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Study of Hydrogenated Silicon Thin Film Deposited by Using Dual-frequency Inductively-coupled Plasma-enhanced Chemical-vapor Deposition

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Microcrystalline silicon thin films were deposited using an inductively-coupled plasma source with an internal linear-type antenna in the dual frequency mode (2 MHz/13.56 MHz), and the characteristics of the thin film and the plasma were investigated as functions of the relative power ratio. The deposition was performed in the SiH_4 depletion condition at a deposition rate of about 10 Å/s to improve the microstructural properties of the film. In the dual-frequency mode, the crystalline volume fraction could be increased by increasing the low-frequency power, which is added to the fixed 13.56 MHz rf power without changing the microstructure factor (R^*), which is related to defects in the crystal structure. The differences appear to be related to the lower-energy ion bombardment of the substrate in the dual-frequency mode. In addition, by increasing the low-frequency power from 0 to 1.5 kW while keeping 3 kW at 13.56 MHz, we were able to change the uniformity of the deposition from 15.5% to less than 10% an improvement.

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I. INTRODUCTION

Microcrystalline silicon has received considerable interest in recent years as a thin-film-transistor (TFT) material and as a narrow-band-gap intrinsic layer for multi-junction silicon solar cells due to its high carrier mobility, superior long-wavelength response, and stability against light-induced degradation [1–3]. Especially, when microcrystalline silicon is used in a silicon solar cell, the thickness of the silicon layer should be more than 1 um because of the indirect energy band gap of microcrystalline silicon. As such, the methods for high-rate, uniform deposition on large areas without deterioration of the film's properties has been extensively investigated with respect to cost-effective mass production.

In general, the properties of a grown silicon thin film, such as crystalline volume fraction, crystalline defects, *etc.*, depend strongly on the deposition conditions. For example, films deposited at high rates tend to show low crystalline volume fraction or poor electrical properties. On the other hand, films deposited at very low rates tend to show high crystalline volume fraction or excellent electrical properties [4, 5]. To obtain high-quality materials at high growth/deposition rates, many deposition techniques or growth methods, such as hot-wire (HW) chemical vapor deposition, electron cyclotron resonance (ECR) plasma deposition, very-high-frequency plasma-enhanced chemical-vapor deposition (VHF PECVD), high-pressure depletion (HPD) methods, *etc.*, have been used [6–9]. Especially, VHF PECVD at the HPD condition [10–12] is considered to be one of the best methods for the deposition of high-quality films at high deposition rates because the high excitation frequency and high pressure conditions increase the gas dissociation rates while decreasing the ion energy bombardment of the substrate by reducing the sheath voltage and decreasing the mean free path. However, due to the standing-wave-effect due to the short wavelength of VHF, it is difficult for VHF plasma to deposit microcrystalline silicon uniformly over a large area. In the fabrication of high-quality silicon thin films, another promising technique of reducing the ion energy bombard-

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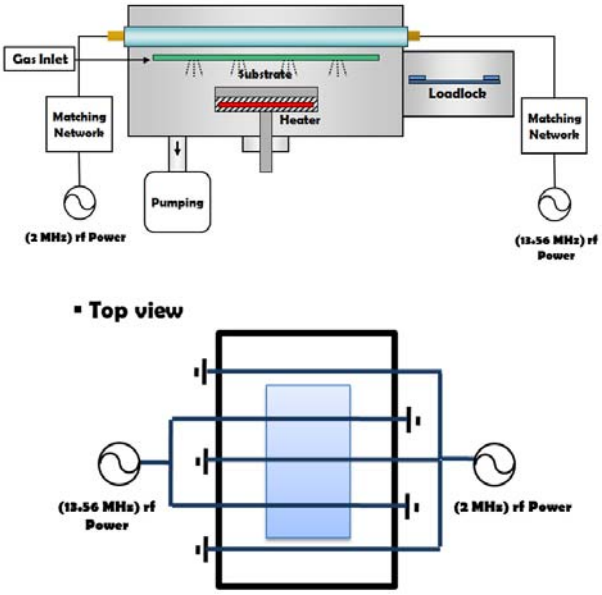

Fig. 1. (Color online) (a) Schematic diagram of the linear internal-type ICP system in this experiment. (b) Configuration of the ICP antenna connection in the dual frequency mode.

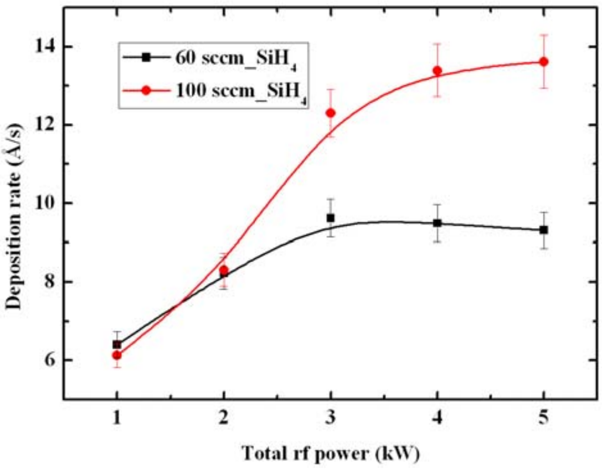

Fig. 2. (Color online) Deposition rate of deposited Si thin films as a function of rf power for a single frequency mode (13.56MHz) with 60 sccm and 100 sccm of SiH_4

ment is the use of a capacitively coupled plasma driven by a dual frequency, which can control the ion flux and the bombardment energy independently by controlling the ratio of high frequency to low frequency [13]. However, this technique also has problems related to scalability and growth rate.

In this study, an internal linear antenna-type inductively coupled plasma (ICP), which is an easily-scalable, high-density plasma source, was used, and a dual frequency mode composed of 2 MHz and 13.56 MHz rf frequencies was introduced to the ICP source antennas. The effect of the dual frequency on the characteristics of the deposited silicon thin films and the internal linear antenna-type ICP were investigated. The experiment was performed in a SiH_4 depletion region, which provided a consistent deposition rate. In this region, the effect of the dual-frequency ICP source on the film's properties can be analyzed without concern about changes in the film's characteristics due to different deposition rates and with the advantage of fully utilizing the SiH_4 gas.

II. EXPERIMENT

Figure 1(a) shows a schematic diagram of the dual frequency (DF) ICP-CVD system used in this experiment. An internal double comb-type ICP antenna was installed in a rectangular chamber with an internal size of 1,020 × 830 mm^2. The antenna consisted of five sets of ceramic-covered, linear Cu tubings, whose diameters were 10 mm, as shown in Fig. 1(b). To make a double comb-type antenna, we alternately connected each set to the power supply through a matching network with the other end of the set grounded. To form a dual-frequency configuration, as shown in Fig. 1(b), we connected a 13.56 MHz power supply to the left side of a comb-type antenna composed of two linear antennas and a 2 MHz power supply to the right side of a comb-type antenna composed of three linear antennas. The ICP source was also operated in the single-frequency mode by connecting both the right and the left antenna sets to the same 13.56 MHz rf power to compare the deposited thin-film's characteristics with those obtained for the thin films deposited with the ICP source operating in the dual-frequency mode. The distance between an antenna and the substrate was 70 mm.

Hydrogenated silicon thin films were deposited both on Eagle XG glasses and p-type Si substrates by using SiH_4 diluted by H_2 at SiH_4 and H_2 flow rates of 60 ∼ 100 sccm and 400 sccm, respectively. For the thin-film deposition in the dual-frequency mode, the 2 MHz rf power was varied from 0 W to 2 kW while the 13.56 MHz rf power was kept at 3 kW. For the thin film deposition in the single frequency mode, the 13.56 MHz rf power was varied from 0 to 6 kW. The operating pressure and the substrate temperature were maintained at 40 mtorr and 180 °C, respectively. Twenty-four Eagle XG glass samples were located on the substrate, and the deposition uniformity was measured using the following relationship:

$$Uniformity(\%) = \frac{deposition\ thickness\ (max) - deposition\ thickness\ (min)}{2 \times average\ deposition\ thickness} \times 100 \quad (1)$$

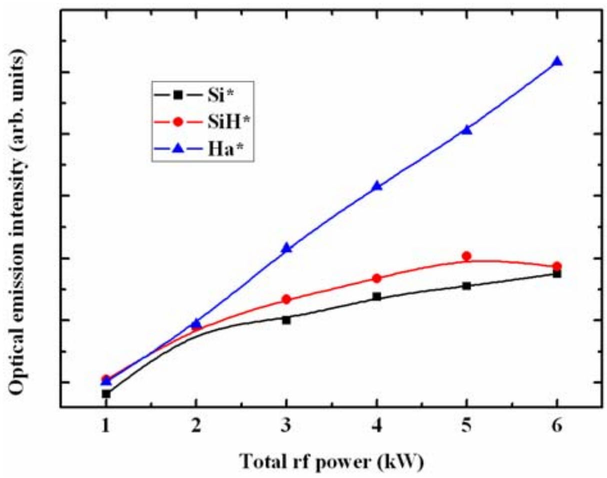

Fig. 3. (Color online) Optical emission intensities of Si, SiH, and H with the increase of rf power from 1 to 6 kW measured by OES for the condition of 60 sccm SiH_4 in Fig. 2.

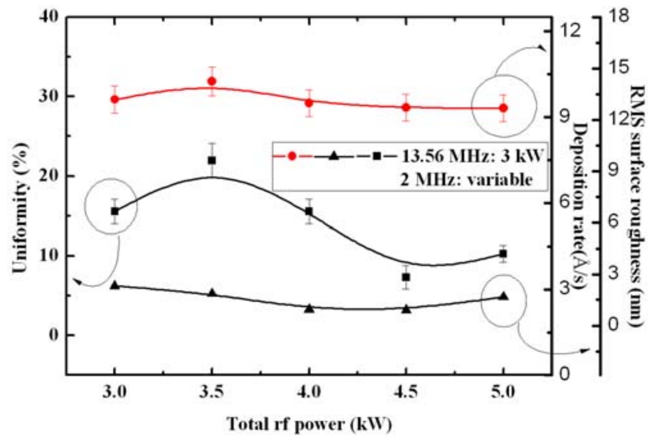

Fig. 4. (Color online) Microcrystalline silicon deposition rate, RMS surface roughness, and the deposition uniformity on the substrate area of 370 × 470 mm^2 measured as a function of 2 MHz rf power added to 3 kW of 13.56 MHz rf power.

The thicknesses of the deposited silicon thin films were measured using a step profiler (Alpha step; Tencor 500). The surface roughness was measured by using atomic force microscopy (AFM; NanoScope IIIA). We used the 300-nm-thick silicon thin films, to measure the crystalline volume fractions of the silicon films by using Raman spectroscopy (Kaiser Optics RXN1), and the microstructure factor(R^*), which indicates defects in a microcrystalline silicon film, by using Fourier-transform-infrared spectroscopy (FTIR; Broker IFS-66/S). The optical emission intensities of species such as Si, SiH, and H due to the dissociation of SiH_4/H_2 plasmas were observed by using optical emission spectroscopy (Andor, Istar).

III. RESULTS AND DISCUSSION

Before the deposition of the microcrystalline silicon thin film in the dual-frequency mode, the silicon was deposited at a single frequency of 13.56 MHz to find the silicon deposition condition for the SiH_4 depletion mode. Figure 2 shows the microcrystalline silicon deposition rate measured as a function of 13.56 MHz rf power in the single-frequency mode for two different SiH_4 flow rates of 60 and 100 sccm at a H_2 flow rate of 400 sccm. As shown in the figure, when the SiH_4 flow rate was 60 sccm, the increase in the 13.56 MHz rf power increased the microcrystalline silicon deposition rate from about 6.5 Å/s at 1 kW to about 9.5 Å/s at 3 kW, but a further increase in the rf power to 5 kW did not change the deposition rate significantly. However, when the SiH_4 flow rate was increased to 100 sccm, the deposition rate at 1 kW was about 6 Å/s; which was similar to that at 60 sccm. An increase in the rf power increased the microcrystalline silicon deposition rate up to 4 kW, but a further increase in the rf power did not increase the deposition rate anymore. The saturation of deposition rates obtained at a 3 kW rf power for a SiH_4 flow rate of 60 sccm and at a 4 kW rf power for a SiH_4 flow rate of 100 sccm is related to the depletion of SiH_4 gas by the full dissociation of the SiH_4 gas molecules fed into the system.

The depletion of SiH_4 at a high rf power at fixed SiH_4 flow rates could also be confirmed by measuring the optical emission intensities of the dissociated species of SiH_4, such as Si, SiH, and H. Figure 3 shows the optical emission intensities of Si, SiH, and H with increasing rf power from 1 to 6 kW measured by using OES for the condition of a 60 sccm SiH_4 flow rate in Fig. 2. As shown in the figure, the increase in the optical emission intensities of Si and SiH with increasing of rf power appears to slow down from about 2 ∼ 3 kW, possibly indicating the start of the depletion mode. The increase in the rf power increased the optical emission intensity of H (H) almost linearly, possibly indicating the continuous dissociation of SiHx by the power delivered to the plasma with increasing rf power. A similar change in the optical emission intensities for the depletion mode of SiH_4 PECVD has been also observed [14]. In fact, even though the silicon deposition rate shown in Fig. 2 was saturated at powers higher than 3 kW, the OES signals of SiH and H still slightly increased with increasing total rf power at total powers higher than 3 kW. The differences between the OES signals and the deposition rate are believed to be from the fact that the OES signals are proportional not only to the concentration of the dissociated species in the plasma but also to the electron density, which tends to increase with increasing total rf power.

To remove the possible effects of the thin film's deposition rate on the change in the thin film's properties such as crystal structure and defects, we carried out an exper-

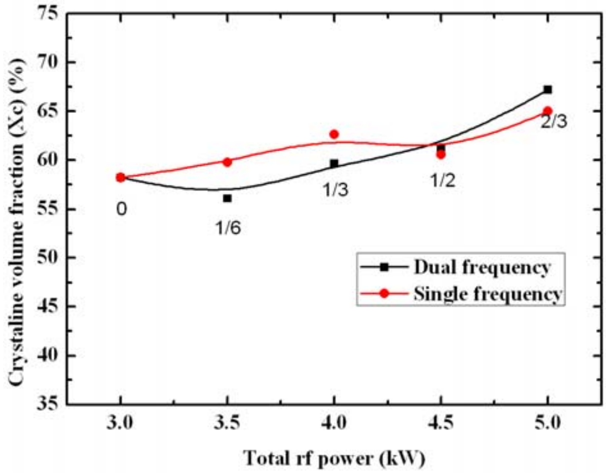

Fig. 5. (Color online) Crystalline volume fraction (Xc) of deposited Si thin films as a function of rf power for the single frequency mode(13.56 MHz) and the dual frequency mode(0 ∼ 2 kW of 2 MHz rf power to 3 kW of 13.56 MHz).

iment at the depletion condition showing similar microcrystalline silicon deposition rates. While obtaining the depletion condition at a 3 kW, 13.56 MHz rf power for the internal linear-type ICP source and a SiH_4 flow rate of 60 sccm, we investigate the effect of the dual-frequency mode on the film's characteristics for CVD by additionally applying a 2 MHz rf power to the ICP source, as described in the experimental section. Figure 4 shows the microcrystalline silicon deposition rate measured as a function of the 2 MHz rf power, which was added to the 3 kW 13.56MHz rf power. As shown in the figure, an increase in the 2 MHz rf power did not increase the deposition rate, which was about 9.5 ∼ 10 Å/s, because the silicon deposition was already in the depletion mode even without the application of the 2 MHz rf power.

Using the microcrystalline silicon thin film deposited with the conditions in Fig. 4, we measured the thin film characteristics. Figure 5 shows the crystal volume fraction measured as a function of total rf power to the ICP source with application of 0 ∼ 2 kW of 2 MHz rf power to the 3 kW of 13.56 MHz. As a reference, the crystalline volume fractions (Xc) of the silicon thin film measured as a function of the 13.56 MHz single-frequency rf power are also shown. The crystalline volume fraction was measured by using Raman spectroscopy by deconvolution of the peaks related to the amorphous silicon (480 cm^{-1}) and the crystalline silicon (510 cm^{-1} and 520 cm^{-1}) and by taking the ratios of their intensities (I) using the equation $Xc=(I_{510}+I_{520})/(I_{480}+I_{510}+I_{520})$. As shown in the figure, the crystalline volume fraction increased from about 55% to 65 ∼ 67.5% with increasing total rf power from 3 to 5 kW for both silicon thin films deposited with the single-frequency ICP source and with the dual-frequency ICP source; therefore, by increasing the total rf power above 3 kW, we were able to increase the crystalline volume fraction at similar deposition rates

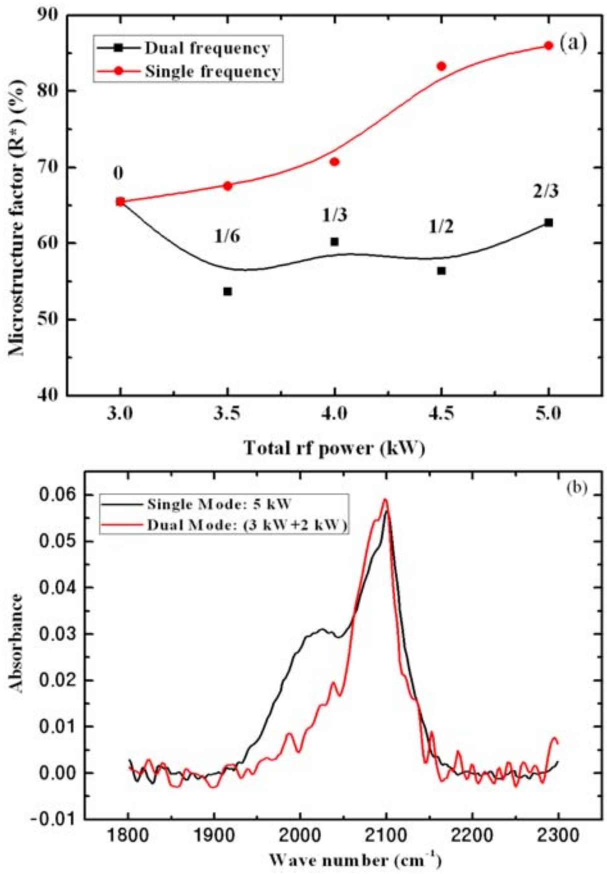

Fig. 6. (Color online) Microstructural factor (R^*) measured using FTIR as a function of total rf power to the ICP source for the microcrystalline silicon thin films deposited with the conditions in Fig. 5. The microstructural factors of the silicon thin film deposited with 13.56 MHz single frequency rf power are also shown as the reference.

of about 9.5 ∼ 10 Å/s. In general, at the depletion condition, the additions of high rf power to the plasma and a small amount of SiH_4 gas to the system, is known to saturate the silicon deposition rate due to the complete consumption of SiH_4. In addition, excess atomic hydrogen it is known to be generally consumed in the plasma by the following reaction when SiH_4 is abundant in the plasma:

$$SiH_4 + H \rightarrow SiH_3 + H_2 \tag{2}$$

However, during the SiH_4 depletion mode, due to the lack of SiH_4, the above reaction is blocked, and the excessive atomic hydrogen available in the plasma tends to increase the crystallinity in the silicon thin film [15].

Figure 6(a) shows the microstructural factor (R^*) measured using FTIR as a function of the total rf power to the ICP source for the microcrystalline silicon thin films deposited under the conditions in Fig. 5. The microstructural factors of the silicon thin films deposited with a 13.56 MHz single frequency rf power were also measured and are shown as the reference (Fig.

6(b)). The microstructural factor was obtained by deconvoluting the FTIR absorption peaks for the low-stretching mode at 2000 cm^{-1} and the high-stretching mode at 2100 cm^{-1} and by using the following equation: $R^*=I(2100)/[I(2100)+I(2000)]$, where I(2000) and I(2100) are the integrated Gaussian peak widths at 2000 cm^{-1} and 2100 cm^{-1}, respectively. The low-stretching mode at 2000 cm^{-1} is related to the monohydride (Si-H) bonding existing near the equilibrium vacancy, and the high-stretching mode at 2100 cm^{-1} is related to the multi-hydride bonding (Si-H_x, $x > 1$) near defects such as voids or grain boundaries in the film [16–18]. In general, the deposition rate, crystallization, and crystal defects are known to be related to each other as trade-offs [17, 19]. For example, the increased crystallization of the film tends to form more silicon microcrystalline grains in the film, whose boundaries are locations of defect generation. The defects near the grain boundaries of a microcrystalline silicon thin film deposited by using PECVD are in the form of SiH_2, which contributes to the high-stretching mode at 2100 cm^{-1}. The high-stretching mode observed in the FTIR absorption spectroscopy, in turn, is known to decrease the electrical properties of the microcrystalline silicon thin film, but for a high quality microcrystalline silicon thin film, a low R^*, which has a low high-stretching mode, is needed.

As shown in Fig. 6(a), for the single-frequency mode, an increase in the rf power continuously increased the R^* from about 65 to 88% due to the increased number of defects related to the SiH_2 bonding near the grain boundaries, as described above. However, when the dual frequency mode was used, with the increase in the total rf power because of the extra 2 MHz rf power added to the 3 kW 13.56 MHz rf power, the R^* was decreased to near 60% at a total rf power of 3.5 kW and remained constant until the total rf power had reached 5.0 kW. The ICP operation at the dual-frequency mode composed of 2 MHz and 13.56 MHz, we investigated previously by our research group [20]. The results showed that, at a fixed total rf power, an increase in the 2 MHz rf power to the ICP source in the dual-frequency mode decreased the energy of the ion bombardment on the substrate while an increase in the 13.56 MHz rf power ratio increased the energy of the ion bombardment on the substrate. The decrease in ion bombardment energy with increasing 2 MHz rf power ratio to the dual-frequency ICP source was related to the lower plasma potential caused by the lower antenna voltage at the higher 2 MHz power ratio because, in the ICP source, a lower frequency shows a lower antenna impedance and a lower antenna voltage at the same rf power. As a result, the low R^* obtained for the multicrystalline silicon thin film deposited in the dual-frequency mode with increasing 2 MHz rf power in Fig. 6(a) is believed to be related to low damage in a growing silicon thin film because of the lower ion bombardment energy.

For the microcrystalline silicon thin film deposited in the dual-frequency mode, the deposition uniformity on a substrate area of 370 × 470 mm^2 was measured as a function of the 2 MHz rf power added to the 3 kW of 13.56 MHz rf power, and the result is shown in Fig. 4, along with the data related to the root mean-squared (RMS) surface roughness measured as a function of the total rf power (3 kW 13.56 MHz + 2 MHz rf power). As shown in the figure, an increase in the 2 MHz rf power from 0 to 2 kW to the dual-frequency ICP source did not change the RMS surface roughness noticeably, although an increase in the 2 MHz rf power generally improved the thin film's deposition uniformity from about 15.5% to less than 10%. A similar improvement in plasma uniformity by application of the dual frequency mode composed of 2 MHz and 13.56 MHz in the double-comb type ICP were observed in our previous research [21]. When a linear-type ICP is operated, the electric field generated in the plasma by the ICP source concentrates near the linear antennas, so the plasma density is always higher near the antenna in the single rf frequency mode. However, when the dual frequency mode composed of 2 MHz and 13.56 MHz is used and rf powers with the different frequencies are alternately applied to the linear antennas in the ICP source, the electric field generated at each antenna is distributed over a larger area, resulting in better plasma uniformity over the substrate area. Therefore, the improved thin-film deposition uniformity in the dual-frequency mode with increasing 2 MHz rf power is believed to be related to the more uniform plasma distribution over the substrate area.

IV. CONCLUSION

Microcrystalline silicon thin films were deposited with SiH_4/H_2 by using an internal linear-type antenna ICP source in the dual frequency mode (2 MHz/13.56 MHz) and the characteristics of the thin films were investigated as functions of the 2 MHz rf power for a 13.56 MHz power of 3 kW. The deposition in the dual frequency mode was performed in the SiH_4 depletion condition at a 3 kW 13.56 MHz rf power at a deposition rate of about 10 Å/s. The silicon thin films that were deposited using the internal linear-type ICP in the dual-frequency mode, instead of the single-frequency mode, not only showed higher crystalline volume fractions without increased defects in the microcrystalline thin films, as measured by using the microcrystalline factor (R^*), but also showed improved deposition uniformity on large area substrates. The fewer micro-crystalline defects and the higher deposition uniformity are believed to be related to the lower-energy ion bombardment and to the spread of the electric field formed by the ICP antenna, respectively. In the dual-frequency mode, which is composed of the lower frequency powers of 1.5 kW and 3 kW at 13.56 MHz, the deposition uniformity was improved to less than 10%.

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