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Studies on Sn Thin Film Decomposition Using VHF hydrogen plasmas

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One of the serious problems of EUV lithography is the accumulation of tin debris on the surface of the condenser mirror, which reduces the reflectance. This study investigated the possibility of using VHF hydrogen plasmas to decompose attached Sn debris. First, a simple VHF hydrogen plasma was generated, and the efficiency and characteristics of Sn removal with respect to hydrogen gas pressure, gas flow rate, and sample temperature were investigated. Regarding the gas pressure dependence of Sn removal, a Sn etching rate of 4.8 nm/min was obtained at 35 Pa. This was more than twice as large as the value previously reported using a RF hydrogen plasma. Furthermore, as a result of combining the hollow cathode discharge, which has an electron confinement effect, with the VHF discharge, the electron density was more than doubled. For this case, the maximum Sn etching rate of 8.3 nm/min was obtained.

Key words: *EUV lithography, Sn debris removal, VHF hydrogen plasma, Hollow-cathode discharge*

1. Introduction

Semiconductor devices are becoming more and more highly integrated. Therefore, a 7 nm node semiconductor process using EUV (Extreme Ultra-Violet) lithography has been started.[1)] The EUV lithography light source uses the resonance line (wavelength 13.5 nm) of tin polyvalent ions from high-temperature and high-density tin plasmas obtained by irradiating tin droplets with a CO_2 laser. At that time, tin debris is generated from the tin droplets and adheres to the EUV condenser mirror, which causes a problem of lowering the reflectance of the mirror. Although 250 W EUV light sources have already been commercialized,[2,3)] it is necessary to further increase the output in the future, and the problem of debris removal will become even more important.

As a countermeasure, it has been proposed to react tin debris with hydrogen atoms to generate volatile gas SnH_4 and remove it from the mirror surface.[4)] In an actual EUV light source device, the chamber is filled with hydrogen gas of about 10 Pa, and hydrogen molecules are dissociated and ionized by EUV light (photon energy 92 eV). Finally, hydrogen atoms are reacted with tin atoms to generate SnH_4, and SnH_4 is exhausted together with hydrogen gas.[5,6)] As a study of the tin removal process, Ugur et al. investigated the decomposition of tin through a chemical reaction using a hydrogen atom flux generated by dissociating hydrogen molecules with a hot filament.[7,8)] As a result, it was reported that one tin atom was removed for every 100,000 hydrogen atoms.

As another method, it was considered to generate a hydrogen plasma and efficiently remove tin by RIE (Reactive Ion Etching) using the energy of hydrogen ions. In that method, Elg et al. reported that SnH_4 generation was promoted by breaking the bond between metal tin atoms with the energy of hydrogen ions.[9,10)] In that study, RF (radio frequency: 13.56 MHz) power was supplied to the powered electrode to irradiate the tin thin film on the electrode surface with hydrogen ions. Hydrogen ions were accelerated through the cathode sheath by the negative bias voltage (-300 V) appearing on the electrode surface. As a result, hydrogen ions obtained energy of approximately 300 eV. Elg et al. have achieved a tin etching rate of 1.7 nm/min. However, Elg et al. concluded that tin etching was independent of gas flow rate and surface temperature, and readhesion was negligible.

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Furthermore, the use of ions of several hundred eV may cause damage due to sputtering on the mirror surface.

The authors have already investigated the dependence of tin removal on hydrogen ion energy.[11] Bias voltages from -50 V to +7.5 V were applied to a Si substrate on which a thin film of tin is deposited (hereinafter, Sn sample) exposed to hydrogen plasma to change the hydrogen ion energy. As a result, it has been clarified that the number of tin atoms removed per hydrogen ion is maximized with hydrogen ion energy of approximately 10 eV.

As for the hydrogen plasma generation method, a higher density plasma can be obtained by using a VHF (very high frequency, 30-300 MHz) power supply. In this study, the possibility of using VHF plasma for tin removal was investigated. By placing a Sn sample on the ground electrode, the voltage of the ion sheath becomes about 10 V, and it is expected that RIE will proceed with maximum efficiency as described above. In this study, we first clarified the basic tin removal characteristics by VHF plasma using three variable parameters: hydrogen gas pressure, hydrogen gas flow rate, and Sn sample temperature. Furthermore, we investigated the possibility of realizing efficient tin removal using RIE by combining VHF discharge with the hollow cathode effect to further increase the electron density.[12, 13]

2. Experimental Setup

A schematic diagram of the experimental equipment is shown in Fig. 1 (a) and 1 (b). In Fig. 1 (a), VHF plasma was generated in the entire chamber, and the tin removal characteristics of the basic VHF plasma were investigated in this arrangement. A 60 MHz VHF power supply was connected to the top electrode to power the device. The inner diameter of the quartz glass tube in the discharge space was 62 mm, and a Sn sample for tin removal experiments was installed at the bottom of the chamber (earth electrode) and fixed with a stainless-steel holding plate (thickness 0.1 mm) and screws. The Sn sample is a 100 nm thick tin film deposited on the surface of a silicon substrate with an area of 15 mm × 15 mm and a thickness of 0.625 mm. The tin film has the same potential as the ground electrode through the holding plate. The port for introducing hydrogen gas and the port for exhausting hydrogen gas were arranged in a straight line, most of the hydrogen gas flowed

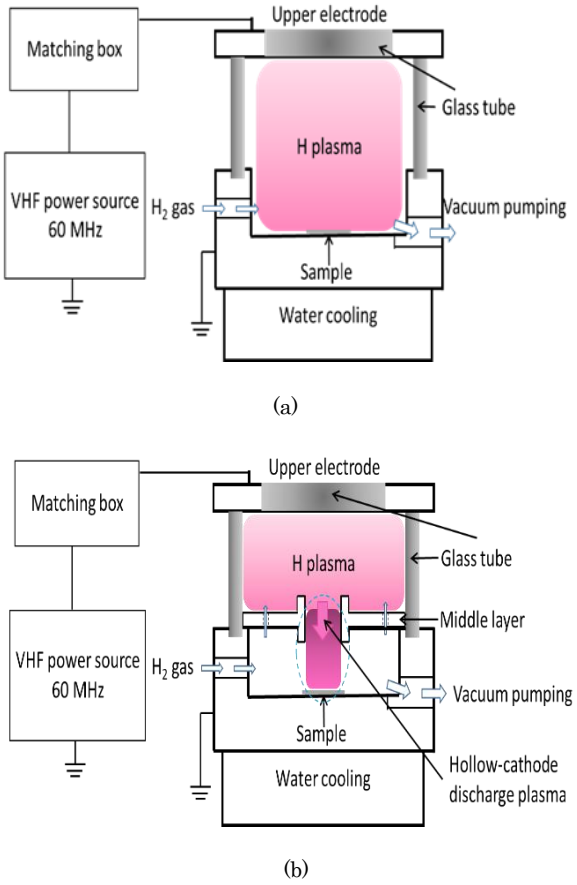


Fig. 1 Schematic of experiment system.

above the sample and the generated SnH_4 molecules were carried away by this flow. The vacuum vessel was evacuated to a pressure of 7×10^{-2} Pa using a turbo molecular pump. Constant temperature water was flowed inside the ground electrode to control the temperature. The Sn sample was brought into close contact with the ground electrode, and the temperature of the Sn sample was also controlled. The power supply was used in the output range of 20 W to 30 W.

As shown in Fig. 1 (b), the vacuum vessel was divided into an upper space and a lower space by a partition metal plate which was at a ground voltage, and a structure having a hollow cathode effect was created in the center of this partition metal plate. The side wall of the upper space was a quartz glass tube, and the height of the space was 30 mm. The VHF plasma was generated in this upper space. The lower space had an inner diameter of 56 mm and a depth of 16 mm and was surrounded by stainless-steel surfaces and a partition metal plate. That is, the entire surrounding surface was at the ground voltage. A metal cylinder with an inner diameter of 16 mm and a height

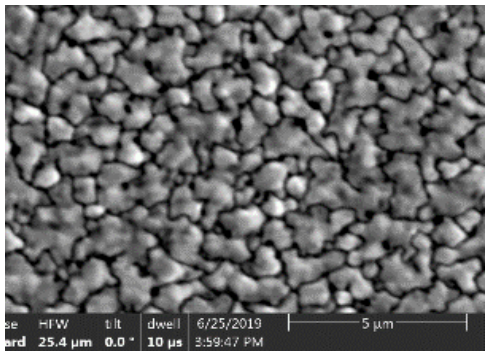
of 19 mm was attached to the center of the partition metal plate. The Sn sample was placed on the bottom surface just below the cylinder. In addition, 20 or more holes with a diameter of 3 mm were made in the partition metal plate around this cylinder so that hydrogen gas introduced from the side surface of the lower space could be supplied to the upper space as well. The hydrogen plasma generated in the upper space was ejected into the lower space through the cylinder in the center of the partition metal plate. The inside of this cylinder caused the hollow cathode effect, and the Sn sample was irradiated with hydrogen plasma having a higher electron density than that of VHF plasma alone. Hollow cathode discharge did not occur in the holes with a diameter of 3 mm.

XRF (X-Ray Fluorescence) and SEM (Scanning Electron Microscope) were used for the evaluation of tin removal. The device used for XRF analysis was Shimadzu EDX800. The actual film thicknesses of the Sn samples were measured by the crystal oscillator method. They were used for calibration during XRF analysis. Before and after the experiment, the amount of tin in the Sn sample was detected as a SnLα signal and converted to film thickness. At the center of the sample, changes in the state of the tin film surface were observed by SEM.

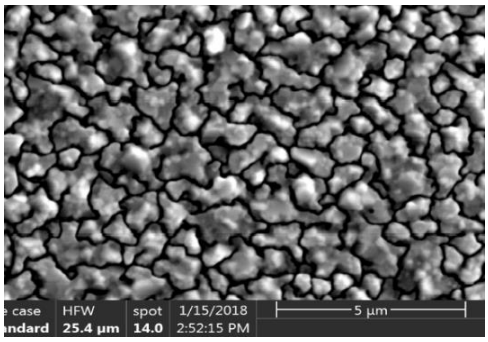
3. Results and Discussion

Figure 2 shows sample-surface observation images by SEM. In these images, the magnification is 5000 times. Figure 2 (a) is an image of the surface of the sample not exposed to plasma. Gray tin is evenly distributed with almost no gaps. Figure 2 (b) is an image when the plasma irradiation time is 10 min. About half of the tin film (thickness 100 nm) has been removed, and the film appears to be uniformly etched. Figure 2 (c) is an image with a plasma irradiation time of 20 min. The part that looks black is the silicon base. Tin remains like islands. In this case, it is considered that the relationship between the amount of Sn removed and the time deviates from the linearity. The etching rate should be determined before the time when half of the tin is removed.

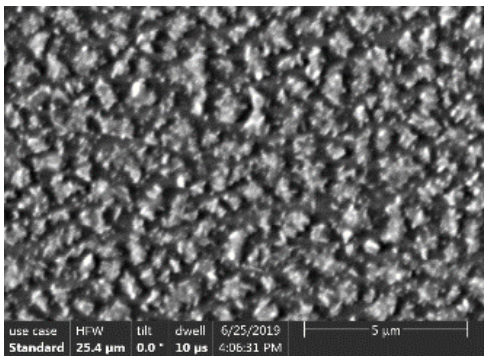
Figure 3 shows the pressure dependence of tin removal. The hydrogen gas pressure was changed to 15, 35, 75 and 150 Pa. The power was fixed at 20 W, the hydrogen gas flow rate was 20 sccm, and the ground electrode



(a)



(b)



(c)

Fig. 2 SEM images of Sn samples for different plasma exposure conditions. (a) no plasma exposure, (b) 10 min plasma exposure and (c) 20 min plasma exposure.

temperature (that is, Sn sample temperature) was fixed at 20 °C. The exposure time of the sample to plasma was 10 min. The tin removal amount is the highest at 35 Pa, which is equivalent to 48 nm thickness. That is, the etching rate is 4.8 nm/min. It is probable that the tin removal amount at the pressure of 35 Pa increased as compared with the case of the pressure of 15 Pa because the electron density became higher and the hydrogen ion flux irradiated to the Sn sample increased. It can be believed that the decrease in tin removal at pressures of 75 and 150 Pa above 35 Pa is due to the fact that SnH_4 exiting the tin surface collides with hydrogen molecules in a short mean free path, increasing the probability of

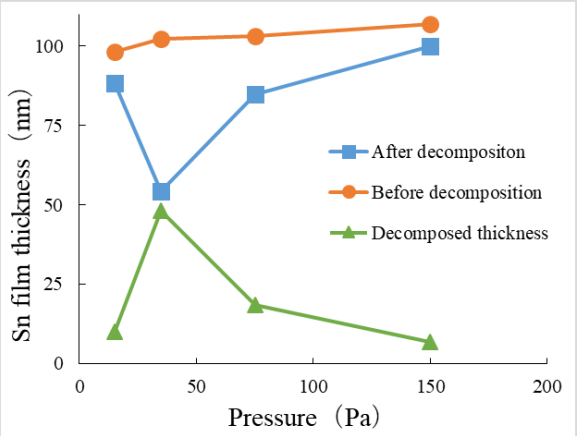


Fig. 3 Dependence of Sn removal on hydrogen gas pressure.

returning to the tin film surface and causing readhesion.

Figure 4 shows the dependence of tin removal on the hydrogen gas flow rate. The power was fixed at 20 W, the hydrogen gas pressure was fixed at 50 Pa, and the Sn sample temperature was fixed at 20 °C. The plasma exposure time was 30 min. As the flow rate increased, the amount of tin removal clearly increased. That is, in tin removal using hydrogen plasma, it is important to quickly carry the generated SnH_4 away from the tin surface by the flow of hydrogen gas.

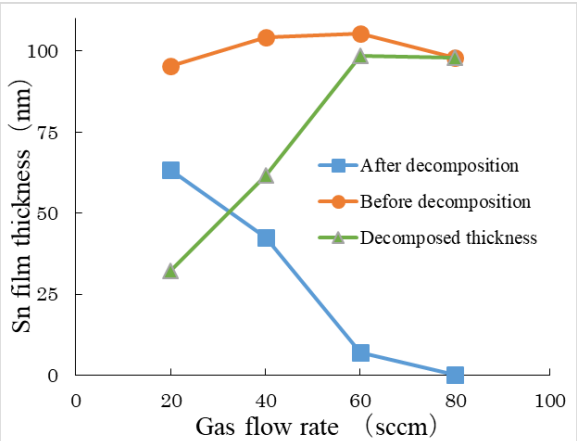


Fig. 4 Dependence of Sn removal on hydrogen gas flow rate.

Figure 5 shows the Sn sample temperature dependence of tin removal. The power was fixed at 20 W, the hydrogen gas pressure was fixed at 50 Pa, and the gas flow rate was fixed at 80 sccm. The plasma exposure time was 30 min. According to the experimental results, almost all tin with a thickness of 100 nm was removed when the Sn sample temperature was 20 °C, but the amount removed was reduced to one-fourth at 60 °C. According to the report of Tamaru,[14] the reaction rate of SnH_4 dissociation increases by about an order of magnitude with a temperature rise of 60 °C. The results of this experiment make us realize how easily readhesion occurs when the temperature of the tin surface is high.

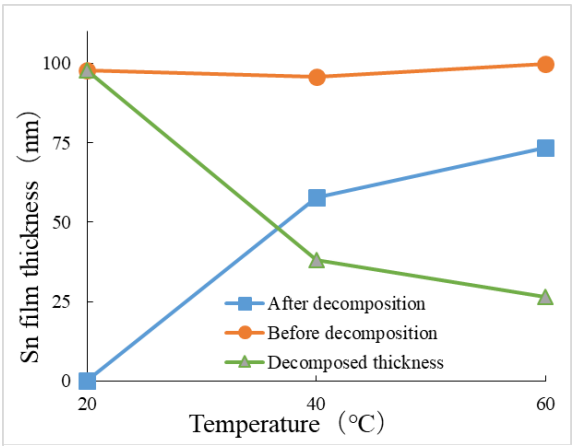


Fig. 5 Dependence of Sn removal on Sn sample temperature.

In the pressure dependence of tin removal, the highest etching rate of 4.8 nm/min was obtained at a gas pressure of 35 Pa. In this case, we evaluate the Sn yield which is the number of tin atoms removed per hydrogen ion. Under the conditions of this experiment, the hydrogen ion was H_3^+.[15] Since the density of metallic tin is 7×10^3 kg/m^3 and the mass of a tin atom is 2.0×10^{-25} kg, the number of tin atoms removed in 10 minutes per unit area of tin film is evaluated as 1.7×10^{21} m^{-2}. On the other hand, the dose amount of hydrogen ions irradiated to the tin film is required. An ion sheath is formed on the surface of the Sn sample at the ground potential exposed to VHF hydrogen plasma, and the Bohm flux of hydrogen ions passing through the sheath end is expressed by the following equation.[16]

$$\Gamma_i = 0.61 n_e \sqrt{\frac{k_B T_e}{m_i}} \qquad (1)$$

Here, k_B is the Boltzmann constant, m_i is the hydrogen ion mass, n_e is the electron density, and T_e is the electron temperature. In order to measure the electron density and electron temperature of the VHF plasma, the probe measurement was performed at a height of about 8 mm from the center bottom of the chamber. The measured values at a pressure of 35 Pa were an electron density of 2.8×10^{15} m^{-3} and an electron temperature of 2.6 eV. From this, the dose amount of hydrogen ions per unit area for 10 minutes is 8.5×10^{21} m^{-2}. That is,

the Sn yield is 0.20. In other words, five hydrogen ions remove one tin atom.

In order to investigate the promotion of tin removal by adding the hollow cathode effect to VHF hydrogen plasma, a tin removal experiment was conducted using the device shown in Fig. 1 (b). From the experimental results of the basic tin removal characteristics in VHF plasma, the optimum conditions were a gas pressure of 35 Pa and a sample temperature of 20 °C, so these conditions were fixed. The power was 30 W. The plasma exposure time was set to 6 min so that the amount of tin film removed did not exceed 50 nm in thickness. In order to investigate the dependence of tin removal on the hydrogen gas flow rate, the change in tin film thickness was measured by changing the hydrogen gas flow rate to 20, 40, and 60 sccm. The results are shown in Table 1. As can be seen from the table, a peak etching rate of 8.3 nm/min was obtained with a hydrogen gas flow rate of 20 sccm. As a result of probe measurement under the cylinder provided in the center of the partition metal plate, an electron density of 6.6 $\times 10^{15}$ m^{-3} and an electron temperature of 3 eV were obtained. When the efficiency as RIE is evaluated based on these data, the Sn yield is 0.12. Taking the reciprocal, this corresponds to the removal of one tin atom by 8.1 hydrogen ions. The efficiency of this tin removal is lower than the above-mentioned maximum value when VHF plasma is used.

As can be seen from Table 1, the results of this experiment incorporating the hollow cathode discharge clearly contradict the results of Fig. 4 in that the amount of Sn removed decreases with the hydrogen gas flow rate. This experimental result suggests that it is out of the optimum conditions. In this arrangement, the flow of hydrogen gas is orthogonal to the plasma ejected from the hollow cathode discharge, and the higher the hydrogen gas flow rate, the more likely it is that the irradiation of the plasma on the Sn sample surface is hindered. This means that, in the current equipment configuration, the relationship of Sn removal with respect to the hydrogen gas flow rate cannot be optimized, and it is necessary to improve the equipment in order to obtain the optimum etching rate.

Table 1 Results of Sn removal by hollow-cathode discharge

Gas flow rate [sccm]	Decomposed thickness of Sn [nm]	Etching rate [nm/min]
20	49.7	8.3
40	48.8	8.1
60	34.7	5.8

4. Conclusion

In this study, in order to clarify the possibility of efficient Sn debris removal by VHF hydrogen plasma, we first investigated the efficiency and characteristics of Sn removal with respect to hydrogen gas pressure, hydrogen gas flow rate, and Sn sample temperature. As a result, an etching rate of 4.8 nm/min was achieved. The following conclusions were obtained from these basic data. (i) The higher the electron density, the better to promote RIE and increase the etching rate. (ii) If the gas pressure is high and SnH_4 is not sufficiently separated from the Sn sample surface, readhesion is likely to occur. (iii) To prevent readhesion, it is effective to increase the gas flow rate and lower the Sn sample temperature. In order to increase electron density, hollow cathode discharge was combined with VHF discharge. As a result, the electron density was more than doubled, and the maximum etching rate of 8.3 nm/min was obtained. However, the Sn yield value for evaluating the efficiency of RIE was reduced to about 60% in the case of VHF discharge alone.

In a device in which the hollow cathode effect is superimposed on the VHF discharge, the etching rate is expected to be further improved by optimizing the gas flow so as to promote the separation of SnH_4 from the tin surface.

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