Outgassing Characteristics of Structural Materials and the Removal of Contaminants from EUVL Masks using 172-nm Radiation

Kazuhiro Hamamoto, Yuzuru Tanaka, Takeo Watanabe, Noriyuki Sakaya*, Morio Hosoya*, Tsutomu Shoki*, Hiroshi Sugahara**, Nobuyuki Hishinuma**, Hideo Hada***
and Hiroo Kinoshita

*Laboratory of Advanced Science and Technology for Industry, University of Hyogo
3-1-2 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1205, Japan*

** HOYA Corporation, Electronics Development Center
3-3-1 Musashino, Akishima-shi, Tokyo 196-8510, Japan*

*** Ushio Inc. Lamp Company
1194 Sazuchi, Bessho-cho, Himeji-shi, Hyogo 671-0224, Japan*

**** Tokyo Ohka Kogyo Co., Ltd.
1590, Tabata, Samukawa-machi, Koza-gun, Kanagawa 253-0114, Japan*

Under EUV radiation, the surfaces of the imaging optics and mask, which are coated with a Mo/Si multilayer, become contaminated with organic compounds. This study examined the rate of outgassing and the species that desorb from materials used in vacuum equipment. The rate of outgassing for metals was found to depend on surface roughness. And most of the desorbed hydrocarbons, which are a primary contaminant, come from the wiring and some other components rather than from the metals used for the stages, even though the metals have a large surface area. Furthermore, since an efficient way of removing carbon contamination from masks and the imaging optics is required, a method of cleaning finished EUVL masks with 172-nm irradiation was investigated. This method restores the reflectivity of a Mo/Si multilayer to its original level, and removes contaminants at the rate of 2 nm/min in a low-pressure environment, which in this study was an initial backpressure in the chamber of 500 Pa provided by a scroll pump, and an O₂ flow to maintain the pressure at 2×10^3 Pa. Irradiation with 172-nm light in a low-pressure environment was found to be an effective way to clean masks.

Keywords: EUVL, contamination, outgassing, 172-nm excimer lamp

1. Introduction

In 2009, the semiconductor industry will require lithography suitable for the 32-nm node. Only extreme ultraviolet lithography (EUVL) has the potential to provide this capability for the mass fabrication of semiconductor devices. R&D on a practical exposure system [1, 2] has already been completed, except in three areas: a high-power EUV source, defect-free mask coating, and contamination control.

Since EUVL is carried out in a vacuum environment, hydrocarbons in the vacuum chamber

that desorb from the photoresist and the structural materials of the storage containers adsorb to the surfaces of the mask and mirrors. SR radiation breaks them down into their constituent elements (C, H, etc.), and the resulting contamination of the reflective mask and imaging optics reduces their reflectivity.

A new resist has been developed that features little outgassing: the gas produced by exposure reaches a pressure of only 1×10^{-8} Pa [3]. However, it is necessary to reduce outgassing from the lithography apparatus. So, this study investigated

the outgassing characteristics of materials used in vacuum equipment. There is a great deal of data on outgassing from the materials of vacuum components during baking [4-7]. However, baking is not feasible for an EUV exposure tool or the EUV microscope used for the inspection of mask defects because this apparatus contains many parts and optics that are aligned very precisely. [8]. So, outgassing from the materials used for vacuum components was examined without heating.

Furthermore, it is necessary to remove the contaminants that adhere to the mask and optics. Two techniques have been developed to accomplish this. The first is the in-situ cleaning of the EUVL imaging optics with synchrotron radiation (SR) [9]. The second is the cleaning of EUVL masks using 172-nm light, which allows the rapid cleaning of large areas.

Since we reported on contaminant removal using SR last year, this paper presents some experimental results on outgassing from the materials used in vacuum components and on mask cleaning with 172-nm light.

2. Contamination

13.5-nm SR interacts very strongly with many types of materials; and the hydrocarbons produced, for example; by the outgassing of the resist in a vacuum decompose and contaminate the Mo/Si multilayers with carbon [10]. This, in turn, not only reduces the reflectivity of the Mo/Si multilayers and degrades the exposure uniformity, but also degrades the resolution of the imaging optics.

Figure 1 is a photograph of a mirror contaminated with carbon during a 10-hour exposure to SR, and Fig. 2 shows that the contamination reduced the reflectivity to 10% or less. Contaminants are deposited at the rate of 0.2 nm/min.

Fig. 1 Photograph of the mirror with contamination.

Figure 3 is a graph of partial pressure versus mass number for the gas in the chamber of the EUV microscope, as measured with a quadrupole mass spectrometer. The total pressure was 2×10^{-5}

Pa. The main substances detected were H_2O , CO , N_2 , and hydrocarbons. So, the components of the equipment should be made of materials that exhibit little outgassing.

Fig. 2 Reflectivity of the contaminated mirror.

Fig. 3 Partial pressure of EUV microscope.

3. Outgassing characteristics of materials used in vacuum components

3.1. Measurement method

The rate of outgassing, surface roughness, and the composition of the residual gas were examined for materials used in vacuum components.

Samples were placed in an ultrasonic bath with acetone for 10 minutes. The testing chamber was first exposed to air for 30 minutes without a sample and then evacuated; and the evacuation time and the pressure in the chamber (P_2) were measured. Next, the chamber was again exposed to air for 30 minutes, a sample was placed inside, and the chamber was evacuated. In this case, only the change in pressure (P_1) was measured.

The rate of outgassing (Pa·m/s) was determined from the formula

$$q = S(P_1 - P_2) / A, \quad (1)$$

where A is the surface area of the sample (m^2) and S is the evacuation rate of the pump (m^3/s). The composition of the residual gas was analyzed with

a quadrupole mass spectrometer (QMA) at the same time as the rate of outgassing was measured.

3.2. Experimental setup

The configuration of the testing chamber is shown in Fig. 4. A turbo molecular pump (TMP) rated at 300 l/s, a QMA (ANELVA, M-QA200F) and a cold cathode gauge (CCG) were connected to the testing chamber, which was made of SUS304 steel. The chamber was 100 mm in diameter and 150 mm high, and had an internal surface area of 0.19 m². The change in internal pressure was measured with the CCG, and the composition of the residual gas species in the chamber was analyzed with the QMA.

Fig. 4 The configuration of testing chamber.

3.3. Samples

One group of samples consisted of stainless steel (SUS304), aluminum alloy (A5052), brass (YBSL2) and Teflon, which are common structural materials for vacuum equipment. In addition, magnesium alloy (AZ31), which is strong and light, was also examined. The samples had dimensions of 50 mm × 50 mm × 10 mm and a surface area of 0.07 m². Regarding surface treatment, all the metal samples were mechanically polished. The surface roughness of samples was measured with both an atomic force microscope (AFM) and a stylus roughness gauge (Dektak).

Furthermore, the motors, wires, and insulating tape used in the construction of a vacuum chamber were investigated. More specifically, the outgassing characteristics were measured for polyvinyl chloride wire, fluorine polymer electric wire, heat-shrinkable tubing, a picomotor, and polyimide tape.

3.4. Results and discussion

Figure 5 shows the rate of outgassing for various materials. The values for stainless steel, aluminum alloy, and other metals are 10 times higher than previously reported data due to the adsorption of water to the surface. These materials can be ranked from the lowest to the highest rate of outgassing in the order brass, A5052, SUS304, AZ31, and Teflon.

Fig. 5 Outgassing speed of various materials.

Table 1 shows the surface roughness of the samples. Except for Teflon, the rate of outgassing is lower for samples with a smaller roughness.

Table 1. Surface roughness of various materials.

Material	Roughness (nm)	
	AFM	Dektak
AZ31	508.11	1704
SUS304	423.02	432.5
Teflon	331.34	2780
A5052	281.76	506.7
Brass	233.14	440.8

Figures 6-9 show the composition of the residual gas after evacuation for 10 hours. For metals, the outgassed species are similar: abundant water, CO, N₂ and a small amount of hydrocarbons. Brass exhibits the least outgassing because it has the smallest surface roughness, even though all the metal samples were subjected to the same surface treatment. Unexpectedly, much more gas desorbed from Teflon than from metals, suggesting that careful consideration must be given to connectors and wires made with Teflon.

Figure 10 shows the rate of outgassing for wiring materials. Clearly, the rate is from 1 to 2 orders of magnitude smaller for fluorine polymer wire than for polyvinyl chloride wire, indicating that the former is more suitable for vacuum

equipment. The species outgassed from wires, tubing, and a picomotor are shown in Figs. 11-14. Polyvinyl chloride wire gives off abundant hydrocarbons. Furthermore, the other samples exhibit greater outgassing than metals do; and clearly, a large amount of hydrocarbons desorb. Since abundant hydrocarbons also outgassed from shrinkable tubing and the picomotor in spite of their small surface area, the materials for wires and motors deserve careful attention.

The key point here is that there is less outgassing from metals with a large surface area than from thin wiring.

Fig. 6 Outgassing species of SUS304.

Fig. 7 Outgassing species from Brass.

Fig. 8 Outgassing species from AZ31.

Fig. 9 Outgassing species from Teflon.

Fig. 10 Outgassing speed of various materials.

Fig. 11 Outgassing species from polyvinyl chloride wire.

Fig. 12 Outgassing species from fluorine polymer wire.

Fig. 13 Outgassing species from shrink tube.

Fig. 14 Outgassing species from picomotor.

4. Mask cleaning using 172-nm light

The possibility of removing contaminants by irradiation with a 172-nm excimer lamp (Ushio Lamp Co.) was examined. The absorption coefficient of molecular oxygen is 20 times larger at a wavelength of 172 nm than at 185 nm. Thus, 172-nm light produces ozone, from which active oxygen is generated. In addition, active oxygen is also directly produced from molecular oxygen irradiated with 172-nm light. Thus, a high density of active oxygen species can be produced, which

should enable the efficient cleaning of masks.

The system is very simple and consists of just a 172-nm lamp and a sample stage. This makes it easy to install in a mask load-lock chamber. Table 2 shows the cleaning conditions. The system can clean an area 8 inches in diameter. In this study, two cleaning environments were investigated: air and a low-pressure environment. For the latter, a scroll pump provided an initial backpressure of 500 Pa in the chamber, and an O₂ flow maintained the pressure at 2×10^{-3} Pa.

Table 2. Conditions for cleaning with 172-nm light.

Light intensity	20 mW/cm ²
Irradiation distance	1 mm
Temperature	Room temperature
Environment	In air or a low-pressure environment

The relationship between cleaning time and the amount of contaminants removed is shown in Fig. 15. Cleaning for about 40 minutes removed a 20-nm-thick layer of contaminants. The removal rate was higher in the low-pressure environment (2 nm/min.) than in air (0.53 nm/min.) because there was less photoabsorption by ambient gases.

Fig. 15 Removal thickness by 172 nm irradiation.

Figure 16 shows the reflectivity of a multilayer before and after cleaning for 40 minutes. This sample was contaminated for 10 hours, and had a reflectivity of 10%. The reflectivity recovered to 50% after contaminant removal in a low-pressure environment.

The change in surface roughness with cleaning time in Fig. 17 shows that irradiation in a vacuum is more effective in reducing roughness than irradiation in air. Thus, it has been demonstrated that irradiation with 172-nm light in

a low-pressure environment is an effective technique for cleaning masks.

Fig. 16 Multilayer reflectivity before and after cleaning.

Fig. 17 Surface roughness of multilayer.

5. Conclusions

- (1) The rate of outgassing from metals was found to depend on surface roughness. In addition, since there is greater outgassing from Teflon than from metals, careful consideration needs to be given to connectors and wires made with Teflon.

- (2) Metal samples with a large surface area exhibited less outgassing than thin wires.
- (3) Irradiation with a 172-nm excimer lamp was found to be an effective off-line process for removing contaminants from finished EUVL masks. This technique is more effective in a low-pressure environment than in air.

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