnO powder. Presence of the cupper on the surface can be result of transport of the anode material.

For measurement of the chemical composition in the bulk, the ion-gun etching was used for remove of the surface layer with thickness about 10 nm. Etching was performed using 200 eV argon ions with normal incidence during 1 minute. Ion current was about 20 nA. In the bulk amount of the impurities was dramatically decreased – concentration of carbon was < 1 at. %, and any copper lines weren't detected.

Etching decreases the resistivity of the film from $2 \cdot 10^6$ down to $3 \cdot 10^4$ Ω·cm. This results shows that some post-deposition treatment of surface is required for removing of the carbon-rich layer from the surface. We expected that argon-hydrogen plasma generated by the plasmatron can be used for this purpose.

The initial optimization of the gas flow rate was performed. It was found that stoichiometry ratio (ZnO) of the zinc and oxygen was achieved at 1.33 Ar/O_2 ratios and further decreasing of the oxygen flow didn't change the chemical composition. At the higher oxygen flow the content of oxygen in the films exceeds the optimum stoichiometry ratio. It is good known that excess of oxygen atoms in the ZnO leads to impetuous increasing of the resistance [6]. Oxygen ratio higher than 1.33 can be used for production of high-resistance films (R > 5 MΩ·cm).

The proper average transmittance of the films in the range 400-800 nm is about 90%

After deposition, series of annealing in hydrogen atmosphere in the wide range of temperatures was done. Because removing of the top layer decrease the resistance, annealing of etched samples was performed. The aim of the annealing was improvement of the structure of the ZnO film and doping it by hydrogen atoms for increasing of the conductivity. X-ray diffraction shows that the crystalline structure of the film was dramatically changed at the annealing temperature more than 500°C. The crystallization occurs in the temperature range between 480 and 500°C, and the diffraction patterns of the annealed films have a peak at 2θ=34.4° 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-crystallization and increasing of the grain size in the film.

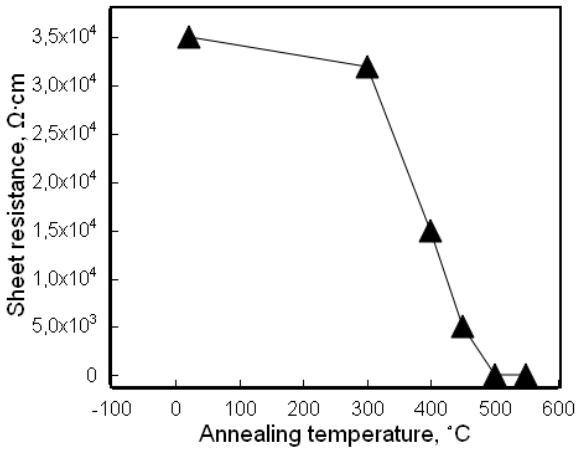

Fig. 1 Sheet resistance of the ZnO film as a function of the annealing temperature in hydrogen atmosphere.

Increasing of the annealing temperature leads to decreasing of the film resistivity. In the range from room temperature to 300°C this change is relative small, but effect of the temperature dramatically increase when the annealing temperature became higher than 300°C. The beginning of changes corresponds to saturation of the films by hydrogen. The further decreasing of the resistivity is the result of crystallization and decreasing of amount of defects in the films.

4. Conclusion

Deposition by a DC Arc plasmatron with further annealing in the hydrogen can be used for low-cost production of zinc oxide films with good electrical and optical properties.

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