

# Hydrogen Plasma Characteristics for Photoresist Stripping Process in a Cylindrical Inductively Coupled Plasma

Seung-Kook Yang, Jung Hee Cho, Seong-Wook Lee, Chang-Won Lee, Sang-Jong Park, and Hee-Sun Chae

**Abstract**—As the feature size of integrated circuits continues to decrease, the challenge of achieving an oxidation-free exposed layer after photoresist (PR) stripping is becoming a critical issue for semiconductor device fabrication. In this article, the hydrogen plasma characteristics in direct plasma and the PR stripping rate in remote plasma were studied using a 120  $\Phi$  cylindrical inductively coupled plasma source. E mode, H mode and E-H mode transitions were observed, which were defined by matching the  $V_{rms}$  and total impedance. In addition, the dependence of the E-H mode transition on pressure was examined and the corresponding plasma instability regions were identified. The plasma density and electron temperature increased gradually under the same process conditions. In contrast, the PR stripping rate decreased with increasing proportion of  $H_2$  gas in mixed  $H_2/N_2$  plasma. The decrease in concentration of reactive radicals for the removal of PR with increasing  $H_2$  gas flow rate suggests that NH radicals have a dominant effect as the main volatile product.

**Index Terms**—Photoresist stripping, hydrogen plasma, E Mode, H Mode, negative ion

## I. INTRODUCTION

Benzene ring-containing PRs are used mainly as the masking material to prevent a reaction with the underlying layers during the semiconductor process. At the end of this procedure, a cleaning process is needed to remove the PR residue selectively and rapidly because the PR is not intended to be an intrinsic component of the device. The current methods for the removal of a PR are largely categorized as wet and dry processes, where dry processes are used more commonly because of their lower cost and high throughput capability in mass production. The dry process proceeds via a chemical reaction between the radicals and bonds in the PR, such as C-O and O-H, using  $O_2$ -based plasma and a high chuck temperature. This is known as the ashing process.

The challenges associated with the ashing process can be categorized roughly into those that originate within the process itself and those due to hardware development. The aspects related to the process involve the acquisition of alternative gas chemistries for the new generation PR stripping protocols. In front-end-of-line (FEOL) processing, ashing by  $O_2$  plasma causes unwanted oxidation at the exposed surfaces, including the Si substrate and metal gate. Under these states, the reliability of the device is affected when either a metal plug with an oxidized surface is deposited into contact and via holes or when a silicon substrate is oxidized because of the increased contact resistivity and dopant loss due to severe silicon loss at the ultra-shallow junction caused by oxidation [1-3]. In back-end-of-line

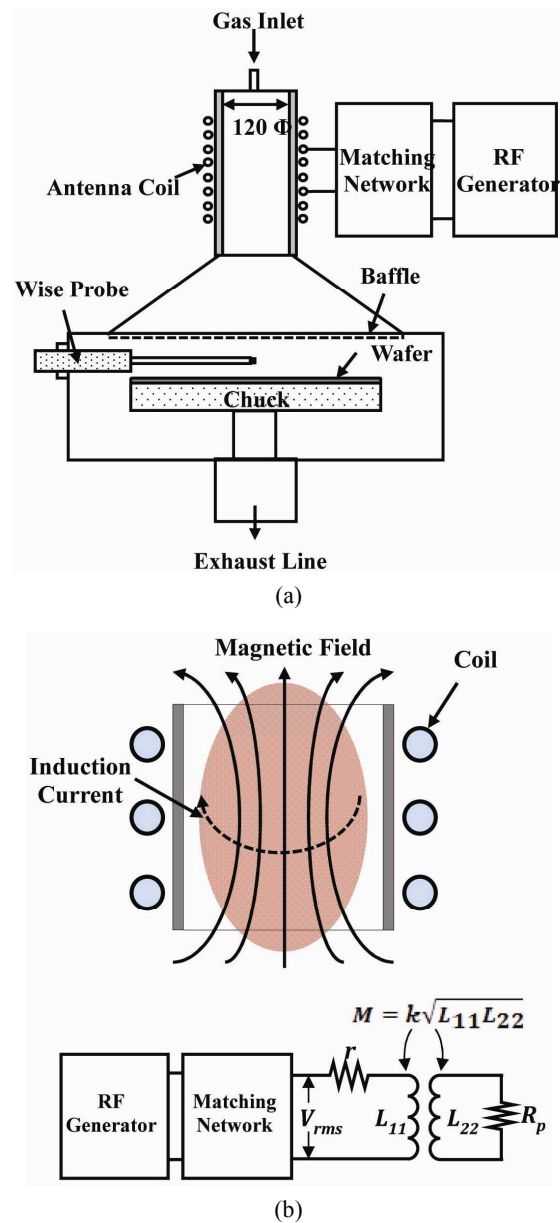
(BEOL) processing, when SiOCH-based low-k dielectric materials are exposed to O<sub>2</sub> plasma, the k-value (permittivity) is enhanced due to the formation of oxygen bonds with methyl groups, which results in porosity [4-6]. Therefore, research on a range of gas chemistries is currently underway to solve the issues involving oxidation and the low-k dielectric material damage during the ashing process. Among the many gas chemistries investigated, the hydrogen gas chemistry has emerged as one of the most promising candidates [7, 8]. The PR stripping process using H<sub>2</sub> plasma has the advantage of decreasing the oxidation rate without additional increases in oxidation due to hydrogen termination [9, 10].

The challenges associated with the hardware involve the development of an applicator tube and plasma source parts with high durability and resilience in the presence of the specific process gas chemistry to be employed. In the case of the conventional ashing process using O<sub>2</sub> plasma, mass production is possible by utilizing a variety of plasma sources, such as microwave, inductively coupled plasma, and a ferrite core in a quartz material-based applicator tube [11]. On the other hand, a range of gas chemistries are needed to synthesize devices. Moreover, the relatively poor mechanical and thermal properties of a quartz applicator tube pose a risk to other parts that may be damaged under the intense radiation of high-temperature plasma, such as hydrogen plasma. These constraints have limited the use of quartz applicator tubes to low RF power only. For industrial applications using high RF power plasma, tubes made from ceramic materials are typically used. The ideal candidate material needs to have good thermal conductivity, excellent thermal shock resistance, and high durability. In addition, the design of the antenna coil is essential for achieving hardware with all the required properties.

In this study, a plasma diagnosis was performed in H<sub>2</sub> plasma using a 120 Φ applicator tube made from a ceramic material for the next generation of PR stripping processes. Based on this analysis, the process windows by the boundary of the E mode, H-mode and E-H mode transition were defined. The PR stripping process was evaluated with different H<sub>2</sub>/N<sub>2</sub> gas mixture ratios, and the PR surface after the stripping process was analyzed by X-ray photoelectron spectroscopy (XPS).

## II. EXPERIMENTAL

As shown in Fig. 1, the plasma source was composed of a cylindrical inductively coupled plasma (ICP) source with a ceramic applicator tube. An applicator tube was manufactured to 120 Φ to help reduce the wafer non-uniformity of both 300 mm and 450 mm platforms. A Faraday shield was used to prevent sputtering damage to the applicator tube. An RF generator (13.56 MHz, TS05-F080-30-C/ASE Co.) from 100 W to 5000 W with a matching network (pi-type auto matcher, AMV-



**Fig. 1.** (a) Schematic diagram of the experimental set-up, (b) structure of ICP source and its circuit model.

5000PSK-FT/ASE Co.) was applied to cover a wide process range. To examine the stripping process, a 300 mm silicon wafer (P-type, 100) was coated with a KrF PR (KY-862A42/Dongwoo Fine-Chem.) using a spin coater (MS212/Opto Fine Tech.). The coating thickness was measured by ellipsometry (RE3100/Rambada ACE Co.) and was found to be approximately 5000 Å ±1%. The process chamber used was a SUPRA V Plus, as a 300 mm Asher of PSK. A baffle was added to obtain a uniform gas and radical flow distribution as well as to prevent plasma damage by ions between the plasma source and chuck, which was heated to 250 °C. The chamber pressure was monitored using a capacitance gauge. The plasma diagnosis was recorded by a wise probe (P&A Solutions Co.) using the floating harmonic method [12], which was performed with the baffle removed from the chamber owing to the low intensity of plasma caused by recombination between the baffle and charged particles. The PR stripping test was performed in the presence of the baffle. The binding energy states of the PR surface were examined by XPS.

### III. RESULTS & DISCUSSION

#### 1. H<sub>2</sub> Plasma Characteristics

The characteristics of H<sub>2</sub> plasma were investigated to develop a new generation PR stripping process. The plasma discharge exists in two different modes: E mode (capacitive) at low power, and H mode (inductive) at high power. The E mode is characterized by a relatively low electron density and low light emission, whereas the H mode has an electron density approximately two orders of magnitude higher than E mode as well as much brighter light emission [13]. Before new gas chemistry was applied to the stripping process, confirmation of the different modes was required to ensure process stability, as the electromagnetic field is altered markedly at the E and H modes and at the E-H transition. Therefore, the source parameters were first examined to determine the unstable regions. Fig. 2 shows the values of V<sub>rms</sub> as a function of the RF power and pressure after the injection of H<sub>2</sub> gas at a flow rate of 10,000 sccm. As shown in Fig. 1(b), V<sub>rms</sub> was used to measure its applied voltage when the rf power was applied to the coil. The measurements were made using a multi-function RF sensor (MRFS)

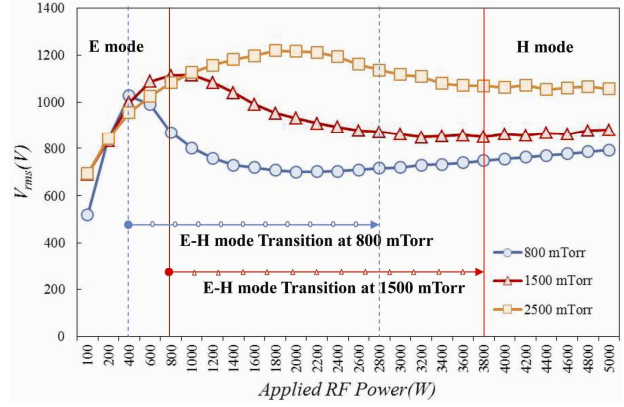


Fig. 2. Change in the E-H mode transition as a function of V<sub>rms</sub> with RF power and pressure (a) 800 mTorr, (b) 1500 mTorr, (c) 2500 mTorr in H<sub>2</sub> plasma.

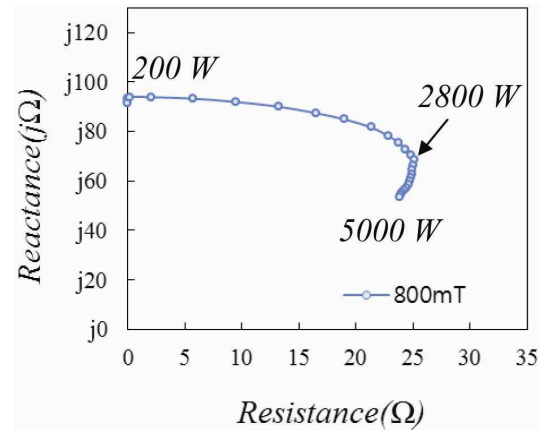
including an RF probe with an auto matcher. V<sub>rms</sub> did not increase linearly with increasing RF power, but increased gradually after the voltage drop at a relatively low input power. Furthermore, as the pressure was increased, the voltage drop occurred over a wider RF range rather than the sharp drop observed at lower pressures. Chung *et al.* reported that this voltage drop accompanies an E-H mode transition, which is affected by the skin depth and pressure [14]. In particular, when the pressure is high, the transition occurs at a much shorter skin depth than the chamber radius and the transition skin depth is inversely proportional to the pressure. Zaplotnik *et al.* reported similar results to those shown in Fig. 2 [15]. Although the analysis of each mode was not clearly defined, it was reported that the E-H mode transition emerged after the voltage drop. The curve transition in Fig. 2 varied with pressure. This suggests that the impedance characteristics are changed as V<sub>rms</sub> is dependent on the total impedance, as shown by Eq. (1), where Z<sub>s</sub> is the total impedance, and L<sub>11</sub> and L<sub>22</sub> denote the antenna inductance and effective inductance, respectively. From Eq. (2), where r is the antenna resistance, and k and R<sub>p</sub> are the coupling constant and plasma resistance, respectively, the total impedance decreased with decreasing plasma resistance as a constant term, and the reactance term reduced as the coupling constant (k) approaches 1.

$$V_{rms} = \sqrt{Re[Z_s]P} \sqrt{1 + \frac{Im[Z_s]^2}{Re[Z_s]^2}} \quad (1)$$

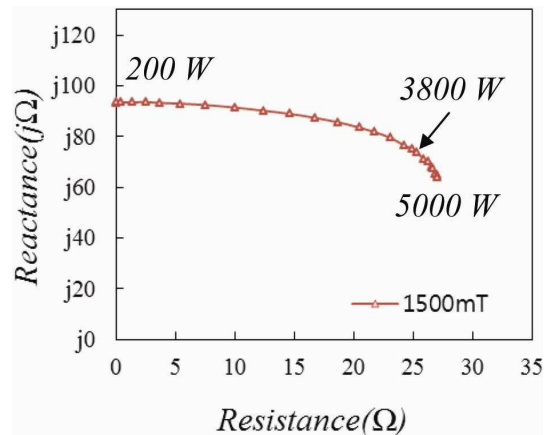
$$Z_s = \left( r + \frac{k^2 R_p L_{11}}{L_{22}} \right) + i\omega L_{11}(1 - k^2) \quad (2)$$

Therefore, the total impedance was measured to confirm these correlation effects (Fig. 3). The results show the resistance as a function of the reactance at different RF powers under each pressure condition. Fig. 3(a) shows that the reactance decreases slowly with increasing RF power and the resistance increases dramatically. This was particularly evident when the RF power was gradually increased after a pressure was fixed at 800 mTorr, where the reactance decreased rapidly at 2800 W, and the resistance showed a slightly decreasing trend. Therefore, the total impedance decreases with decreasing reactance and resistance, indicating conversion to the H mode. This result occurred at precisely 2800 W, which is the point at which  $V_{rms}$  begins to increase after the voltage drop shown in Fig. 2. In Fig. 3(b), although an inflection point similar that observed for 800 mTorr was not present, the reactance decreased rapidly at 3800 W. This is similar to that observed at the point at which  $V_{rms}$  begins to increase after its initial voltage drop in Fig. 2. In Fig. 3(c), an inflection point was not observed because the  $V_{rms}$  did not increase after the voltage drop at 2500 mTorr in Fig. 2. Overall, the correlation between  $V_{rms}$  and total impedance, as defined in Eq. (1), can be used to verify each mode.

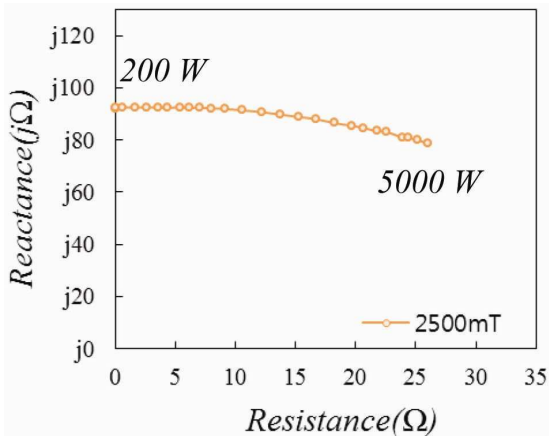
Fig. 4 shows how the ion density and electron temperature varied with pressure and RF power in  $H_2$  plasma. Both the ion density and electron temperature increased with increasing RF power, and decreased with increasing pressure. The increase in electron temperature with RF power can be explained by the fact that hydrogen is not ionized easily by the input power, which means that the energy obtained by the electrons is rarely transferred effectively to the hydrogen atoms. Therefore, when using  $H_2$  gas only, the increase in electron temperature with RF power suggests a decrease in plasma efficiency in terms of the plasma density. The decrease in both the ion density and electron temperature with increasing pressure is because electron energy can be exhausted by a collision between electrons and hydrogen particles in the plasma. In particular, there were some ranges in which both the ion density and electron temperature could not be measured, despite the high RF power. With increasing pressure, these ranges became wider and appeared in the intermediate regions regardless of whether the RF power was low or high. This was attributed to the deviation of pressure from the measuring



(a)



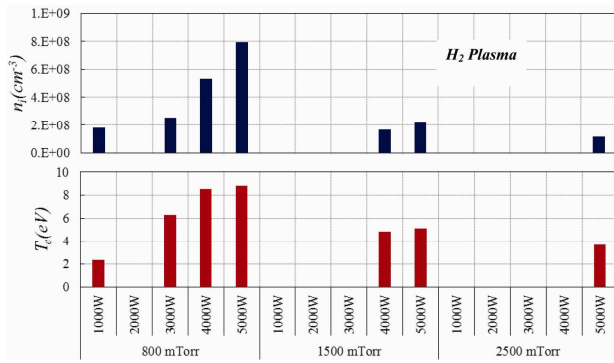
(b)



(c)

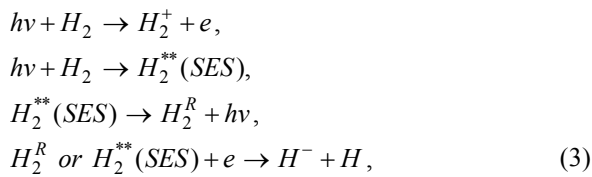
**Fig. 3.** Variation in the total impedance characteristics with RF power and pressure in  $H_2$  Plasma. Peak Characteristics of  $V_{rms}$  in Fig. 2 correspond precisely to an inflection point in the impedance characteristics.

range of the Wise probe [12] due to the low plasma density. These regions are described as instability regions because the plasma is unstable under these conditions

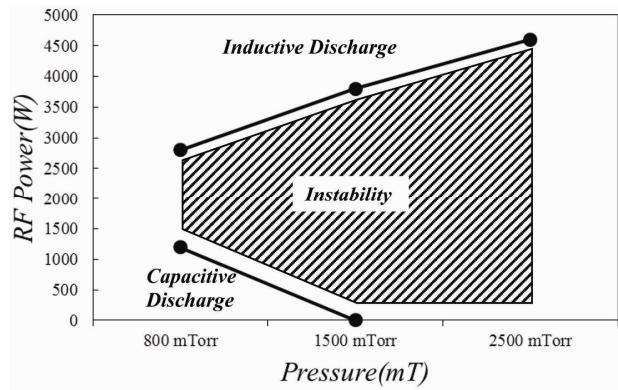


**Fig. 4.** Ion density ( $n_i$ ) and electron temperature ( $T_e$ ) variations with RF power and pressure in  $H_2$  plasma. Non-measurement regions are observed in  $H_2$  plasma.

[16]. Fig. 5 shows the instability regions found in Fig. 4 in graphical form as functions of the pressure and RF power. At 800 mTorr, the regions at low RF power were assigned as capacitive discharge (E mode) and regions at high RF power, whereas the areas above the instability region were classified as an inductive discharge (H mode). As shown in Fig. 4, the instability region expanded with increasing pressure. The explanations for the cause of these instability regions reported in the literature are related to negative ions in plasma [16].  $H_2$  gas chemistry leads to the formation of negative ions in  $H_2$  plasma, primarily because of the dissociative electron attachment to vibrationally excited molecules [17-19]. The mechanism for the formation of  $H^-$  negative ions in  $H_2$  plasma and the rates of dissociative attachment in  $H_2$  are strongly dependent on the electronic excitation involving super-excited states (SES) in the ionization continuum, as shown by Eq. (3) [20].



where  $H_2^R$  denotes the high Rydberg states of hydrogen formed by the rapid radiative decay of the super-excited state, SES ( $\tau^{SES} < 10^{-14}$  s). These super-excited states can be formed easily at low pressure with high-density plasma. As reported previously, under a reduced pressure, the increased production of negative ions creates a further dependence on the pressure [20]. On the other hand, most reports show the opposite in that there is a



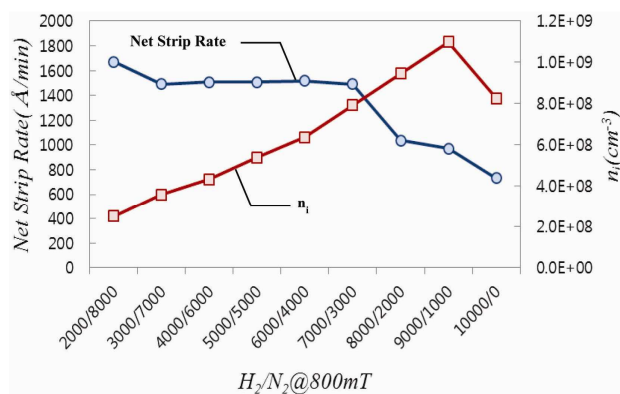
**Fig. 5.** Windows of instability observed in  $H_2$  plasma. The regions show a trend dependence on pressure.

decrease in the concentration of negative ions with decreasing mean attachment rate due to the increasing pressure (Fig. 5). If the correlation between negative ions and instability regions is accurate then the instability regions should shrink with increasing pressure. In this experimental system, it was impossible to evaluate the plasma characteristics, such as dominant ions and active species, in more detail. Considering the observed expansion of the instability region with increasing pressure, the main cause of this behavior appears to be related to a range of E-H mode transitions rather than a negative ion effect. The efficiency of energy transfer towards gas particles is decreased by a change in the electromagnetic field with decreasing skin-depth under the E-H mode transition, which is an intermediate step between the E and H modes. Hence, the plasma density is also decreased. Furthermore, the instability region is expanded due to an enhancement of the energy dispersion effect with increasing pressure.

Overall, when plasma consisting solely of  $H_2$  gas is used for PR stripping, the results suggest that there is a small process window due to the wide instability regions formed with increasing pressure.

## 2. PR Stripping Process using $H_2/N_2$ Plasma

To perform the PR stripping process was performed under a fixed pressure of 800 mTorr, which provides the broadest window of the plasma stability, a chuck temperature of 250 °C and an applied RF power for discharge of 5000 W. The net PR stripping rate was calculated by subtracting the shrinkage rate due to removal by the chuck temperature from the total PR

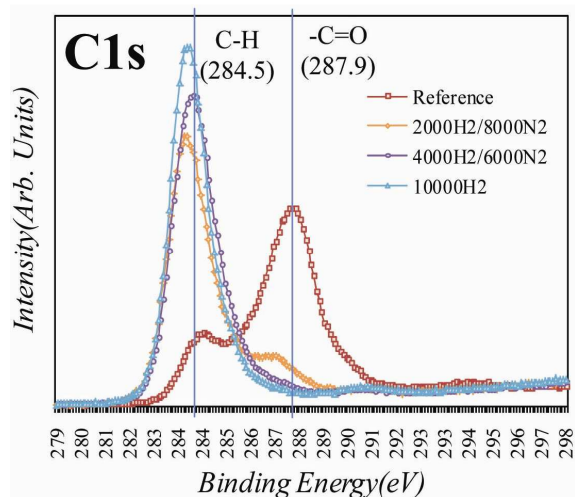


**Fig. 6.** Dependence of the net strip rate of photoresist on the H<sub>2</sub>/N<sub>2</sub> gas mixture ratio at 5000W rf power. PR strip rate decreases and the plasma density increases with increasing H<sub>2</sub> gas flow rate.

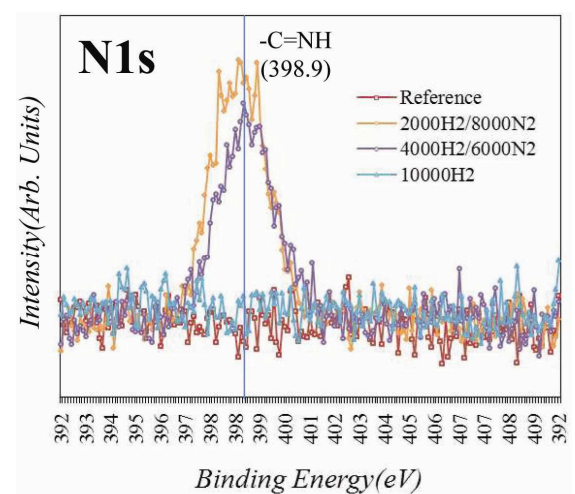
stripping rate, giving a value based solely on removal with plasma. A relatively high RF power of 5000 W was applied to avoid the E-H mode transition. To improve the plasma stability and density, N<sub>2</sub> gas was injected in addition to H<sub>2</sub> gas. This is analogous to the addition of N<sub>2</sub> to O<sub>2</sub> in the conventional ashing process.

Fig. 6 shows the PR stripping rate and ion density as a function of the gas mixture ratio. The PR stripping rate remained constant with increasing proportion of H<sub>2</sub> gas up to 7000 H<sub>2</sub>/3000 N<sub>2</sub>, where it decreased significantly. The ion density was observed to increase linearly with increasing amount of H<sub>2</sub>, reaching a peak at 9000 H<sub>2</sub>/1000 N<sub>2</sub> then decreasing. In the conventional O<sub>2</sub>/N<sub>2</sub> plasma ashing process, the ashing rate increased with increasing ion density by increasing the abundant OH radicals, but the use of H<sub>2</sub>/N<sub>2</sub> plasma had the opposite effect.

One possible explanation for this is that a high proportion of H<sub>2</sub> lacks the reactive radicals to strip PR. A second possibility is that H<sub>2</sub> plasma accelerates the hardening of the PR surface under these conditions resulting in a decrease in PR stripping rate. Owing to the experimental setup, it was not possible to determine directly whether the product volatility was a factor. Therefore, the PR surface was analyzed by XPS after the stripping process to determine the cause of the decreased stripping rate. Fig. 7 shows the XPS C 1s and N 1s spectra obtained after the PR stripping process using a range of gas compositions at 5000 W RF and 800 mTorr. The C 1s peak corresponding to the -C≡O bond decreased compared to the unstripped PR reference. This



(a)



(b)

**Fig. 7.** XP spectra of the PR surface after stripping in H<sub>2</sub>/N<sub>2</sub> gas mixture (a) C 1s, (b) N 1s. NH radicals perform the role of a main reactive radical to form a volatile product with PR.

is due likely to the formation of a volatile product containing O-H bonds after a reaction with H<sub>2</sub> plasma during the PR stripping process. On the other hand, the intensity of the C-H bond peak increased gradually with increasing H<sub>2</sub> gas proportion, with pure H<sub>2</sub> plasma showing the highest intensity. On the other hand, because the H<sub>2</sub> gas flow rates and PR stripping rate are inversely proportional to each other, the C-H bond does not appear to be the main volatile product in the PR stripping process in H<sub>2</sub>/N<sub>2</sub> plasma. As expected, no nitrogen peak was observed for the native PR reference or the sample treated with H<sub>2</sub> plasma only (Fig. 7(b)). The intensity of the -C=NH peak increased with increasing H<sub>2</sub> gas

proportion, which corresponds to the PR stripping rate shown in Fig. 6. Therefore, when PR was stripped with  $H_2/N_2$  plasma, it is likely that the main volatile product was NH content. The decrease in the formation of this product with increasing proportion of  $H_2$  is a probable cause of the decreased PR stripping rate.

#### IV. CONCLUSIONS

In this study, the use of  $H_2$  plasma for PR stripping using a cylindrical ICP source was investigated. The plasma characteristics were assessed and the process window was determined before analyzing the stripping process itself. A more expanded E-H mode transition region appeared with increasing pressure, and the regions of plasma instability could be identified. These instability regions could be avoided clearly by decreasing the pressure. To understand the mechanism of KrF PR stripping in  $H_2/N_2$  plasma, the PR stripping rate was evaluated in terms of the increasing proportion of  $H_2$  gas in the mixture at 800 mTorr. The ion density increased with increasing proportion of  $H_2$  gas, whereas the PR stripping rate decreased. XPS showed that the PR stripping rate in  $H_2/N_2$  plasma was affected dominantly by the formation of an NH-containing volatile product during PR removal.

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