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Removal of photoresist film coated on silicon substrate by means of atmospheric pressure non-equilibrium plasma

Dai Kumagai, Kazuo Sugiyama*, Kazutoshi Kiyokawa
Hideki Kurokawa, and Hiroshi Miura
Faculty of Engineering, Saitama University, Shimo-Okubo 255 ,Urawa , Saitama, 338-8570, JAPAN
*Fax: 048-858-3505, e-mail: sugi@apc.saitama-u.ac.jp

We found that an atmospheric pressure plasma could be generated by microwave irradiation to electrically conductive and heat-resistive materials such as $La_{0.6}Sr_{0.4}CoO_3$. Electron and gas temperature measurements showed that this atmospheric pressure plasma is in a non-equilibrium state. As an application using this plasma, we tried to remove photoresist on silicon substrate. Consequently, the resist could be removed with an argon or argon-oxygen plasma treatment. The plasma treatment effect was advanced by increasing the plasma treatment time and oxygen concentration. Plasma gas temperature increased with the increase in oxygen concentration. Optical emission spectroscopy indicated that a large amount of oxygen radicals existed in the plasma. The existence of oxygen radicals was considered to be effective in removing of photoresist.

Key words: photoresist, non-equilibrium plasma, atmospheric pressure

1. INTRODUCTION

In industrial plasma processing, vacuum systems are widely used for thin film formations and surface treatments [1-4] with reference to the productions of display panels, solar cells, semiconductors, etc. However, a cost reduction can be brought about, provided that the vacuum system is not necessary. Therefore a plasma process that does not require vacuum systems, that is, an atmospheric pressure non-equilibrium plasma, is an important subject, today.

Hence, several trials concerning the atmospheric pressure non-equilibrium plasma have been tried [5-10]. In a related matter, when trying to prepare perovskite type oxide powders by microwave heating, we found that an atmospheric pressure plasma is generated around the powders (plasma-generative materials) [11-18]. Taking into account the current state of the plasma processing mentioned above, we started to examine the atmospheric non-equilibrium plasma process with an aim towards industrial and practical applications. The removal of photoresist on a silicon substrate was tried using the plasma as a surface treatment. As a result, the resist could be removed by an argon or an argon-oxygen plasma treatment. To evaluate the effect of the plasma, fundamental parameters, such as optical emissions and gas temperatures, were also measured.

2. EXPERIMENTAL

The experimental apparatus used to generate the atmospheric pressure plasma is shown in Fig. 1. This apparatus consists essentially of a microwave generator, a wave guide unit, and a reactor. A quartz tube (18 mm O.D) was used as the reactor. Gas inlet and outlet lines were connected to the reactor. The sides of the quartz tube were dented so that a bulk sample could be set inside. It had already been found that electrically conductive and heat-resistive properties were important for the plasma-generative materials, and that silicon was one of the proper materials to generate the plasma. In this experiment a lump type of silicon was used as a plasma generative-material.

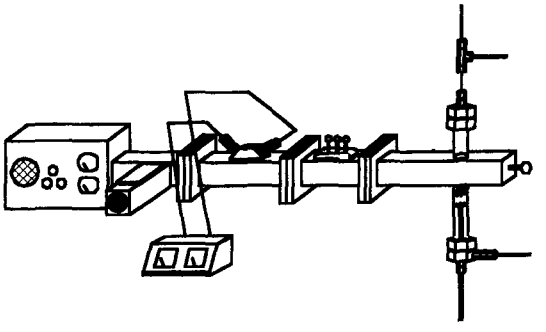

Fig. 1 Experimental apparatus. This apparatus was made up of a microwave generator, a waveguide unit, and a reactor. The inner reactor space attained a plasma state.

The procedure for the plasma generation is described below. After the silicon lump sample (1.1 g) was placed in the reactor, argon and oxygen were introduced into the reactor. Next the microwave power was turned on. When the impedance was adjusted, the inner reactor space attained a plasma state.

In this experiment a silicon wafer on which photoresist had been coated was used as the substrate to be treated. Photoresist used in this experiment was

composed of novolac resin and naphthoquinone azide (photosensitizer), and the thickness of photoresist layer was 1.1 μm. The shape of the substrate was a square with a side 10 mm long. A gas mixture of argon and oxygen was used and a total flow rate was kept at 1.5 L/min. The microwave (2.45 GHz) power was 400 W. To evaluate the treatment's effect the composition of surfaces were analyzed with an X-ray photoelectron spectroscopy (XPS). The substrate was also treated by heating at 800 K as a control experiment.

A multi channel type spectrometer was used to analyze optical emission species in the plasma in order to characterize the plasma. The emissions were observed from a circular hole which had been made in a waveguide wall. A thermocouple was inserted into the reactor from the lower part of the reactor, and the temperature was measured. This temperature is expressed as a gas temperature in this paper because of its close relationship with the gas temperature.

3. RESULTS AND DISCUSSION

At first, the outside appearance, or the color, of the surface of treated substrates was investigated. The color of an untreated surface is originally dark green due to the existence of the photoresist. After heat-treatment in air (control experiment) a change in the surface color was not observed. In this case, the heat-treatment time and the temperature of the hot plate were 3 min and 800 K, respectively. On the other hand, after plasma-treatment, the silver area or the optical interference were observed on the surface. In this case, the microwave power and the treatment time were 400 W and 60 sec, respectively. Then the surface of the heat-treated substrate and the silver surface of plasma-treated one were analyzed with XPS.

The XPS profiles are shown in Fig. 2. These two profiles are the results of the (a) heat-treatment and (b) plasma-treatment mentioned above. In the case of (a), a peak of C_{1s} was clearly observed on the surface. This result shows the simple heat-treatment could not remove the photoresist on the substrate even at 800 K. On the other hand, after the plasma-treatment the C_{1s} peak was drastically decreased, and the peaks of Si_{2s} and Si_{2p} appeared as shown. So this result could be evidence of the removal of the photoresist. In short silver color originated from the silicon surface, so it expressed complete treatment effect.

Next for the purpose of investigating the effects of the plasma treatment conditions, such as treatment time and oxygen concentration, a "removal ratio" was defined as (size of silver area / maximum size of silver area) × 100 [%]. Here, "silver area" means "completely treated area" as mentioned. In this experiment the maximum treatment area was limited to about 0.8 cm^2 because of plasma size and experimental conditions such as the size of quartz tube reactor. Therefore an area of 0.8 cm^2 was used as a present standard, or "maximum size of silver area" for the relative evaluation of plasma treatment effects.

Fig. 3 shows the results of the relationship between the treatment time and the removal ratio of; (a) argon plasma, and (b) argon-oxygen plasma. On either (a) or (b), the total gas flow rate and the microwave power were 1.5 L/min and 400 W, respectively. In the case of (b) the oxygen concentration was 1.3 vol.%. The plasma-treatment effect was advanced with an increase in the treatment time and in the oxygen concentration. It could be considered that interatomic bonds of photoresist were cut by energy transfer from the activated species in plasma to the photoresist consisting

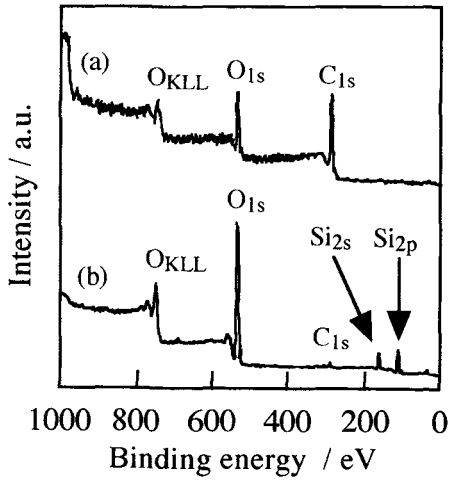

Fig. 2 XPS profiles of substrate surfaces. Each profiles shows (a) heat-treated surface on hot plate at 800 K in air, (b) plasma-treated surface, respectively. After plasma-treatment the C_{1s} peaks was drastically decreased and Si_{2s} and Si_{2p} peaks appeared as shown.

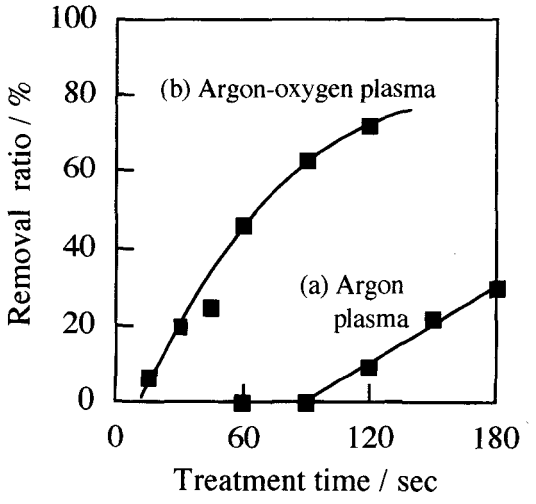

Fig. 3 Relation between treatment time and removal ratio ; (a) argon plasma and (b) argon-oxygen plasma. The plasma-treatment effect was advanced with an increase in the treatment time and with oxygen gas.

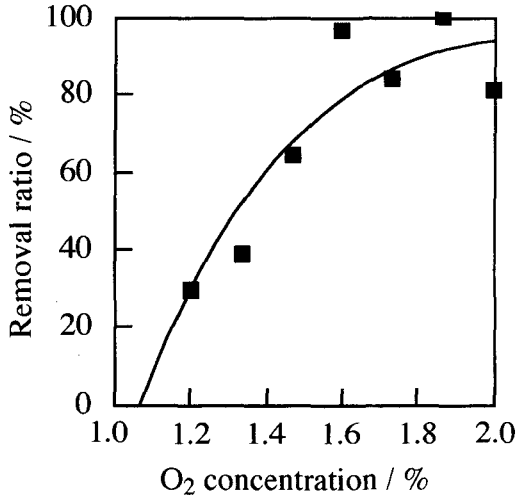

Fig. 4 Removal ratio when oxygen concentration was varied. There was a tendency for the removal ratio to increase gradually with increasing oxygen concentration.

of organic compounds, and that then the photoresist was changed into volatile compounds.

The plasma-treatment effect was confirmed as mentioned. Fig. 4 shows the removal ratio when the oxygen concentration was varied. Total gas flow rate and the microwave power were 1.5 L/min and 400 W, respectively. The removal ratio was increased with an increase in the oxygen concentration. In short it was found that the argon-oxygen plasma treatment was more effective to remove the photoresist than the argon plasma treatment.

Next the fundamental plasma parameters, such as the optical emission and the gas temperature, were measured.

Fig. 5 shows the optical emission spectrum of a plasma produced using a gas mixture of argon and oxygen (2 vol.%). A peak at 777 nm originating from oxygen radical stood out clearly, and the others between 700 - 900 nm arose from activated argon atom (4s-4p transition) [19,20]. These results indicate that oxygen atoms were effectively activated in the atmospheric pressure plasma.

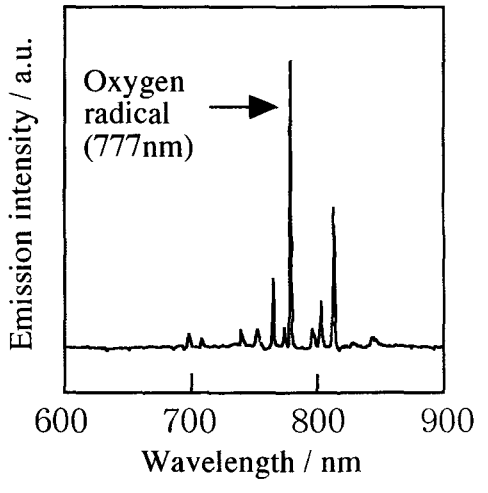

Fig. 5 The optical emission spectrum of a plasma which was generated by a gas mixture of argon and oxygen (2 vol.%). A oxygen peak at 777 nm stood out clearly. The others between 700 and 900 nm originated from argon atom (4s-4p transition).

The upward tendency of the emission intensity of oxygen radical was observed by increasing the oxygen concentration. On the other hand the intensity of the peak at 811 nm originating from activated argon atoms was decreased. The results were shown in Fig. 6. These results indicate the number of activated species was decreased by increasing the oxygen concentration. Therefore, it was considered that the quantity of the

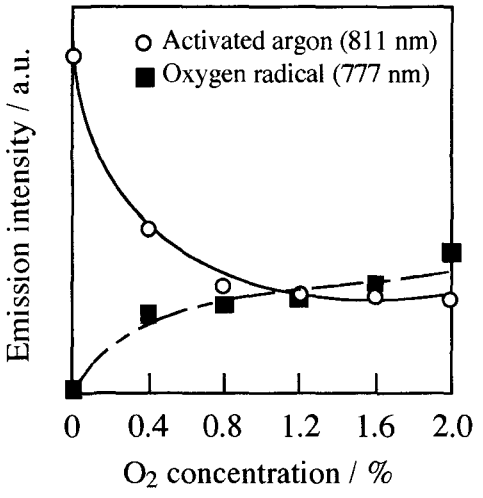

Fig. 6 Relation between oxygen concentration and optical emission. The upward tendency of the emission intensity of oxygen radical was observed by increasing the oxygen concentration. Conversely intensity at 811 nm originating from activated argon was decreased.

photoresist decomposed by activated argon atoms was decreased, and that the plasma treatment effect could be controlled by varying the oxygen concentration.

These results indicate that the ashing process would occur by the oxygen-added plasma. In the plasma ashing process, the oxygen radicals would extract hydrogen atoms from the photoresist, and would cut into C-C bonds of the photoresist.

Fig. 7 shows the gas temperature in an atmospheric pressure plasma produced using a gas mixture of argon and oxygen. This gas temperature was measured by using a thermocouple covered with a quartz tube which was used to prevent contamination Each measurement's condition was kept for more than 5 min in consideration of thermal equilibration. The total gas flow rate and the microwave power were 1.5 L/min and 400 W, respectively. The tip of the thermocouple was set at the same position as the substrate's. The

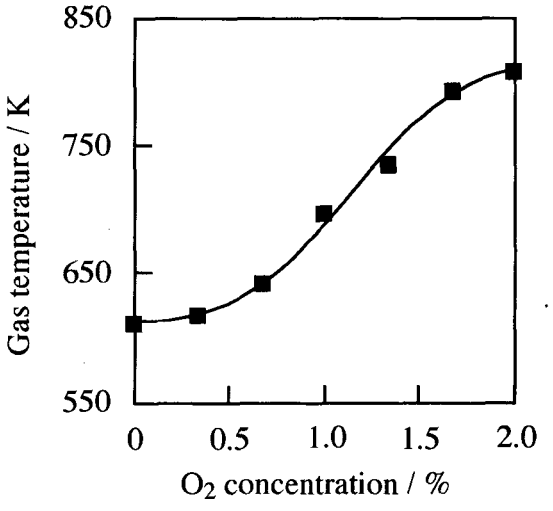

Fig. 7 Gas temperature in an atmospheric pressure plasma of argon and oxygen gas mixture. There was a tendency for the gas temperature to increase gradually with increasing oxygen concentration.

oxygen concentration was varied from 0.0 to 2.0 vol.%. There was a tendency for the gas temperature to increase with an increase in concentration. At a 2.0 vol.%, for example, the gas temperature was about 800 K. Although this temperature sounds relatively high, the simple heat-treatment at 800 K could not remove the photoresist as shown in Fig. 2. Therefore it is considered that the plasma-treatment effect was greater than the heat-treatment effect. In this experiment the distance between plasma-generative material and substrate (or thermocouple) was fixed at 4 cm, taking high rate of plasma-treatment into consideration so the gas temperature was relatively high. If it is necessary to lower treatment temperature, the substrate should be kept at a distance of more than 4 cm although the longer treatment time would be required to remove the photoresist.

4. CONCLUSIONS

The findings of the current experiments concerning the removing of photoresist on a silicon substrate could be summarized as follows:

1. The photoresist on a silicon substrate was removed by an atmospheric pressure plasma treatment using a gas mixture of argon and oxygen.
2. The plasma-treatment effect was advanced with an increase in the treatment time and the oxygen concentration.
3. The optical emission of oxygen radical was clearly observed in the plasma, and the intensity was increased with an increase in the oxygen concentration.
4. It was considered that the ashing process was caused by the existence of oxygen radical added to the plasma.

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