Investigation of Contamination Removal from Finished EUVL Mask

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During extreme ultraviolet lithography, the surfaces of the imaging optics and mask become contaminated with organic compounds. As more and more contaminants are deposited on a Mo/Si multilayer, the reflectivity and exposure intensity become lower, and the resolution of the imaging optics is degraded. A novel in-situ method of removing contaminants without heating has been developed. In an O$_2$ atmosphere at a pressure of 5.0 $\times$ 10$^{-2}$ Pa and at an electron beam current of the synchrotron storage ring of 150 mA, it removes a 0.1-$\mu$m-thick layer of contamination in 7 hours. The removal of the contamination restores the reflectivity of a Mo/Si multilayer without causing any surface damage.

Keywords: EUVL, contamination, multilayer, reflectivity

1. Introduction

In 2007, the semiconductor industry will require lithography suitable for the 50-nm node. Extreme ultraviolet lithography (EUVL) has the potential to provide this capability for the mass fabrication of semiconductor devices. Basic research on a practical exposure system[1] has already been completed, except in three areas: a high-power EUV source, defect-free mask coating, and contamination control.

For a throughput of 80 wafers per hour, the Mo/Si multilayers used in EUVL require a reflectivity of 68%. This throughput can be maintained as long as the drop in reflectivity is less than 2%, which corresponds to a layer of carbon contamination 3 nm thick. However, the interaction between materials and 13.5-nm synchrotron radiation (SR) is very strong; and the hydrocarbons produced, for example, by the outgassing of the resist in a vacuum decompose and contaminate the Mo/Si multilayers with carbon.

This, in turn, not only reduces the reflectivity of the Mo/Si multilayers and degrades the exposure uniformity, but it also degrades the resolution of the imaging optics. So, a method of contamination removal is essential for a practical EUVL system. This paper describes a dry-etching technique without heating for the in-situ cleaning of EUVL masks and mirrors.

2. Mechanism by which contaminants are removed

EUVL is carried out in a vacuum. The hydrocarbons in the vacuum chamber that come from the outgassing of the photoresist and from the storage containers adsorb to the surfaces of the mask and mirrors; and the SR radiation breaks them down into their constituent elements (C, H, etc), as shown in Fig. 1.
Contaminants can be removed either by a wet process or by dry cleaning. Currently, the most commonly used wet process for cleaning EUVL masks is RCA [3]. However, it suffers from the drawback that the solvent causes the contaminants to re-adhere to the cleaned surface. This makes it unsuitable for cleaning a mask with fine patterns for the 50-nm node.

Two common methods of dry cleaning are plasma ashing with activated oxygen and UV+O₃ cleaning. Dry cleaning has the following advantages over wet cleaning:

1. Contaminants do not re-adhere.

2. The selectivity, uniformity, and repeatability are good.

3. It is environmentally friendly.

4. The process is safe.

However, its disadvantages are that it causes surface damage and some contaminants are deposited on the sidewall of the chamber. A previous study [2] revealed that UV+O₃ cleaning removes carbon contamination when the substrate temperature is 150°C. However, a cleaning method for EUVL must be performed in situ and without heating so that the extremely precise alignment of the imaging optics required for high resolution is not affected.

In this study, Auger electron spectroscopy (AES) was used to analyze the composition of the contamination layer as a function of depth. Figure 2 shows AES spectra for the surface of an EUVL mask contaminated with hydrocarbons. C and O were detected at sputtering times from 10 to 170 min from the surface. Since the ratio of C to O is 96:4, the main contaminant is clearly carbon. In deeper regions, Ta was detected. These spectra correspond to the mask structure. Based on these results, an attempt was made to remove the carbon by employing 13.5-nm SR in an O₃-rich atmosphere, as illustrated in Fig. 3.

Fig. 2. AES spectrum of contamination of mask
3. Experimental setup

Contamination removal experiments were carried out on the BL-3 beam line of the NewSUBARU electron storage ring at the Nishi-Harima SPring-8 site. Figure 4 shows the configuration. SR generated by the bending magnets of the storage ring is collimated by two toroidal mirrors (M1 and M2) and directed toward the testing chamber by the movable mirror M3. The mask was directly irradiated with “white” SR. The samples were 0.5-mm-thick polished silicon wafers covered with a Mo/Si multilayer and a TaBN absorber film [4].

The irradiated area on a mask was 20 mm in diameter.

Figure 5 shows the configuration of the testing chamber. The incident angle of the mask was 10°. In order to analyze the effect of adding O₂ during EUV irradiation in real time, the light reflected from the mask was detected with a GaAsP photodiode. The oxygen flow rate was regulated with a gas flow controller (STEC).

Figure 6 is a photograph of a 4-inch-square region of a mask used as a sample. It is negative-type mask covered with a TaBN absorber film, and was used for several months in exposure experiments. The contamination covers a 70 mm × 10 mm region at the top of the figure.

The thickness and roughness of the contaminated region were measured with a non-contact optical thickness measuring system (NANOMETRICS M5100A) and an atomic force microscope (AFM), respectively. The contamination was 170 nm thick in Part A and 40 nm thick in Part B. The reflectivity was measured before and after cleaning with the reflectometer of the NewSUBARU.

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4. Results and discussion

Figure 7 shows how the reflectivity measured with the photodiode changes over time, or in other words, with the dose of EUV radiation in an O₂-rich atmosphere. Clearly, the normalized reflectivity of a mask increases in proportion to the dose. These data show how effective EUV irradiation in an O₂-rich atmosphere is.

4.1. Dependence of amount of contamination removed on dose

Figure 8 shows the results of irradiating Part A of the mask at a storage ring current of 120 mA for 3 hours. A 50-nm-thick layer of carbon contamination was etched off. In this experiment, the initial backpressure of the chamber was $5 \times 10^{-5}$ Pa, and an O₂ flow rate of 6 sccm kept the pressure at $5 \times 10^{-2}$ Pa.

Figure 9 shows the results of further irradiation at a storage ring current of 135 mA for 3 hours, which removed a 60-nm-thick layer of contamination. As can be seen, the contamination was completely removed, and the reflectivity is the same as that of the uncontaminated region.

Figure 10 is a graph of the thickness of the layer removed versus dose. It shows that irradiation at a storage ring current of 130 mA for 7 hours removes a 0.1-μm-thick layer. The curve suggests that two different growth rates are involved: an initial fast rate, which is dominant up to a thickness of about 40 nm, and a much slower, asymmetric rate. The fact that the growth rate depends on thickness indicates that the mechanism involved is not direct photo-induced cracking, but rather photoelectron-induced cracking.

Fig. 7. Effectiveness of cleaning method

Fig. 8. The results of irradiating Part A of the mask

Fig. 9. The further irradiation result

Fig. 10. Dependence of amount of contamination removed on exposure dose
4.2. Reflectivity measurements

The reflectivity was measured before and after cleaning with the reflectometer on the BL-10 beam line of the NewSUBARU. Figure 11 shows the measurement points on a sample mask. Points A to D were covered with contamination, but E was not.

![Figure 11. Measurement point of sample mask](image)

Figure 12 shows the reflectivity before cleaning. The values were 28%, 32%, 34%, 38%, and 34% for Points A through E, respectively. Figure 13 shows the results of irradiating the contaminated region in an O₂-rich atmosphere. Cleaning restored the reflectivity to 58%, which is same as for the uncontaminated region of Point E. Furthermore, the surface roughness of the cleaned region was found to be the same as that of the region that was not irradiated, as expected from the reflectivity measurements.

So, EUV irradiation in an O₂-rich atmosphere has been demonstrated to be a very effective way of removing contamination without any damage and without heating.

![Figure 12. Reflectivity before cleaning](image)

![Figure 13. Reflectivity after cleaning](image)

5. Conclusion

A novel in-situ method of removing contamination without heating has been developed that consists of EUV irradiation in an O₂-rich atmosphere. At a storage ring current of 150 mA and an O₂ pressure of \(5.0 \times 10^{-2}\) Pa, it removes a 0.1-μm-thick layer of contamination in 7 hours.

This method of cleaning restored the reflectivity of a Mo/Si multilayer without any surface damage. So, it can be concluded that EUV irradiation in an O₂-rich atmosphere is an effective way of removing contamination without surface damage and without heating.

References