Significant Improvement of Copper Dry Etching Property of a High-Pressure Hydrogen-Based Plasma by Nitrogen Gas Addition

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ABSTRACT: The characteristics of copper (Cu) isotropic dry etching using a hydrogen-based plasma generated at 13.3 kPa (100 Torr) were improved dramatically by simply introducing a moderate amount of N₂ gas into the process atmosphere. A maximum Cu etch rate of 2.4 μm/min was obtained by nitrogen addition at a H₂ mixture ratio (C_H₂) of 0.9 and an input power of 70 W. The etch rate for the optimally N₂-addicted plasma was 8 times higher than that for the pure H₂ plasma. The Cu etch rate increased with increasing input power. The maximum etch rate reached 3.1 μm/min at an input power of 100 W and a C_H₂ of 0.9. The surface roughness of the etched copper decreased as a result of optimum N₂ addition. Furthermore, N₂ addition also improved the etch selectivity between Cu and SiO₂ such that the selectivity ratio reached 190. Finally, selective etching of a trench-patterned Si wafer with an electroplated Cu layer was demonstrated.

1. INTRODUCTION

A precise chemical etching technique for a metal is an essential manufacturing technology for the fabrication of various devices, including microelectronic devices, microelectromechanical systems, and optical devices. Above all, copper (Cu) is a ubiquitous industrial metal because of its low electrical resistivity and earthy abundance. However, when Cu microstructures are prepared, the use of harmful chemicals is necessary in either dry or wet etching. It is well known that Cu wet etching requires nitric acid, sulfuric acid, or a mixture of hydrochloric acid and hydroperoxide and shows isotropic etching behavior. These wet etching techniques are frequently used for the fabrication of printed circuit boards, and their etching rates typically attain tens of micrometers per minute. In contrast, when dry etching is performed on Cu at a considerably high rate, chlorine-related gases are used as typical etchant gases for the Cu metal. One of the motivations for performing dry etching processes using chlorine-related gases is to achieve anisotropic etching. In chlorine-related gas dry etching processes, the gas species that is mixed into the process atmosphere is also known to strongly affect both the etch rate and the etch anisotropy. On the other hand, Hess et al. revealed that the hydrogen plasma can etch Cu at relatively low temperatures. From the viewpoint of avoiding the use of hazardous chemicals, hydrogen etching appears to be more attractive than chlorine etching. However, the etch rate that was obtained using a low-pressure pure hydrogen plasma was 13 nm/min and a higher rate is desirable for both a wider range of applications (i.e., other than microelectronic Cu wiring) and higher production throughput.

We therefore attempted to use a subatmospheric-pressure pure hydrogen plasma for Cu isotropic dry etching to achieve higher etching rates and obtain meaningful etch rates as high as 500 nm/min. However, the etched surface became rough because of the many pits and voids that formed after etching. This surface roughening was presumed to result from the excess hydrogen content in the Cu bulk because vast numbers of hydrogen atoms can easily diffuse into the metal when the Cu surface is exposed to the high-density H₂ plasma. It is also well known that hydrogen atoms tend to create vacancies in the metal because of the energetic stability of the vacancy–hydrogen complex, so these nonequilibrium vacancies tend to segregate, resulting in void formation in the Cu bulk. As a result, the roughness of the etched surface was considered to originate from these preformed voids. If the above surface roughening mechanism is accepted, prevention of atomic H diffusion into the Cu bulk seems to be a possible solution for surface roughness suppression. In hydrogen-using industries, such as thermal nuclear fusion and oil production, metal surfaces are often coated using a low hydrogen permeation layer to prevent hydrogen embrittlement of the metal. In the cases of Al and Ti metals, alumina and titanium oxide exhibit low permeability because of their low hydrogen diffusivity. In contrast, an iron nitride layer grown using plasma acts as a hydrogen trapping layer. Therefore, if surface-refining gases, which transform surfaces from metallic to nonmetallic bonds,
are supplied simultaneously to the plasma during Cu etching, an improvement in etched surface roughness can be expected because of the suppression of hydrogen diffusion into the metal. We focused on nitrogen gas as the surface-reforming gas because $N_2$ is a stable and inexpensive gas and Cu$_3$N is a nonmetallic and covalent material.24

Therefore, in this report, to improve the surface roughness and the etch rate in Cu etching using a subatmospheric-pressure hydrogen-based plasma, we have investigated the effects of addition of $N_2$ to the plasma on the Cu etching properties and have achieved dramatic improvements in the copper etching properties when using a high-pressure hydrogen-based plasma.

2. EXPERIMENTAL SECTION

The experimental setup that was used in this study is shown in Figure 1a. The apparatus has also been described in detail in a previous report.14 The Cu samples were 1 mm thick rolled Cu plates with a purity of 99.9%. Additionally, 0.7 mm thick SiO$_2$ glass was used to evaluate the etch selectivity. Trench-patterned wafers with electroplated Cu layers were also used to verify the feasibility of the process as a Cu wiring process. The samples were mounted on a Cu stage, and the stage temperature was maintained at 0 °C by circulating a coolant. The sample stage was grounded, so the Cu sample bias was 0 V. An In–Ga alloy was pasted on the bottom sample surface to improve the thermal conductivity between the stage and the sample. After loading the sample on the stage, the etch chamber was evacuated to a pressure of less than $10^{-3}$ Pa. Then, a $N_2$ and H$_2$ gas mixture was introduced into the chamber at a total pressure of 13.3 kPa (100 Torr). To provide insight into the role of nitrogen addition, Ar and He were also used as alternative additive gases in place of $N_2$.

The hydrogen mixture ratio ($C_{H_2}$) of the process gas was adjusted using mass flow controllers. The process gases were supplied directly to the plasma at a total flow rate of 10 standard liters per minute (SLM) through the pipe electrode, and the process chamber pressure was maintained at 13.3 kPa during the experiments by adjusting the exhaust conductance. The plasma gap between the pipe electrode and the sample was set at 0.7 mm. In this etching system, the Cu etch rate is also dependent on this plasma gap value and the etch rate generally decreases as the gap value increases. Very high frequency (VHF; 150 MHz) plasma input power ($W_{VHF}$) was supplied to the plasma gap through an impedance matching unit without any blocking capacitors to generate the plasma, and this power was varied as an experimental parameter. The VHF driving frequency was selected to generate a more localized high-density plasma around the apex of the pipe electrode when compared to that generated using a radio frequency (RF) source. Figure 1b,c shows photographs of the H$_2$-based plasmas generated at hydrogen mixture ratios of 1 and 0.9, respectively. The images show that the optical emission intensity around the apex of the pipe electrode is stronger than that in any other region in the setup. However, all aspects of the two plasmas seem to be almost identical, regardless of the hydrogen mixture ratio. The surface profile of the etched sample was obtained using a stylus surface profiler (Tokyo Seimitsu, Surfcom 590A). As mentioned in our previous report,14 because the etching depth shows a distribution along the radial direction of the electrode, the etch rate ($R_{etch}$) was calculated from the etched valley depth obtained and the etching time. The surface morphology of the sample was observed using a scanning electron microscope (SEM; Hitachi, S-4800). The surface roughness of the sample was evaluated using a laser scanning microscope (Keyence, VK-9710). Additionally, an optical emission diagnosis of the plasma was conducted using an optical spectrometer (Ocean Optics, HR-4000CG-UV-NIR).

3. RESULTS AND DISCUSSION

Figure 2 shows the effect of the addition of nitrogen on the etch rate ($R_{etch}$) obtained at an input power ($W_{VHF}$) of 70 W. The etching time was kept at 20 min. In Figure 2, the etch rates obtained for the He and Ar dilutions are also shown for a...
comparison of the additive gas effects. As shown in Figure 2, for the N2 gas addition, Cu etching was hardly observed when C_{H2} was less than 0.1 and R_{etch} increased with increasing C_{H2} until C_{H2} increased to 0.9. However, R_{etch} decreased with increasing C_{H2} above a value of 0.9 and R_{etch} reduced to 0.3 μm/min at a C_{H2} of 1. The maximum R_{etch} achieved by the nitrogen-added plasma was 2.4 μm/min at a C_{H2} of 0.9. From this result, R_{etch} was increased 8-fold by the addition of 1 SLM of N2 gas when compared to that of pure H2 plasma. On the other hand, for the He-added plasma, the etch rates were reduced by He gas addition when compared to that of the pure H2 plasma and did not show any remarkable C_{H2} dependence. Similarly, for the Ar-added plasma, the etch rates were almost the same as that of the pure H2 plasma and were independent of C_{H2}. In the pure hydrogen plasma used in this study, H^+ and H2 are the main ion species because H_2^+ ions react promptly with H2 molecules to form stable H^+ ions because of the short mean free path of the high-pressure process. Although Ar is heavier than H^+, H_2^+, and N2^+, addition of Ar did not affect the Cu etch rate at all. Therefore, physical sputtering by ions does not seem to be the sole cause of copper etching. A typical photograph of a Cu sample that was etched by the pure H2 plasma is shown in the inset of Figure 2. To indicate the positional relationship between the plasma electrode and the Cu sample, a schematic of the area around the electrode is also shown. Etching does not occur beneath the electrode central hole, and the maximum etched depth could be obtained beneath the electrode wall. Furthermore, a discolored area can be observed outside the plasma. This is caused by redeposition of a portion of the Cu etching product because the process gas was blown out of the central hole in the pipe electrode in this study. Therefore, if this redeposition is to be avoided, suction should be used to remove the process gas from the central hole.

Magnified photographs of the Cu samples that were etched by the nitrogen-added plasma at C_{H2} values of 1 and 0.9 are shown in Figure 3a,b, respectively. Figure 3d,e shows surface SEM images of the Cu samples when etched at C_{H2} values of 1 and 0.9, respectively. Additionally, a photograph and a surface SEM image of the as-received Cu sample are shown in Figure 3c,f, respectively. The as-received Cu sample shows fine scratches occurring in the same direction on its surface due to the rolling process. This roll mark can be observed in the SEM image shown in Figure 3f. As shown in Figure 3a,b, the appearances of the etched Cu samples clearly differed from each other. When the pure H2 plasma was used, the surface around the arrow, which indicated the deepest position of the etched valley, showed no gloss and was rough. In contrast, when using the 10% N2-added plasma, the etched surface area was shinier than that obtained using the pure H2 plasma. These differences among the appearance of the samples originated from the microscopic surface structure of the etched sample, as shown in Figure 3d,e. The roll mark existed on the as-received Cu sample vanished from both etched surfaces. When the pure H2 plasma was used, many bumps and voids with approximate diameters of a few hundred nanometers were observed on the surface. In contrast, when the 10% N2-added plasma was used, the surface morphology became smoother and the void density decreased drastically, although a few bumps and voids were still observed. Moreover, the contrast, which was caused by the different crystalline grain orientation, could be observed (see the arrows in Figure 3e). The surface roughness values (130 × 130 μm^2) measured by a laser microscope were R_a = 0.29 μm and R_a = 0.06 μm for the pure H2 plasma and the 10% N2-added plasma, respectively. N2 addition to the hydrogen plasma thus revealed...
improvements in both the Cu etch rate and the etched surface roughness. Figure 4a shows a photograph of the pure H₂ plasma generated at a plasma gap of 1 mm and an input power of 100 W.

Figure 4. (a) Photograph of the pure H₂ plasma generated at a plasma gap of 1 mm and an input power of 100 W. The H₂ pressure and H₂ flow rate were 100 Torr and 10 SLM, respectively. (b) Photograph of the plasma in (a) observed through an optical filter at a wavelength of 656 nm, which corresponds to the Balmer line of atomic hydrogen (Hₐ). (c) Optical emission spectra (OES) of the hydrogen-based plasma. Plasma was generated under the same experimental conditions used in Figure 2. The emission from the plasma was collected using an ultraviolet transmitting optical fiber that was attached 2 cm away from the plasma.

The H₂ pressure and H₂ flow rate are 100 Torr and 10 SLM, respectively. Figure 4a shows that the plasma optical emission region exists near the two electrode surfaces. Moreover, a relatively dark region when compared with the bright region near the electrodes can be observed around the center of the plasma gap. This spatial emission distribution of the plasma becomes much more obvious in Figure 4b. Figure 4b shows a photograph of the plasma when observed through an optical filter at a wavelength of 656 nm, which corresponds with the Balmer line of atomic hydrogen (Hₐ). As shown in Figure 4b, the intensity saturation region in the photograph indicates that the high-density atomic hydrogen is generated at the apex of the electrode and below the electrode wall. It is also confirmed that the luminous region is distributed around the surfaces of the two electrodes. When compared with the luminous region around the electrode surface, hydrogen generation is not as remarkable as around the center of the gap. The column connecting the electrode to the sample and the spark are not observed in the plasma gap. This spatial distribution in the plasma luminous region indicates that the plasma is sustained in the γ-mode, which is largely dominated by secondary electron emission from the metal electrode.²⁶

Figure 4c shows the optical emission spectra (OES) of the various plasmas during Cu etching. With the exception of the pure N₂ plasma, H₂ could be observed at the wavelength of 656.6 nm but the Balmer line of atomic hydrogen (Hₐ) at 486 nm was barely visible. The hydrogen line ratios (H₁/Hₐ) between H₂ and N₂ that were obtained at various N₂ mixture ratios are remarkably lower than that of the methane-containing low-pressure hydrogen plasma at 20 mTorr.²⁷ Because the average electron energy is reported to range from 2.5 to 3.0 eV in that low-pressure hydrogen plasma, the electron energy of the plasma in this study is estimated to be much lower than 2.5 eV. This reduction in the electron energy is related to the high process pressure and the use of the VHF plasma driving frequency, which is higher than RF.²⁸ Moreover, since no etching was observed without H₂ gas, the presence of atomic hydrogen was thus of primary importance to the copper dry etching process. However, the H₂ emission intensity of the pure hydrogen plasma was slightly higher than that of the 10% N₂-added plasma, although the etch rate of the 10% N₂-added plasma was 6 times higher than that of the pure hydrogen plasma. This result indicates that the increase in the Cu etching rate by N₂ addition is not due to the increased atomic hydrogen density of the 10% N₂-added plasma but is caused by other mechanisms. In contrast, the OES of the N₂-added plasma showed that broad emission bands from the excited nitrogen molecules were observed in the wavelength range from 300 to 400 nm (second positive system) and in the range from 550 to 800 nm (first positive system).²⁹,³⁰ Emission from N₂⁺ was also observed at 391.3 nm, and its emission intensity relative to the other nitrogen-related emissions increased with increasing CuVHF from 0 to 0.9. Although an emission from an NH radical appears at 337 nm, this band was overlapped by the N₂ second positive system and the two emissions were unable to be separated. However, in this H₂ and N₂ gas mixture plasma, it was confirmed by gas-phase Fourier transform infrared spectroscopy that ammonia was produced (data not shown). Ammonia production in the plasma usually required a NH radical as an intermediate product,³¹ and NH radicals were typically generated via the following reaction processes.³²−³⁴

\[
\begin{align*}
N^+ + H_2 &\rightarrow NH + H \\
N_2^+ + H_2 + e^- &\rightarrow 2NH \\
N_2^+ + H + e^- &\rightarrow NH + N
\end{align*}
\]

From the above equations, NH radical formation requires N₂⁺ or an N atom in addition to an H atom. Then, the NH radical can be produced in the plasma and contributes to the nitridation of the copper surface. With regard to Cu, though strong emission lines could be observed at 324.8, 327.4, and 321.8 nm, a more remarkable emission comparable to that from the H atom was not observed. This lack of emission from the Cu atoms could be explained in two ways: either most of the etched Cu evaporated in the form of copper compounds, such as copper hydride, or the emission from the Cu atoms was diminished because of quenching by H₂ molecules. Figure 5 shows the W_VHF dependence of Retch that was obtained at a CuVHF of 0.9. The Cu etch rates obtained by the pure H₂ plasma are also shown in Figure 5. Retch increased linearly as W_VHF increased from 40 to 100 W. The sample temperature near the surface also increased by plasma heating as W_VHF increased. In particular, for the pure H₂ plasma, it was estimated that the temperature near the sample surface increased from 50 to 250 °C as W_VHF increased from 40 to 100 W based on ultrafine diameter (d = 80 μm) sheath thermocouple measurements, although the Cu sample was chilled from its bottom surface by the Cu stage at 0 °C. Retch reached 3.1 μm/min at 100 W. In comparison with the rates for the pure H₂ plasma, all etch rates obtained were dramatically improved by the addition of N₂. Similar to the etching behavior of the N₂-added plasma, Retch for the pure H₂ plasma increased linearly with increasing W_VHF. However, the gradient between Retch and W_VHF became larger for the N₂-added plasma when compared to that for the pure H₂.
Figure 5. Input VHF power dependence of the Cu etch rate (○) for the 10% N2-added plasma. For comparison, Cu etch rates obtained by the pure H2 (○) and etch rate for SiO2 glass (△) by the 10% N2-added plasma are also shown. The stage temperature and total flow rate are 0 °C and 10 SLM, respectively.

plasma. This different gradient implied that the generation of nitriding species and nitridation of the Cu surface occurred as a renewed rate-limiting process for Cu etching with N2 addition. In addition, Figure 5 also shows $R_{\text{etch}}$ for SiO2 when using the N2-added plasma at 100 W. The $R_{\text{etch}}$ obtained was 16.4 nm/min, which was lower than that for the pure hydrogen plasma, because the $R_{\text{etch}}$ for SiO2 by the pure H2 plasma was 45 nm/min. The etching rate ratio between SiO2 and Cu was 11, for N2 addition also has an effect on the etching behavior strongly. The proposed etching model is shown in Figure 6. In the case where nitrogen is added to the process atmosphere, a thin nitride layer would be formed by nitrogen radicals. If stoichiometric Cu3N is formed as this nitride layer, the bond lengths of Cu–Cu in metallic Cu and Cu–N in Cu3N would be 2.56 and 1.91 Å, respectively. Therefore, the Cu3N structure is denser than that of metallic copper and the nitride layer would act as a barrier layer for reactive radicals because its structure is denser than that of metallic Cu. This barrier effect is expected to be effective for both the nitriding species and atomic hydrogen. Therefore, the formation of a thick nitride layer and diffusion of excess hydrogen into the metal would be inhibited. Suppression of the excess hydrogen diffusion into the metal leads to the inhibition of excess void formation in the Cu bulk, as shown in Figure 6b. Furthermore, Cu3N appears to be a covalent compound, which means that the defective nitride layer will contain multiple dangling bonds. Therefore, a lot of atomic hydrogen would be accumulated in the nitride layer due to dense nitride structure and trapping by the dangling bonds. In contrast, it was reported that pyrolysis of Cu3N becomes remarkable in a vacuum atmosphere when the sample temperature exceeds 350 °C.34 Cu3N does not seem as thermodynamically stable as other nitrides, e.g., AlN and Si3N4. It is thus expected that copper nitride will react easily with atomic hydrogen. If a thin Cu3N layer covered the Cu surface, Cu hydride was proposed to be formed via the following reaction

$$2\text{Cu}_3\text{N} + 6\text{H} \rightarrow 6\text{CuH} + \text{N}_2$$ (4)

The formation enthalpies for Cu3N, H, and CuH are known to be 74.5,47 472, and 27.5 kJ/mol, respectively. Although the enthalpies for Cu3N and CuH are unfortunately unknown, given that the enthalpies for Cu3N and CuH are equal to that for CuO, the reaction in eq 4 would be possible below 1000 °C in the presence of atomic hydrogen. Therefore, hydrogen atom accumulation in the nitride layer appears to enhance the reaction between Cu and H while suppressing void formation in the Cu bulk, unlike pure hydrogen plasma. Choi et al. reported that Cu can be etched using a low-pressure pure methane plasma at higher etch rates than a low-pressure pure hydrogen plasma.27 In their report, it was estimated that the etch products were changed from unstable CuH species to relatively stable CH3Cu or CH4CuH species by changing the process atmosphere from pure H2 to pure CH4. In contrast, in this study, copper etching did not occur under the pure N2 plasma. The copper etching only proceeded when the process atmosphere contained hydrogen gas. Therefore, copper etching appears to be preceded by copper hydride formation. It was also reported that CuH shows relatively low vapor pressure.20 Ion bombardment may thus enhance the vaporization of CuH. In this study, the mean free paths of the particles at the process pressure of 100 Torr at room temperature and 600 K are approximately 3.5 and 7.1 μm, respectively. If an electron temperature of 0.8 eV and an electron density of 1013 cm−3 are assumed, the Debye length (in meters) is estimated to be 2.1 μm according to the following equation

$$\lambda_{\text{De}} = 7.43 \sqrt{\frac{T_e}{n_e}}$$ (5)

where $T_e$ and $n_e$ are the electron temperature (in volts) and the electron density, respectively. If the sheath thickness is only several times longer than the Debye length, the sheath thickness is calculated to be ~8 μm. When the gas temperature is sufficiently higher than room temperature, the mean free path becomes comparable to the sheath thickness. In this case, the
ions in the plasma could be accelerated in the sheath region with relatively fewer collisions among the particles and ion impingement on the CuH surface appears to be a possible candidate for CuH vaporization enhancement. In this case, nitrogen addition may also enhance the ion impingement effect by forming heavier ion species such as N³⁺ rather than H⁺ in the pure H₂ plasma. However, because no etch rate enhancements by Ar dilution were observed, ion bombardment does not appear to play a main role in etch rate enhancement in the N₂-addited plasma. At the present stage, although the detailed mechanism of etching enhancement based on N₂ addition is yet to be clarified, surface nitridation plays an important role in Cu etching.

Figure 7a,b shows cross-sectional SEM images of the trench-patterned Si wafer before and after 10% N₂-addited plasma etching, respectively. Figure 7c shows a bird’s-eye view SEM image of the N₂-addited plasma-etched sample. The plasma exposure time and W_{VHF} were 1 min and 40 W, respectively. As shown in Figure 7, the superfluous Cu film was removed by plasma etching, leaving the required Cu film in the trench. In addition, the TaN film acted as an etch barrier for the N₂-added plasma. In contrast, Figure 7d shows a bird’s-eye view SEM image of the sample after pure H₂ plasma etching. The etching time and W_{VHF} were 3 min and 70 W, respectively. The pure H₂ plasma-etched surface was rougher than that etched using the N₂-added plasma. Furthermore, a porous structure containing a lot of voids was observed on the pure H₂ plasma-etched surface. Since the surface roughness of Cu wiring is correlated to its resistivity,

In this study, to improve the dry etching properties of Cu when using the high-pressure hydrogen-based plasma, nitrogen gas was added to the plasma atmosphere. A maximum Cu etch rate of 2.4 μm/min was obtained with nitrogen addition at a H₂ mixture ratio (C_{H₂}) of 0.9 and an input power of 70 W. This Cu etch rate is 8 times higher than that of the pure hydrogen plasma. Furthermore, nitrogen addition at the C_{H₂} of 0.9 changed the surface roughness and morphology of the etched surface dramatically. The etched surface became smooth with nitrogen addition reducing the density of nanosized voids. The plasma optical emission spectra indicated that the increase of the copper etch rate obtained by adding N₂ gas was not due to the increase of atomic hydrogen density in the 10% N₂-added plasma. The Cu etch rate increased with increasing input power. The maximum etching rate attained was 3.1 μm/min at an input power of 100 W and a C_{H₂} of 0.9. On the other hand, the etch rate for SiO₂ decreased with nitrogen addition when compared to that for the pure hydrogen plasma. This also indicated that the increased Cu etch rate with nitrogen addition was not induced by increased atomic hydrogen density but by nitrogen-related surface reactions. As a result, the etch selectivity between SiO₂ and Cu reached 190. Using this selectivity, the unnecessary Cu film was removed, leaving the required Cu film in the trench. We conclude that this etching method has demonstrated a partial capability for use as an alternative Cu wiring technique.

4. CONCLUSIONS

In this study, to improve the dry etching properties of Cu when using the high-pressure hydrogen-based plasma, nitrogen gas was added to the plasma atmosphere. A maximum Cu etch rate of 2.4 μm/min was obtained with nitrogen addition at a H₂ mixture ratio (C_{H₂}) of 0.9 and an input power of 70 W. This Cu etch rate is 8 times higher than that of the pure hydrogen plasma. Furthermore, nitrogen addition at the C_{H₂} of 0.9 changed the surface roughness and morphology of the etched surface dramatically. The etched surface became smooth with nitrogen addition reducing the density of nanosized voids. The plasma optical emission spectra indicated that the increase of the copper etch rate obtained by adding N₂ gas was not due to the increase of atomic hydrogen density in the 10% N₂-added plasma. The Cu etch rate increased with increasing input power. The maximum etching rate attained was 3.1 μm/min at an input power of 100 W and a C_{H₂} of 0.9. On the other hand, the etch rate for SiO₂ decreased with nitrogen addition when compared to that for the pure hydrogen plasma. This also indicated that the increased Cu etch rate with nitrogen addition was not induced by increased atomic hydrogen density but by nitrogen-related surface reactions. As a result, the etch selectivity between SiO₂ and Cu reached 190. Using this selectivity, the unnecessary Cu film was removed, leaving the required Cu film in the trench. We conclude that this etching method has demonstrated a partial capability for use as an alternative Cu wiring technique.

ACKNOWLEDGMENTS

This work was partly supported by KAKENHI (16H04245, 18K188090).

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