Effect of Hydrogen Ion Energy in the Process of Reactive Ion Etching of Sn Thin Films by Hydrogen Plasmas

Mengran JI, Ryo NAGATA and Kiichiro UCHINO

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816-8580, Japan

One of the problems in extreme ultraviolet (EUV) lithography is the deterioration in the reflectivity of the EUV mirror owing to the deposition of tin (Sn) debris. Such Sn adhesion films can be etched by hydrogen ions and atoms through a chemical reaction, forming a volatile SnH_4 gas. In this study, the dependence of the hydrogen ion energy on the Sn etching was investigated. Samples covered by Sn thin films and with various applied bias voltages were exposed to hydrogen plasmas. The etched thicknesses of the Sn films were quantitatively analyzed using X-ray fluorescence. As a result, it was found that the threshold ion energy is approximately 7 eV, and that the peak of the Sn atom yield per hydrogen ion, which is the value indicating the efficiency of the reactive ion etching, is obtained at a hydrogen ion energy of approximately 14 eV.

1. Introduction

Extreme ultraviolet (EUV) lithography, employing a light wavelength of 13.5 nm, has been successfully applied in the mass production of semiconductors using 7-nm node processes [1]. EUV lithography uses emissions from multiply charged tin (Sn) ions, as generated by the laser irradiation of tin droplets with diameters of approximately $20\,\mu m$. Currently available sources for EUV lithography systems are typically based on high-density hot Sn plasmas [2, 3]. Sn droplets bombarded by lasers produce Sn debris adhering to the surface of the collection mirror, resulting in the deterioration of the reflectance. Therefore, it is necessary to efficiently decompose the Sn debris adhered to the mirror surface.

Studies have proposed etching the Sn debris through a chemical reaction between a Sn atom and four hydrogen atomic radicals, thereby producing the volatile molecule SnH_4 [4, 5]. Ugur [5] produced hydrogen atoms using a hot filament method, and introduced them to the surface of Sn thin films. The decrease in the thin films was quantitatively measured, and it was found that approximately 90 000 hydrogen atoms were necessary to produce one SnH_4 molecule [5]. In a real EUV system, EUV photons (energy 92 eV) dissociate hydrogen gas, which fills the EUV source chamber at approximately 10 Pa; the generated SnH_4 molecules from the Sn etching are evacuated from the chamber, together with the hydrogen gas. Elg *et al.* [6] proposed an additional Sn removal system based on using an EUV mirror as a powered electrode, and produced a hydrogen plasma using a radio frequency power source at a frequency of 13.56 MHz. The plasma could directly supply hydrogen atoms to the surface of the EUV mirror. Subsequently, Elg *et al.* also claimed [7] that reactive ion etching, which utilizes hydrogen ion energy, can more efficiently remove Sn films adhered on an EUV mirror surface than etching using hydrogen atoms alone. In their experimental device, a self-bias voltage of approximately −300 V appeared at the powered electrode simulating the EUV mirror, and the average hydrogen energy was estimated to be more than 300 eV [6].

Reactive ion etching has already been investigated as a method for removing carbon (C) thin films deposited on an EUV mirror surface [8–10]. The method utilizes the synergistic effects between hydrogen atoms and argon or hydrogen ions to etch C and generate CH_4 (or other volatile hydro-carbon molecules).

In this C etching, the bond energy of the C is approximately 7 eV, and it has been found that the etching progresses as the ion energy increases [8, 10]. In contrast, the bond energy of Sn is as low as approximately 3 eV (as described later); therefore, the hydrogen ion energy dependence of the Sn etching is considered as different from that of the C etching. The authors obtained a much higher Sn etched thickness per minute than those obtained by Elg *et al.* [7]. We used a very high-frequency (VHF) hydrogen plasma, and samples with Sn thin films (hereafter referred to as "Sn samples") were set on a grounded electrode [11]. The hydrogen ions impinging on the Sn sample through the ion sheath should have had energies of approximately 10 eV.

Based on the above, we investigated the dependence

author's e-mail: ji.mengran.266@s.kyushu-u.ac.jp

of the hydrogen energy on the Sn etching. We applied various bias voltages to Sn samples, and arranged the plasma so as to be at a stable space potential, so that we could examine the threshold hydrogen ion energy for Sn etching (currently thought to be a few eV).

2. Experimental Setup and Methods

The Sn samples were Si substrates with an area of 15×15 mm^2 and thickness of 0.625 mm. The samples were covered by deposited Sn thin films, each with a thickness of approximately 100 nm. The etched thicknesses of the Sn thin films were quantitatively measured via X-ray fluorescence (XRF) analysis. The details of the analysis will be described later.

A schematic diagram of the experimental device is shown in Fig. 1 (a). The vacuum chamber was divided into upper and lower spaces by a metal partitioning plate with a thickness of 3 mm. The side wall of the upper space was a quartz glass tube with an inner diameter of 62 mm. The upper surface of the upper space was the powered electrode, and the spacing between the powered electrode and partitioning plate at the ground potential was approximately 30 mm. A VHF power source at a frequency of 60 MHz

(a)

(b)

Fig. 1 (a) Schematic of the experimental setup. (b) Schematic of the side view of the DC bias structure.

supplied a power of 15 W to the powered electrode, and the hydrogen plasmas were produced in the upper space.

The lower space was formed in a stainless-steel block with an outer radius of 112 mm. The lower space had a radius of 56 mm and cutting depth of 16 mm. The ceiling of this space comprised the partitioning metal plate. As the stainless-steel block was grounded, the lower space was surrounded by a circular side wall at the ground voltage. At the bottom of this lower space, a structure was installed to apply DC bias voltages to the Sn samples. The height of the surface of the Sn sample was 3 mm from the bottom. The electron density and electron temperature were measured using a Langmuir probe at 4 mm above the Sn surface (7 mm above the bottom surface). The measuring part of the probe comprised cylindrical tungsten with a length of 10 mm and diameter of 0.5 mm. The probe was inserted through a port hole provided on the side wall with a diameter of 6 mm (the center height was 7 mm from the bottom). There were three other holes with the same diameter, which were used for gas pressure monitoring, H$_2$ gas introduction, and lead wire introduction for the DC bias voltage. At the outside of the vacuum chamber, a small resistor was inserted into the lead wire circuit, and the voltage across the resistor was measured to determine the current flowing into the Sn sample. In addition, the voltage on the sample side was measured. A port hole with a diameter of 12 mm was also provided on the side wall, through which the vacuum chamber was evacuated.

A hole with a diameter of 26 mm was made in the center of the partitioning metal plate, and two metal meshes were attached to both the upper and lower surfaces of the partitioning metal plate. The VHF hydrogen plasma generated in the upper space passed through these meshes by diffusion, and by the gas flow owing to the evacuation from the lower space. The Sn sample was exposed to the hydrogen plasma that entered the lower space in this way. As described above, the lower space was surrounded by the metal of the grounded potential, and therefore, the fluctuation of the space potential of the plasma in the lower space was much smaller than that of the plasma in the upper space, where the potential fluctuation was large. As a result, the potential of a Sn sample surface potentially floated with respect to the chamber could be determined using the bias voltage. In fact, fluctuations of approximately ± 0.1 V appeared in the floating voltages of the Sn samples. Simultaneously, the mesh spacing (1.55 mm) and wire diameter (0.2 mm) were adjusted to secure the electron density in the middle of 10^{15} m^{-3}, so that sufficient Sn etching would occur.

Over 20 holes (each with a diameter of approximately 3 mm) were made around the hole with the diameter of 26 mm on the partitioning metal plate. We intended to supply the hydrogen gas supplied to the lower space to the upper space as well, i.e., through the hole with a diameter of 26 mm and these small holes. Under a gas pressure of 30 Pa, no hollow cathode discharge occurred in these small
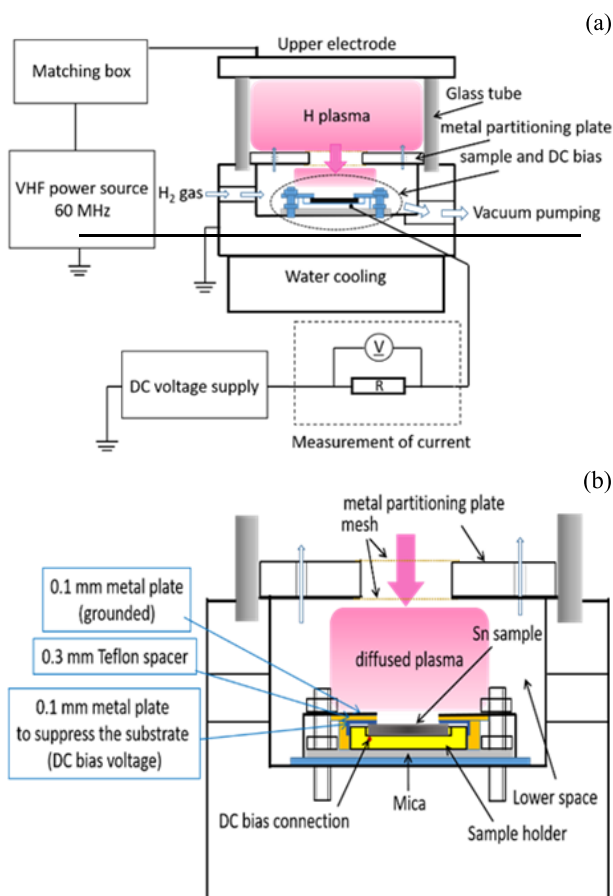
holes, i.e., there was no plasma supply to the lower space through these holes.

As shown in Fig. 1 (b), the lower space was provided with a structure for applying a bias voltage to the Sn sample. From the bottom of the lower space, the following elements were layered in order: a metal base plate (thickness 1 mm), mica plate (thickness 0.2 mm) for insulation, metal substrate holder surrounded by a Teflon spacer (both thicknesses 1.5 mm), Sn substrate (0.62 mm buried in the substrate holder and approximately 0.12 mm above the substrate holder surface), press metal plate (thickness 0.1 mm) at the bias voltage, Teflon spacer (thickness 0.3 mm), and grounded metal plate (thickness 0.1 mm). These elements were then fixed with screw rods and nuts at the four corners. A $12 \times 12 \, \text{mm}^2$ area square hole was drilled in the center of the press metal plate, Teflon spacer, and grounded metal plate. As described above, the sample holder was connected to a DC power supply, so that a bias voltage could be applied from the outside.

After evacuating the vacuum vessel to 4×10^{-2} Pa, hydrogen gas was flowed at a rate of 40 sccm using a mass flow controller, and was adjusted with a butterfly valve to maintain the pressure at 30 Pa. All measurements in this study were performed at this gas pressure.

For some Sn samples, the actual film thickness was measured by the crystal oscillator method; these were used as calibration samples. As the thickness of the Sn film (target value 100 nm) varied by ±10%, the Sn Lα signal of the XRF was calibrated using the calibration samples. First, the film thicknesses of the Sn samples were measured before exposure to the hydrogen plasma. Then, the film thicknesses were measured again after the experiment, to quantify the amount of Sn removed by the plasma exposure.

3. Experimental Results and Discussion

As described in Sec. 2, the electron density and electron temperature above the Sn sample were measured using a Langmuir probe, and an example of the current-voltage characteristic curve is shown in Fig. 2. The electron temperature was evaluated as $T_e = 2.8 \, \text{eV}$ from a logarithmic plot of the electron current with respect to the voltage. From the ion saturation current at the floating voltage, the electron density was evaluated as $n_e = 5 \times 10^{15} \, \text{m}^{-3}$. The floating voltage of the Sn sample was $V_f = 3.2$ V. Under the experimental conditions of this study, most of the hydrogen ions were H_3^+ when calculated according to Ref. [12], so it was assumed that all hydrogen ions were H_3^+. The measured value of the plasma potential V_p was 7.5 V when evaluated from the current-voltage characteristics using an Sn sample. As the electrons of the diffused plasma were collected by using the 12-mm square Sn sample as a probe, it is highly possible that the plasma was disturbed. According to probe theory, the difference between
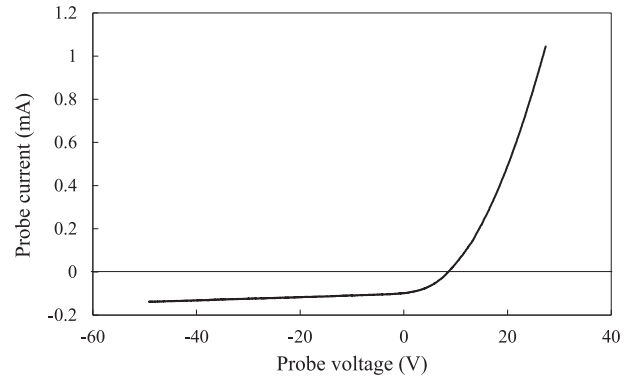

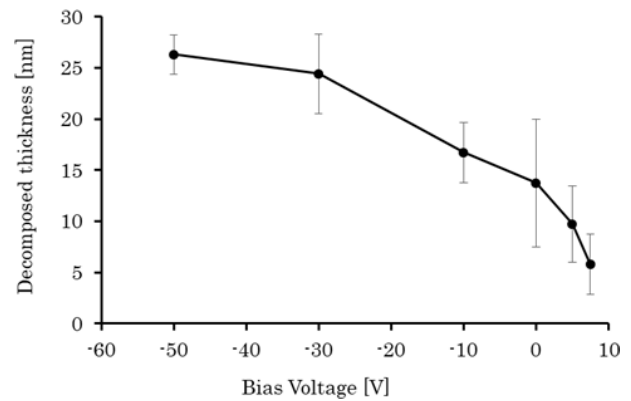Fig. 2   Probe characteristic I - V curve.

Fig. 3   Decomposed thickness of Sn film after plasma exposure of 15 minutes as a function of the DC bias voltage.

V_p and V_f can be expressed as follows [13]:

$$|V_p - V_f| = (T_e/2)(1 + \ln(m_i/(2\pi m_e))), \quad (1)$$

where m_i is the mass of the hydrogen ion (3 amu), and m_e is the mass of the electron. From this, we can evaluate $|V_p - V_f| = 10.9$ V; in the following, we consider $V_p = 14.1$ V.

The DC bias voltage V_b was varied at 7.5, 5, 0, −10, −30, and −50 V, and was applied to the Sn samples. The Sn samples were exposed to hydrogen plasma for 15 min, and the Sn etched thicknesses were examined. The results are shown in Fig. 3. The error bars in the figure illustrate the standard deviations from the results of five to six measurements at each bias voltage.

The current flowing into the Sn sample at each DC bias was also measured. The results are shown in Fig. 4. This result is basically a current-voltage characteristic curve of the saturated ion current, based on using the Sn sample as a planar probe. On the negative side of the DC bias voltage of −10 V, there is no influence of the electron current, i.e., it is purely ion current. Because the measurement points for the DC bias voltages −10, −20, and −30 V are on one straight line, the fitted line (shown in Fig. 4 by a red line) was extended to 3.2 V (floating voltage) to es-

Table 1   Values to evaluate Sn etching efficiency for each DC bias voltage. The last row shows the resultant efficiency as the number of removed Sn atoms per one hydrogen ion.

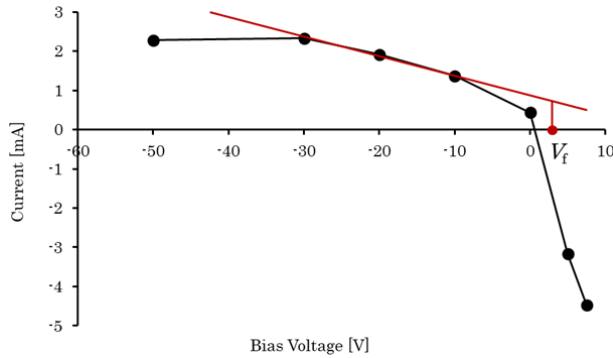| Bias voltage (V)	7.5	5	3.2	0	·10	·30	·50
Sheath voltage (V)	6.6	9.1	10.9	14.1	24.1	44.1	64.1
Ion current (mA)	0.74	0.74	0.74	0.89	1.37	2.33	2.28
Thickness of ion sheath (mm)	0.26	0.34	0.39	0.47	0.70	1.10	1.46
Sn yield (×10⁻² atoms/ion)	0.75	1.25	—	1.47	1.16	1.00	1.10

Fig. 4   Current flowing into Sn sample during plasma exposure as a function of the DC bias voltage.

timate the ion currents, as in the probe analysis. Table 1 shows the value of the ion current obtained in this way as an underlined value with respect to the DC bias voltage. Table 1 also shows the thickness of the ion sheath d_s. The following equation was used for this calculation [13]:

$$d_s = 0.47\lambda_D(2V_0/T_e)^{0.75}, \tag{2}$$

where λ_D is the Debye length, and V_0 is the voltage applied to the ion sheath (= $V_s - V_b$).

As mentioned in Sec. 2, the plasma exposure area of the Sn sample is limited to 12×12 mm² by the grounded metal plate. The Sn sample surface is 0.5 mm lower than the metal plate surface. At a floating voltage of 3.2 V, the sheath thickness $d_s = 0.39$ mm; therefore, the area of the ion sheath can be considered as 12×12 mm². The ion current is estimated as a product of the Bohm flux, elementary charge, and surface area of the sheath. The ion current value obtained in this way is 0.66 mA, which is in good agreement with the ion current value of 0.74 mA at a floating voltage of 3.2 V (Table 1). The situations are the same for $V_b = 5$ and 7.5 V; therefore, both ion current values are considered as 0.74 mA, as shown in Table 1.

The last row of Table 1 shows the Sn atom yield which is the number of Sn atoms removed per hydrogen ion, and this value is considered to indicate the efficiency of the reactive ion etching. The values of the Sn yield are obtained from the total amount of removed Sn atoms as evaluated from Fig. 3, divided by the total amount of hydrogen ions after 15 min of plasma exposure. At a bias voltage of 0 V, the Sn yield has the maximum value, meaning that one Sn

atom is removed per (approximately) 70 hydrogen ions.

The Sn etched thickness using hydrogen atoms alone was investigated, under the condition that the influence of the hydrogen ions was almost eliminated. Specifically, a grounded metal mesh was placed approximately 2 mm above the grounded metal plate, and a +7.5 V bias was applied to the Sn sample. As a result, the Sn etched thickness (removed after 15 min of plasma exposure) was 1.2 nm on average for the four measurements. Considering the reported fact [5] that 9×10^4 hydrogen atoms are necessary to remove one Sn atom, the hydrogen atom density can be evaluated as 8×10^{18} m⁻³ (dissociation degree of approximately 0.1%) from this etched thickness. It can be seen from Fig. 3 that the Sn etched thicknesses for bias voltages below 5 V are more than 10 nm. Therefore, it was confirmed that etching involving hydrogen ions is at least an order of magnitude more dominant than that using atoms alone.

We also can consider the binding energy of Sn in a metal bond. The standard sublimation enthalpy of metallic β phase tin is 302.1 kJ/mol, and the tin metal has a body-centered cubic structure with four bonds between atoms. The binding energy per Sn atom can be obtained from the standard sublimation enthalpy [8]; as calculated in eV units, the value is 3.1 eV, i.e., 0.78 eV per bond.

As mentioned in the introduction, reactive ion etching has been examined for the removal of C films deposited on an EUV mirror [8–10], and Hoph's model [8] has been proposed as the mechanism. According to the model, when the bond between carbons (bonding energy 7.4 eV) is broken by the energy of the ions, a bond between the carbon and hydrogen is formed by the flux of the hydrogen atoms, which is more than two orders of magnitude higher than the ion flux. From this chemical reaction, volatile and stable hydrocarbon molecules (CH_4, etc.) are generated. In the experiments of Hoph et al. [8], argon ion energies in the range of 20 - 800 eV were investigated, and it was found that the erosion yield of the carbon increased monotonically with the argon ion energy. Sputtering occurs depending on the energy of argon ions, and even if hydrocarbon molecules are formed relatively deep from the surface, the stable hydrocarbon molecules diffuse to the surface, and are discharged into the gas phase. Such a process has been examined theoretically [10], and comparisons with experimental results have shown the usefulness of this model. Similar results were obtained by Dolgov et al. [9] using

hydrogen plasma (hydrogen ion energies 20 - 100 eV).

In contrast, the Sn decomposition is not a monotonically increasing function of the hydrogen ion energy, as shown in the last row of Table 1. A bias voltage of +7.5 V (hydrogen ion energy of approximately 7 eV) is the threshold for Sn etching, and the Sn yield becomes maximum between a bias voltage of 0 V and floating voltage of 3.2 V (hydrogen ion energy of approximately 10 - 14 eV). At higher hydrogen ion energies, the Sn yield drops, or remains at a nearly constant value. One reason for the hydrogen ion-energy dependence of the Sn yield is that the difference in mass between an H_3^+ ion and Sn atom is large. When considered as a simple head-on collision between rigid spheres, the energy that H_3^+ ions (mass 3 amu) can give to Sn atoms (mass approximately 119 amu) is approximately four times the mass ratio, i.e., approximately 10% of the ion energy. Moreover, 10% of the threshold energy of the Sn decomposition is equal to the energy of one Sn metal bond. Another reason could be that SnH_4 is an unstable molecule. It has been shown by Tamaru [14] that the activation energy for the dissociation of SnH_4 on a Sn surface is approximately 0.4 eV per molecule. Therefore, the exothermic reaction of $SnH_4 \rightarrow Sn + 2H_2$ spontaneously proceeds, even at room temperature. Furthermore, as SnH_4 is 10 times heavier than CH_4, it is difficult for SnH_4 to escape via diffusion from the inside of the Sn film to the surface. The reactive ion etching for Sn decomposition is considered to occur only at a very shallow position from the surface of the Sn film. When a penetration depth of the H_3^+ ions into the Sn film is calculated using the "Stopping and Range of Ions in Matter" code [15], most of the ions penetrate to a depth of 2 nm or more from the film surface, at an ion energy of 30 eV or higher. The contribution of these ions to the Sn decomposition may be small.

4. Conclusion

In this study, we investigated the ion energy dependence of Sn reactive ion etching by hydrogen atoms and ions. The Sn atom yield per hydrogen ion did not increase with the ion energy (contrary to the results reported for C-film etching) and became constant or decreased with hydrogen ion energies of approximately 30 eV or more. The threshold ion energy for Sn etching was 10 eV or less, and the peak of the Sn yield appeared when the ion energy was approximately 10 - 14 eV. This means that it is efficient to use the floating voltage in hydrogen plasma when removing the Sn film adhered to an EUV mirror, which is electrically insulating. This result is quite favorable for the actual decomposition of Sn debris films from EUV mirrors.

[1] *News* release by TSMC, Oct 7, 2019, https://www.tsmc.com/tsmcdotcom/PRListingNewsAction.do?action=detail&language=E&newsid=THHIHIPGTH
[2] H. Mizoguchi *et al.*, Proc. SPIE **8679**, 86790A (2013).
[3] H. Tanaka *et al.*, Appl. Phys. Lett. **87**, 5 (2005).
[4] M.M.J.W. van Herpen *et al.*, Chem. Phys. Lett. **484**, 197 (2010).
[5] D. Ugur *et al.*, Chem. Phys. Lett. **552**, 122 (2012).
[6] D.T. Elg *et al.*, J. Vac. Sci. Technol. A, Vac. Surf. Film. **34-2**, 021305 (2016).
[7] D.T. Elg *et al.*, Plasma Chem. Plasma Process. **38**, 223 (2018).
[8] C. Hopf, A. von Keudell and W. Jacob, J. Appl. Phys. **94**, 2373 (2003).
[9] A. Dolgov *et al.*, J. Phys. D Appl. Phys. **47**, 65205 (2014).
[10] S. Liu, J. Sun, S. Dai, T. Stirner and D. Wang, J. Appl. Phys. **108**, 073302 (2010).
[11] M. Ji, R. Nagata, K. Uchino, Engineering Sciences Report, Kyushu University **42**, 12 (2021).
[12] L. St-Onge and M. Moisan, Plasma Chem. Plasma Process. **14**, 87 (1994).
[13] M.A. Lieberman and A.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, 2nd ed. (Wiley, Hoboken, NJ, 2005).
[14] K. Tamaru, J. Phys. Chem. **60**, 610 (1956).
[15] J.F. Ziegler *et al.*, Nucl. Instrum. Methods Phys. Res. B **268**, 1818 (2010).