Novel Ozone-based Contamination Cleaning for EUV Optics

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Since contaminants on EUV optics, including mirrors and masks, reduce the throughput in EUV lithography, they must be removed. Various cleaning techniques have been developed to do that, such as plasma cleaning, UV and ozone cleaning, hydrogen radical cleaning[1], in situ EUV cleaning with oxidative gasses, etc. They have removal rates of 0.01-1 nm/min for carbon contamination under almost ideal conditions; so the actual rates in a production tool will be lower. In HVM, the contamination rate might be dramatically higher, necessitating an even more efficient cleaning technique. Here, we describe a new carbon contamination cleaning technique that uses pure ozone gas.

Recently, Meidensha developed a new method of removing photoresist with pure ozone gas[2]. The method, which we call the gas addition method, efficiently removes photoresist at room temperature just through the supply of gas, in contrast to other reported ozone processes, which generally need an elevated temperature or irradiation with UV light. Since the gas addition method is easy to use and causes no plasma or heat damage, we tried using it to remove carbon contamination from EUV optics, even though the carbon is rigid and chemically very stable, unlike an organic compound, such as a photoresist.

Figure 1 illustrates the cleaning apparatus used in this study. The sample is placed in a vacuum chamber, and ethylene gas flows over it. Then, ~100% pure ozone gas from a Meiden Pure-Ozone Generator is fed in.

The sample contained patches of simulated carbon contamination deposited on a Si

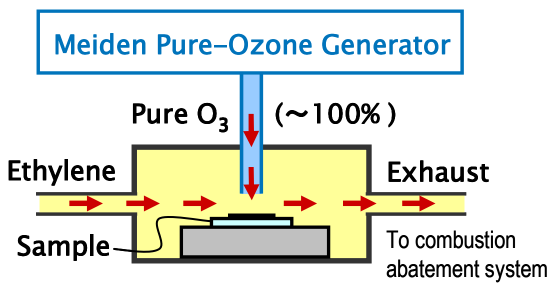

Fig. 1: Schematic diagram of apparatus.

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[1] H. Oizumi et al., Proc. SPIE Vol. 5751, 1149 (2005); Anazawa et al., EIPBN2008, 5B-3.
[2] Toshinori Miura et al., ECS Trans. 19, 423 (2009).

wafer using phenanthrene gas and the electron beam of a SEM. Initially, the patches had thicknesses of 12, 34, 82, 230, and 620 nm [left to right in Fig. 2(a)]. One minute of cleaning at room temperature reduced the thicknesses to 0, 0, 0, 140, and 530 nm, respectively [Fig. 2(b)]. So, carbon is removed at the rate of 90 nm/min. This is two to three orders of magnitude higher than the rates for the other techniques mentioned above.

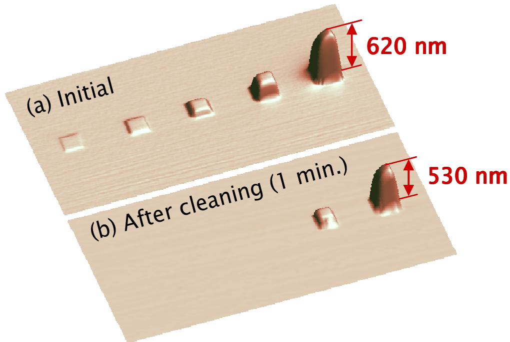

Fig. 2: AFM images of carbon patches (a) before and (b) after 1 min. of cleaning.

We speculate that the removal mechanism is as follows: Ozone reacts readily with the double bond of ethylene to form ozonide, an unstable intermediate. The decomposition of ozonide produces a variety of active species, such as oxygen radicals, hydroxyl radicals, and atomic hydrogen[3]. These species react with the carbon.

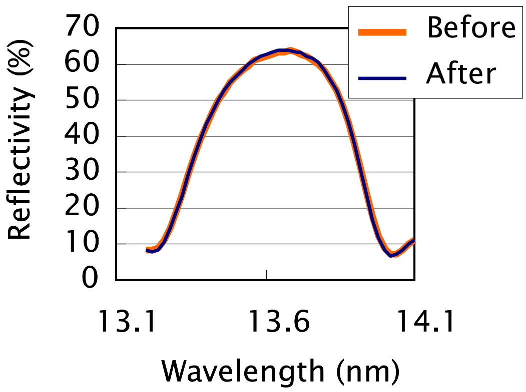

Fig. 3: EUV reflectivity of Si-capped multilayer mirror before (orange) and after (blue) 1 min. of cleaning.

We examined the ability of EUV masks to withstand our cleaning technique and found that the reflectivity of a Si-capped EUV mask blank was virtually unchanged after 1 minute of cleaning (Fig. 3).

In the presentation, the details of our cleaning technique and the durability of various materials used in EUV masks will be discussed.

This work was supported by NEDO (New Energy and Industrial Technology Development Organization).

[3] John T. Herron and Robert E. Huie, J. Am. Chem. Soc. 99, 5430 (1977).