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To cite this article: H Itoh *et al* 2013 *J. Phys.: Conf. Ser.* **441** 012019

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A Development of Atmospheric Pressure Plasma Equipment and Its Applications for Treatment of Ag Films Formed from Nano-Particle Ink

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Abstract. We have developed an equipment of atmospheric pressure plasma with two micro-wave guide antennas, which have a discharge line with 41 slots. The antennas are set against a stage with a heater in a process chamber. A process gas, which is a 1 % H_2 gas diluted by Ar gas and its flow rate is 20 standard litter per minute (slm), flows into the micro-wave guide and goes to a process chamber through each slots. A micro-wave is introduced to the micro-wave guide and the atmospheric pressure plasma grows at each slots. We obtained the electron density of 1×10^{15} cm^{-3} and the H radical density of 1×10^{-16} cm^{-3} at the slot on the condition of a 10 GHz, 1.5 kWatt, pulsed micro-wave with 2.5 pulsed voltage, 4 kHz pulsed frequency, and a duty ratio of 0.16. We applied this system to improve the quality of the spin-coated Ag firm formed from Ag nano-particle ink. This Ag film showed a resistivity of 32 $\mu\Omega$ cm after annealing on the condition of 180 $^{\circ}$C for 30 minutes recommended by the maker (The bulk resistivity of Ag is 1.6 $\mu\Omega$ cm). In order to make the annealing time shorter, we studied the effect of atmospheric plasma treatment of Ag film. We obtained the Ag film of the 5.7 $\mu\Omega$ cm resistivity after the atmospheric pressure plasma treatment under 180 °C for 5 min.

1. Introduction

Recently, the Atmospheric pressure plasma (AP-Plasma) has been investigated extensively. The AP-Plasma has a potential of large area, and high-speed surface treatment and it is useful for the many production lines. The AP-Plasma has high electron density and is able to produce high radical density of a process gas [1]. Then, we have developed a microwave AP-Plasma equipment with 1-meter-length plasma-head.

One of AP-Plasma applications is surface treatment of substrate for the printable electronics, because the AP-Plasma needs no expensive vacuum system and is suitable to apply an continues treatment of substrate surface, for example, hydrophilic treatment, hydrophobic treatment, and surface cleaning. We carried out to improve a quality of Ag film spin-coated using Ag nano-ink by our AP-Plasma equipment and the AP-Plasma produced high quality Ag film under simple treatment, lower process temperature, and shorter process time.

2. Experimental

Figure 1 shows our experimental system. The upper figure shows a horizontal view of our experimental system, and the middle figure shows a vertical view of our experimental system. This system has two microwave rectangle wave guides, and each wave guide has one slot line consisted of 41 slots. The length of the microwave antenna is 1-meter.

The microwave antenna was combined to a treatment chamber to change and to maintain the uniform gas condition. This system has no dielectric plate between the antenna and treatment chamber. We can introduce a process gas into this rectangle wave guide antenna and introduce a process gas into the treatment chamber through the antenna. There is a movable stage to hold a substrate in the treatment chamber, and this stage has a hot plate to heat a substrate.

The power source of microwave produces pulsed microwaves and its frequency is 10 GHz. Maximum output power is 1.5 kW, and pulse width is the value between 5 and 50 μs, and its duty ratio is a value between 0 and 50 %.
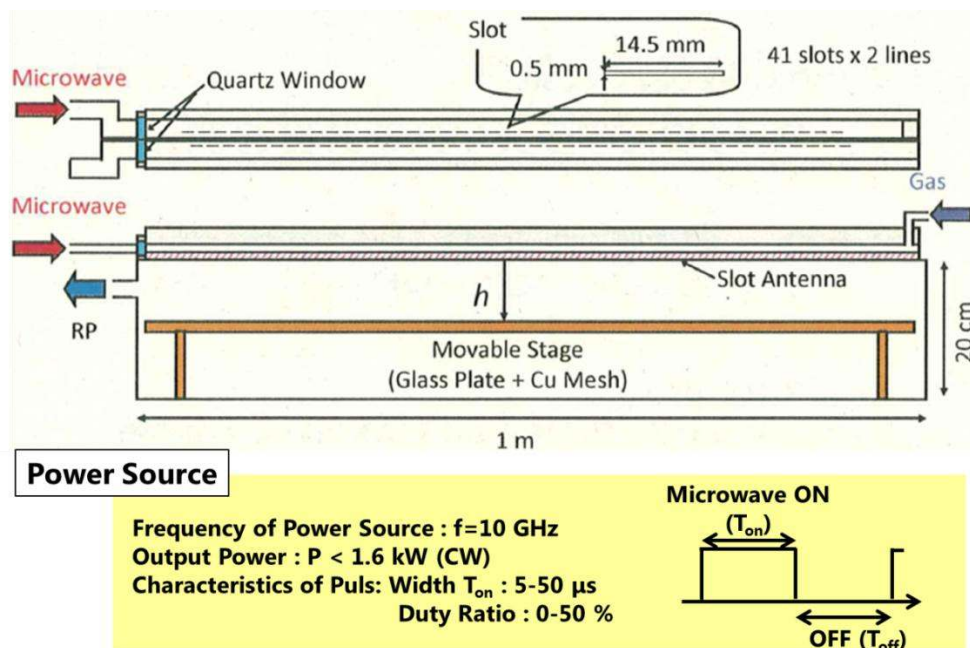

Figure 1.   A schematic diagram of experimental apparatus.

Table 1 shows experimental conditions, measurement method of gas temperature (Tg), electron density (n_e), and hydrogen radical density ([H]) and detail of application of AP-Plasma for the improvement of the quality of Ag film deposited by spin coated method using Ag nano-ink. The process gas is the argon diluted 1 % hydrogen molecule. The flow rate of process gas is 20 slm or 50 slm, and its pressure is 1 atom in the treatment chamber. Substrate used for experiments are Si (100) chips of 15 mm×15 mm, and substrate temperature is a value between room temperature and 180 °C. Process time is a value between 5 min and 30 min.

In order to estimate the gas temperature and electron density, we measured the optical emission of N_2 and H_2 gases, respectively, introduced at a mixing ratio of less than 0.1 % in the main discharge gas. We measured optical emissions using an optical fiver and a spectrometer (SpectraPro 750, Acton Research Corporation, USA). The gas temperature was estimated by the curve fitting between experimental and simulated results of the emission of N_2 2nd Positive Band ($C^3\prod_u - B^3\prod_g$) [2]. The electron density was estimated by the curve fitting between experimental and simulation results of the optical emission spectra of H_β including the Doppler, pressure, instrumental, and Stark broadening effects [3]. H radical concentration was measured by VUVAS method [4].

Table1. List of experimental condition, measurement method of T_g, n_e and hydrogen radical concentration [H], and detail of application of the improvement of Ag film deposited by spin coated method using Ag nano-ink.

Experimental Condition	Process Gas	Pressure (aton)	Flow Rate (slm)	T_{sub} (°C)	Process Time (min)
	1 % H_2 in Ar	1	20, 50	15 – 180	5 – 30

Measurements of T_g, n_e and [H]	Gas Temperature (T_g)	Electron Density (n_e)	Hydrogen Radical Concentration
	Curve Fitting of N_2 2nd Positive Band	Curve Fitting of H_β Spectra Broadening	VUVAS

Application (Ag film)	Material	Material Maker	Deposition Method	Annealing
	Ag nano-ink	DIC Corporation	Spin Coated Method	Hot Plate in Air

We carried out to improve Ag film quality spin-coated using Ag nano-ink by our AP-Plasma equipment and the AP-Plasma produced high quality Ag film under simple treatment, lower process temperature, and shorter process time. We used Ag nano-ink (JAGT-05) produced by DIC Corporation. The Ag nano-ink consisted of Ag nano-particles with a mean diameter of 10 – 50 nm in the solvent of water or alcohol. Ag film was deposited by a spin coating method and was annealed using a hot plate in the air. It is believed that Ag nano-ink is a promising material to produce electrical lines and electro-rods of devices in the printable electronics which does not need expensive manufacturing tools.

3. Results

3.1. Dependence of Electron density and Gas Temperature on Process Parameters

Figure 2 shows the dependence of the electron density and the gas temperature on the process parameters. The left vertical axis is electron density, and the right vertical axis is gas temperature in each figure. The electron density is at around the value of 5×10^{15} cm^{-3}, and the gas temperature is at around the value of 1000 K.

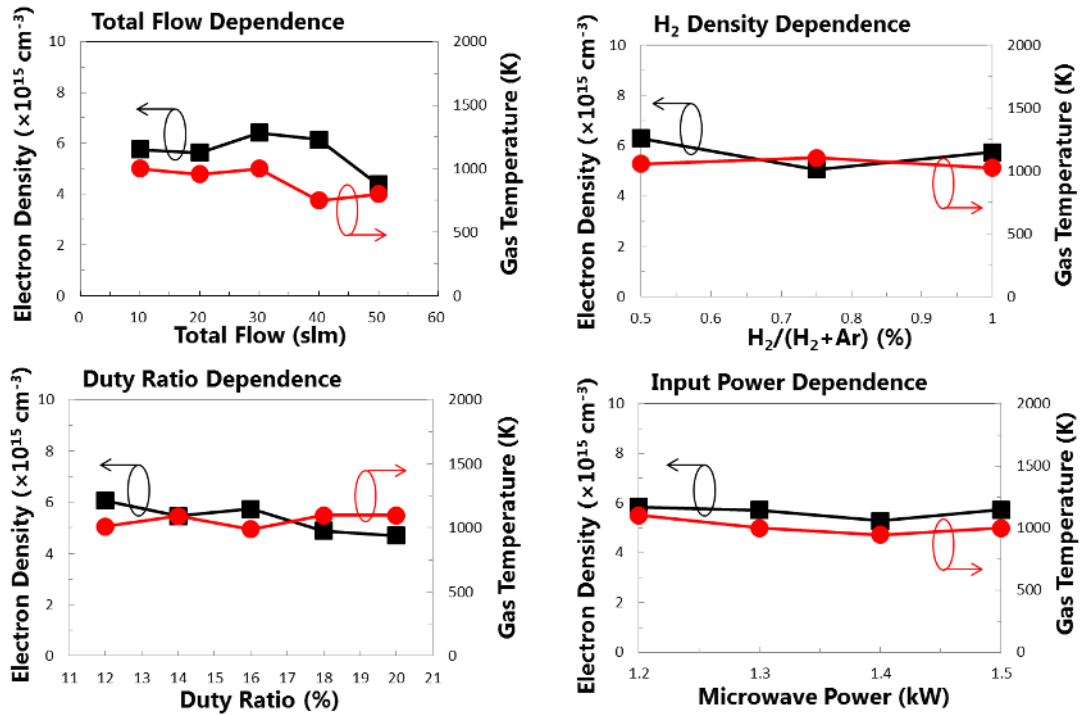**Figure 2.** Dependence of electron density and gas temperature on process parameters.

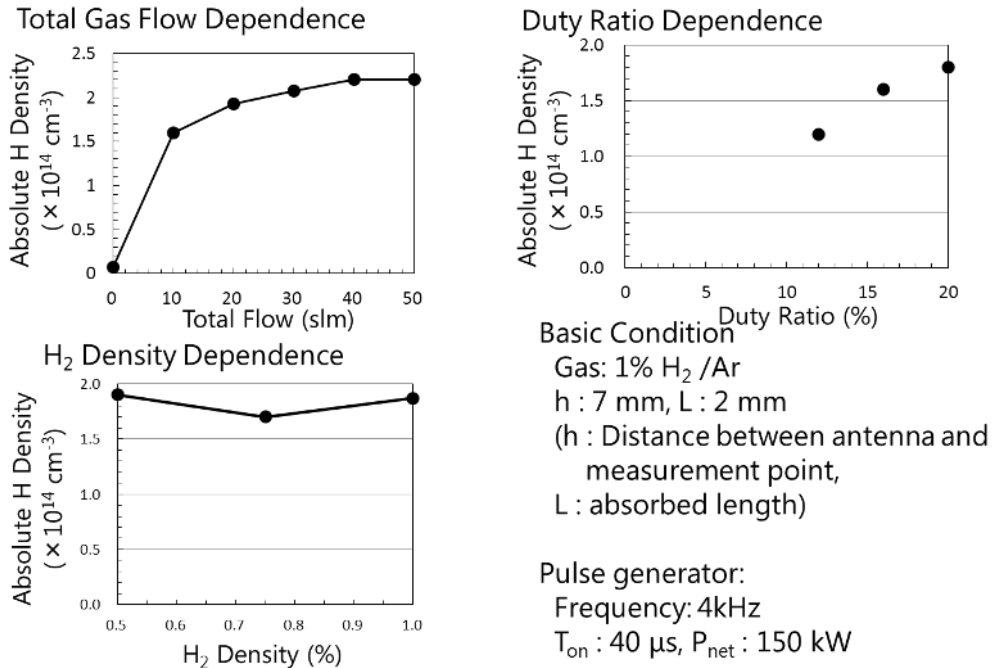*3.2. Dependence of H density on process parameters*

Figure 3. Dependence of H radical density on process parameters.

Figure 3 shows the dependence of the hydrogen (H) radical density on process parameters. The absolute density of H radicals increases rapidly with the increase of the total flow rate from 0 standard-litter-per-minute (slm) to 10 slm, and then the hydrogen radical absolute density increases slightly with the increase of total flow rate.

The dependence of the H radical absolute density shows no significant dependence on the hydrogen molecule (H_2) density and increases proportionally with the duty ratio.

3.3. Dependence of H radical density on the distance from slot antenna

H radicals are deactivated and recombined by many collisions in the atmospheric pressure condition. Figure 4 shows the dependence of H radical density on the distance between the slot antenna and the measuring point. The slope of the decay of the case of the 10 slm total gas flow is larger than that of the case of 50 slm. We can use, however, the high-density H radicals larger than the order of 10^{14} cm^{-3} in the region of the distance less than 5 mm from the slot antenna.
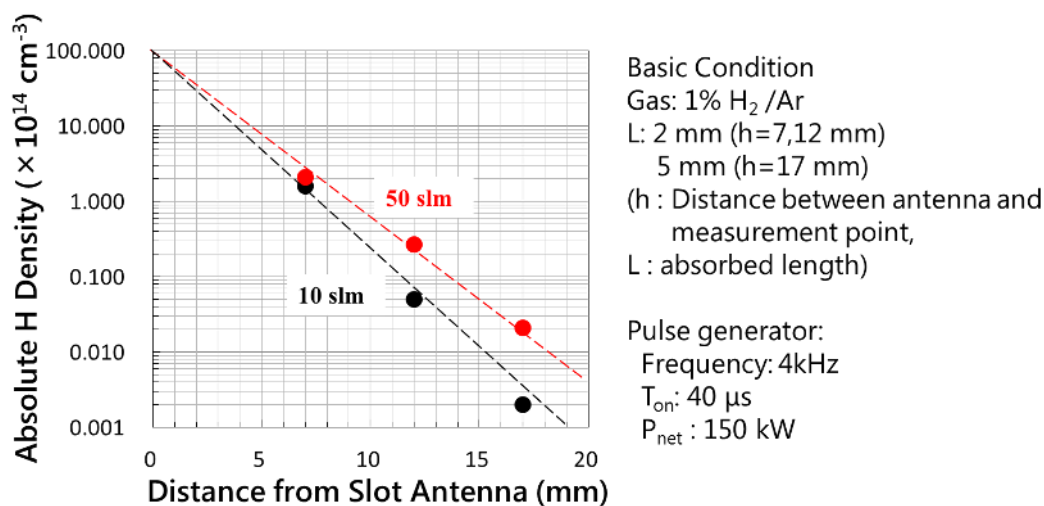

Figure 4. Dependence of H radical density on the distance from the slot antenna.

3.4. Ag Film Spin-Coated using Ag Nano-Ink: Treatment under the Condition recommended by the Ink-Maker

I show one of applications of our atmospheric pressure plasma to improve the film quality of Ag film spin-coated using Ag nano-ink. Figure 5 shows the characteristics of Ag film under the condition recommended by the ink-maker, DIC Corporation. Ag film is spin-coated using the amount of 1 ml Ag nano-ink under the coating condition of 2000 rpm and 10 seconds. And then, the film is under the thermal treatment of 180 $^{\circ}$C and 30 minutes in the air.
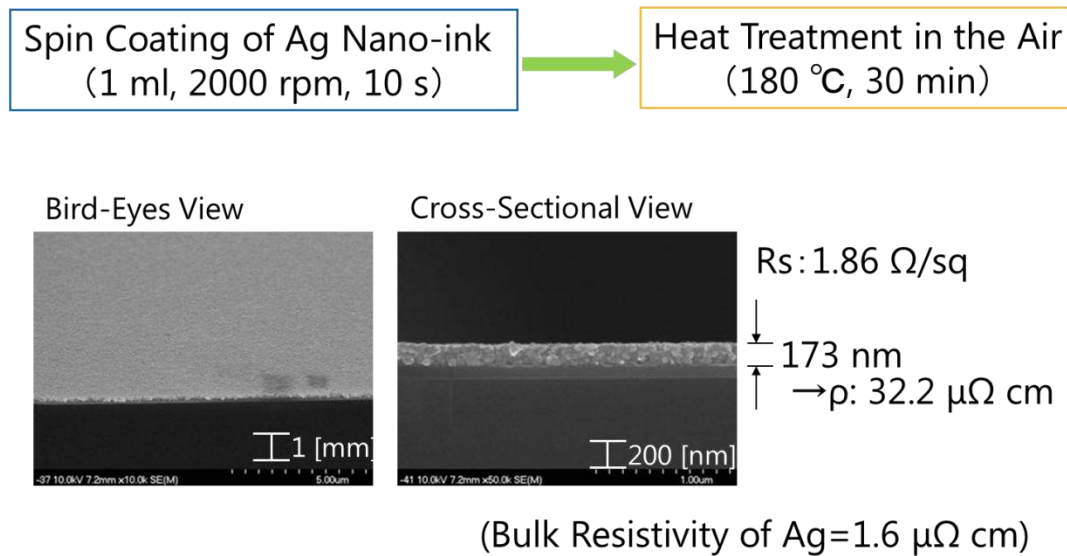
Figure 5. Ag film spin-coated using Ag nano-ink . The treatment is carried out under the condition recommended by the ink-maker.

The surface morphology of the Ag film is very smooth, as shown these two SEM micrographs in Figure 5. The resistivity of this Ag film is 32 μΩ cm. The bulk resistivity of Ag is 1.6 μΩ cm and then the resistivity of this film is about 20 times larger than that of the bulk value.

3.5. Heat and AP-Plasma Treatment in the H_2/Ar Atmospheric Pressure

Figure 6 shows the bird-eyes view and cross-sectional view of Ag film after treatment of only 180 °C heat treatment, only AP-Plasma treatment, and both heat and AP-Plasma treatment. The treatment time is 10 min.

 All Ag films have a smooth surface and uniform thickness. However, the resistivity of either thermal only or AP-Plasma only treatment is very, very high. And the resistivity of Ag film after the both thermal and AP-Plasma treatment for 10 minutes is about 32 μΩ cm. This value is the same as the value after the ink-maker recommended treatment, that is, 30 minutes anneal time.
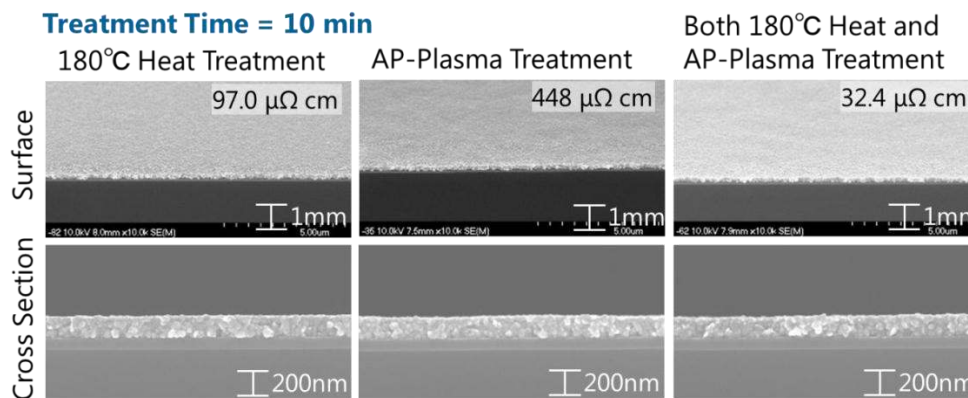

Figure 6. Heat and AP-Plasma treatment in the H_2/Ar atmospheric pressure.

3.6. Pre-Thermal Treatment to Reduce Ink Solvent

We found that the pre-thermal treatment after coating is effective to reduce the resistivity of the Ag film, as shown in Figure 7, which shows the effect of pre-thermal treatment. We carried out to do both AP-Plasma and 180 °C thermal treatment after 5 min pre-thermal treatment. In the case of 100 °C 5 min pre-thermal treatment, the resistivity of Ag film is 5.25 μΩ cm. Ag film has no grain boundary.

We believe that hydrogen radicals in the AP-Plasma of hydrogen and Ar mixture gas react on residuals of solvent in the Ag film and promote the grain growth of Ag film and then the Ag film produces a lower resistivity of 5.25 μΩ cm. Only the plasma treatment cannot reduce the residue of solvent effectively and both the plasma and heat treatments are useful to reduce the resistivity of Ag film.
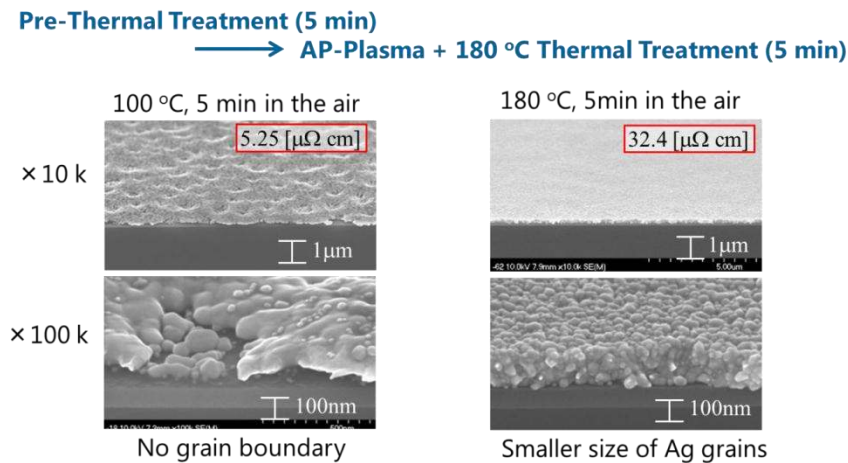

Figure 7. Pre-thermal treatment to reduce film resistivity.

4. Conclusions

We developed the microwave atmospheric pressure plasma system with 1-m-length antenna. This system yields the high electron density of 10^{15} cm^{-3} and produces high H radical densities of 10^{16} cm^{-3} at slots. We applied this system for the treatment of Ag film spin-coated using Ag nano-ink and obtained the high-quality Ag film with the resistivity of 5.25 μΩ cm for shorter process time.

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