Deposition of ZnO Film by Using an Atmospheric Pressure Cold Plasma Generator

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ABSTRACT

Under atmospheric pressure, homogenous nonequilibrium low temperature plasma was generated by an rf (13.56 MHz) excitation of He gas. Using this cold plasma, ZnO films were deposited on glass substrates exposed to air at room temperature by feeding bisdipivaloylmethanato zinc into the plasma with He carrier gas. Thickness and electrical resistance of the films were then measured. Rf power dependence, anode and cathode gap on the thickness as well as electrical resistance were then investigated.

Keywords: transparent electrical conductive ZnO film, atmospheric pressure, cold plasma generator, bisdipivaloylmethanato zinc, He gas.

1. INTRODUCTION

Transparent electrical conductive zinc oxide (ZnO) films have generated much attention as low-cost transparent electrodes for solar cells such as amorphous silicon (a-Si) or copper indium diselenide ($CuInSe_2$) [1]. ZnO films are usually prepared by methods such as metalorganic chemical vapor deposition (MOCVD) / chemical vapor deposition (CVD) [2-3] and sputtering (SP) [4-5]. Most of these however require sophisticated and costly apparatus making it unsuitable for large area production.

Recently, we developed a shower-type plasma generator (plasma torch). It is composed of a cylindrical Al cathode and Al plate anode. The homogeneous nonequilibrium plasma called glow plasma was generated by an rf excitation of flowing He gas at 1 atm. In this paper, we report on the application of the atmospheric pressure cold plasma torch to the deposition of ZnO films by feeding bisdipivaloylmethanato zinc (DPM_2Zn) into the plasma. The influence of He gas flow rate, rf power, anode and cathode gap on the deposited ZnO films are discussed.

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2. EXPERIMENTAL

The atmospheric pressure cold plasma torch used in this study is schematically illustrated in Fig. 1. The torch is made of a 100 mm high Teflon tubing (50 mm in diameter at its top and 90 mm at its bottom, this part being fixed to the cathode). The cathode is composed of a disk (90 mm in diameter, 10 mm thick) and a cylinder (50 mm in diameter, 20 mm high) connected to an rf (13.56 MHz) generator. 33 holes with diameters of 0.5 mm each were drilled into the cathode for the purpose of introducing He gas into the gap. The grounded anode is an Al plate fixed on to a platform. Corning glass (#7059) substrate was placed on top of the anode plate. The space between the anode and cathode (gap) can be manipulated by adjusting the height of the platform.

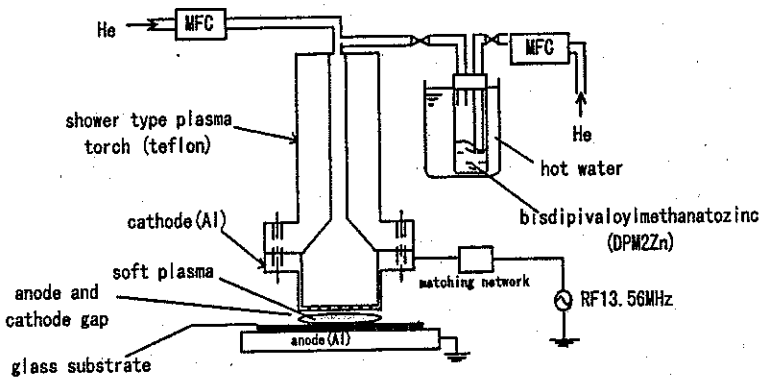

Fig. 1 Schematic diagram of the atmospheric pressure cold plasma torch.

Table 1 shows deposition conditions for our experiment. Plasma was generated by flowing He plasma gas (1800 sccm) and He carrier gas (200 sccm) through the inner space of the cathode down to the gap, where it was excited by a 30 - 50 W radio frequency. DPM_2Zn was vaporized by hot water and carried by the He flow for introduction into the plasma generated at the gap. The experiment was conducted for various gap widths (0.5 - 1.4 mm) and deposition times (10 - 40 min).

Table 1 Deposition conditions

substrate	#7059 glass
substrate temperature	room temperature
source material	bisdipivaloylmethanatozinc
source material temp.	96 ℃
He plasma gas flow rate	1800 sccm
He carrier gas flow rate	200 sccm
rf power	30 - 50 W
deposition time	10 - 40 min
anode - cathode gap	0.5 - 1.4 mm

Film thickness was measured with a surface texture measuring instrument (Surfcom 570A, Tokyo Seimitsu Co., Ltd.). Electrical resistance of the film was tested with a multimeter (E2373A, Hewlett Packard Co., Ltd.).

3. RESULT AND DISCUSSION

3.1 Glow discharge range

Under normal atmospheric pressure, arc discharge is the most commonly observed phenomenon. However, the plasma generator we developed using Al as the cathode has a thin coating of alumina resulting from a process using natural oxidation which enables glow discharge to occur instead of arc discharge. Fig. 2 shows the range of glow discharge in our experiment. The horizontal and vertical axes indicate the length of the anode-cathode gap and the rf power, respectively. When the gap is less than 3.5 mm and rf power between 5 to 60-100 W, stable glow discharge was observed. For gaps of 3.5 mm and above, glow discharge ceased to exist.

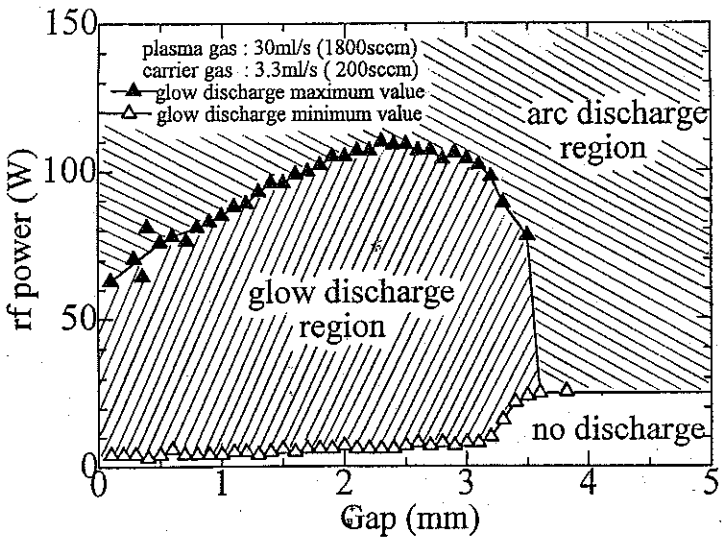

Fig. 2 Grow discharge region of the torch.

3.2 The external appearance of a typical ZnO sample

Fig. 3 shows the diagram of a typical ZnO sample deposited with the cold plasma torch. Spot-like films with diameters of approximately 1.5 mm were deposited directly under the holes drilled into the cathode. Transparent films were deposited when the gap was small but as the gap increased in size, colored films began replacing the transparent ones. This can be attributed to the fact that when the gap is small, more DPM_2Zn is decomposed by the plasma due to the higher rf power per cubic unit.

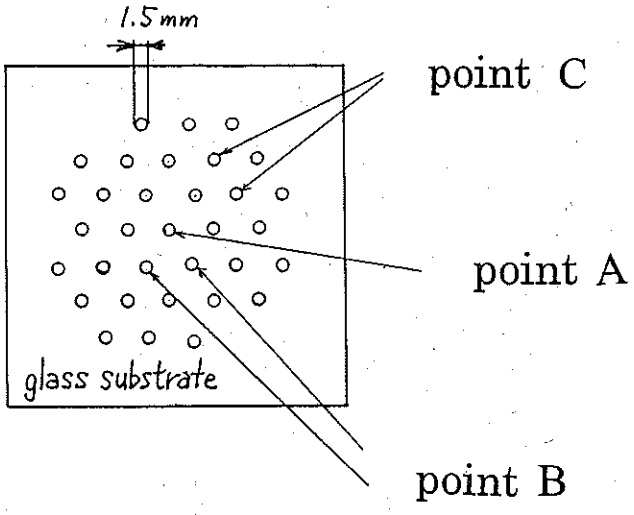

Fig. 3 Schematic diagram of points A, B and C on the ZnO film.

3.3 Film thickness

We marked the ZnO films on the glass substrate A (center film), B (7 mm from the

center) and C (14 mm from the center) as shown in Fig. 3. The film deposited on point A is thinnest, yet it grows thicker as it proceeds from B to C. It seems that due to the difference of the flow rate at the center and surrounding area of the cathode, variation in film thickness is inevitable.

Fig. 4 shows the relation between the deposition time and film thickness. When the gap was small, thicker films were deposited, which similarly applies for longer deposition times. For films of less than approximately 1 μ m, thickness increased linearly against time but for larger values, this rule no longer applied. From SEM observations of these films, it was found that for thicker films, the surface was very uneven, possibly attesting to the extreme increase in overall thickness.

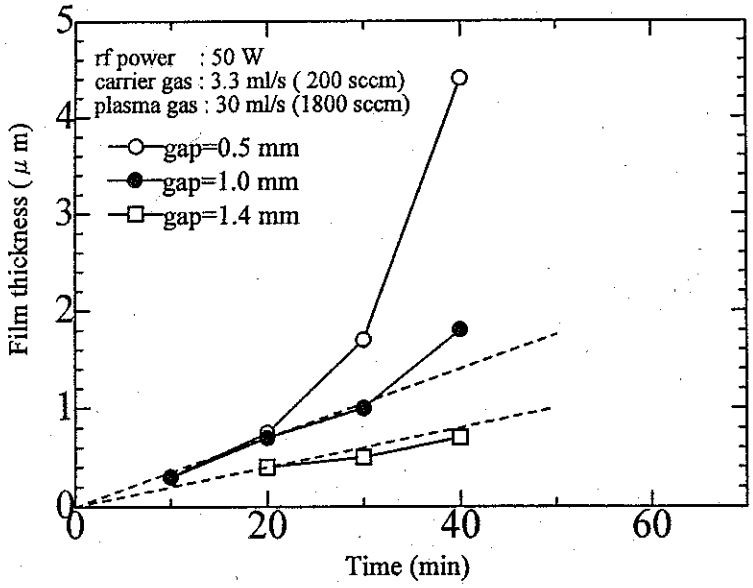

Fig. 4 The relation between the deposition time and film thickness.

3.4 Electrical resistance

Fig. 5 shows the resistance of the conductive ZnO films over periods of 20 min with the rf power set at 35 W. It was observed that when the gap was narrowed, electrical resistance decreased. Resistance dropped to a minimum 4 k Ω when the gap was fixed at 0.5 mm. Fig. 6 shows the film thickness for the same samples as Fig 5. It was also observed that as the gap narrowed, film thickness increased two-fold indicating that the deposited ZnO film has a low resistivity value.

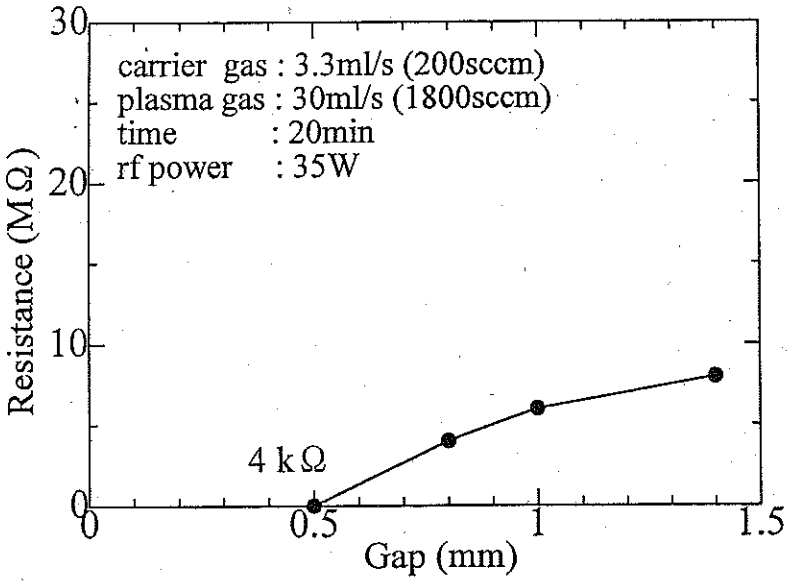

Fig. 5 Resistance of the conductive deposited ZnO film.

4. CONCLUSION

The atmospheric pressure cold plasma torch developed in our experiment was successful in generating stable glow discharge. We utilized this torch to deposit ZnO films and the results obtained are as follows.

1) By feeding DPM_2Zn into the plasma, we were successful in depositing transparent electrical conductive ZnO films.

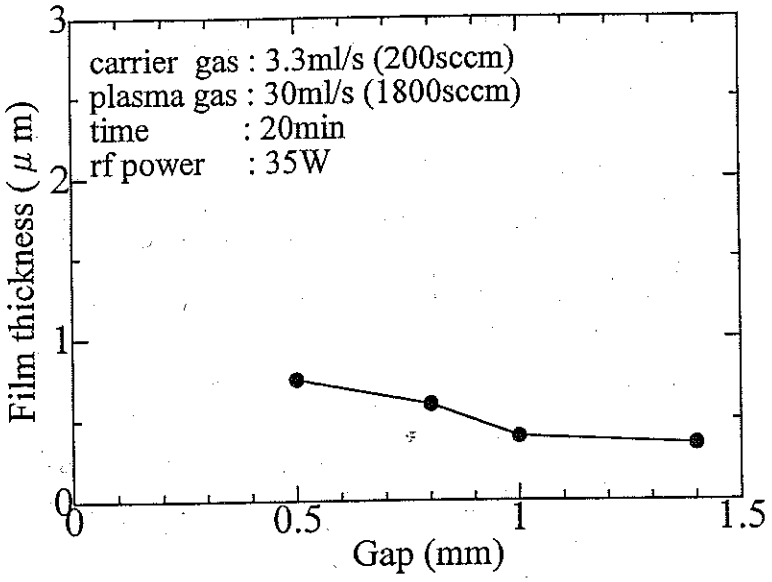

Fig. 6 The film thickness of the same samples as Fig. 5.

2) Succesfl deposition of a ZnO sample, 1.5 μm thick with a low resistance of 4 kΩ was carried out for 20 min with a gap of 0.5 mm at an rf power of 35 W.

Until now, only spot-like films have been deposited. Further studies and experiments in reference to the cathode are in progress to enable better quality ZnO to be produced in the near future.

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