



Resist outgassing assessment for multi electron beams lithography



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ABSTRACT

The outgassing of e-beam resist materials has to be carefully considered in the research and development of multi e-beams lithography. The release of hydrocarbonaceous species by outgassing in high-vacuum e-beam exposure tool is indeed unavoidable and may lead to premature contamination of optics projection systems. Such a contamination may affect the incident electrons path and hence the final imaging performances. In this work, we present an experimental methodology for the purpose of e-beam resist outgassing qualification. A specific experimental setup was designed in CEA-Leti in order to perform electron bombardment of the e-beam resists coated on 100 mm silicon wafers and to monitor the induced outgassing phenomena. The wafer stage was designed in order to allow suitable displacements of the resist coated surface with respect to the incident e-beam. In addition, the wafer can be exposed through specific silicon micromachined membranes (called mimic) that are representative of the optics projection system usually embedded in real multi e-beam exposure tools. Finally, a Quadrupole Mass Spectrometer (QMS) is plugged into the vacuum chamber and enables in situ analysis of the by-products outgassing. Combining this tool with the Thermo Desorption–Gas Chromatography coupled to Mass Spectroscopy and Flame Ion Detector (TD/GC/MS–FID) analysis, we could not only determine the outgassing amount of four different resists but also identify all by-products outgassed and their origin. This paper also shows that the use of a thin top-coat can considerably reduce the outgassing. The outgassing amount as well as the top-coat efficiency was shown to be dependent on the resist chemical properties.

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1. Introduction

It is well known that under electron bombardment, the resist outgassing leads to the release of hydrocarbonaceous molecules (CxHy) in the vicinity of the exposed wafers. Currently, inside single electron beam lithography tool, the contamination of the optics projection system due to this resist outgassing is not critical. However, in incoming parallel e-beams exposure tools, based on the use of several thousand electron beams, the optics projection system contamination issue can no longer be neglected. Consequently, it becomes mandatory to carefully analyze the resist outgassing mechanisms and their contribution to the contamination layer growth inside the tools. It is worth noticing that since the last decade, several research groups acting on the development of the EUV lithography have been addressing similar

resist outgassing issues [1,2] by using various experimental approaches. According to previously published results [3–7], Photo Acid Generator (PAG) and Leaving Groups (LG) have been shown to be important contributors of the total outgassed species at 193 and 248 nm DUV radiation as well as under EUV exposure [8,9]. Recent work [10] has showed that the outgassing amount depends on the PAG's cation size as well as on the resist's components properties. In collaboration with Mapper Lithography, the purpose of our current experimental investigations is to determine under which conditions, the contamination layer induced by resist outgassing may obstruct the mimic holes and modify, thereby, the e-beams paths characteristics. In this paper, we will describe the experimental setup used for those analyses and comparatively investigate the outgassing of four different resist formulations. The effect of additional thin polymeric films deposited on the top of the resists will also be investigated in terms of outgassing reduction. The obtained results are discussed with highlights on the resist material's properties and sizes.

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2. Theoretical background

In general, at equilibrium conditions, the pressure P (Pa) inside a vacuum chamber is expressed as following [9]:

$$P = \frac{F}{S} \quad (1)$$

where F ($\text{Pa m}^3 \text{s}^{-1}$) is the release rate of the outgassed species from the inner-chamber walls and S ($\text{m}^3 \text{s}^{-1}$) is the effective pumping speed.

By combining the ideal gas equation,

$$P \cdot V = n \cdot R \cdot T \quad (2)$$

where n is the number of moles, V is the chamber volume, R is the gas constant and T is the gas temperature,

with Eq. (1), the resist outgassing amount per incident electron Q (molecules electron $^{-1}$), the outgassing amount per area unit N (molecules cm $^{-2}$) and the outgassing rate N' (molecules cm $^{-2}$ s $^{-1}$) can be calculated respectively as follows:

$$Q = \sum_{i=45 \text{ amu}}^{200 \text{ amu}} \Delta P_i \left(\frac{S \cdot N_A \cdot q_{e^-}}{R \cdot T \cdot I} \right) \quad (3)$$

$$N = \sum_{i=45 \text{ amu}}^{200 \text{ amu}} \Delta P_i \left(\frac{S \cdot N_A \cdot t}{R \cdot T \cdot A} \right) = \sum_{i=45 \text{ amu}}^{200 \text{ amu}} \Delta P_i \left(\frac{S \cdot N_A \cdot D}{R \cdot T \cdot I} \right) \quad (4)$$

$$N' = \sum_{i=45 \text{ amu}}^{200 \text{ amu}} \Delta P_i \left(\frac{S \cdot N_A}{R \cdot T \cdot A} \right) = \sum_{i=45 \text{ amu}}^{200 \text{ amu}} \Delta P_i \left(\frac{S \cdot N_A \cdot D}{R \cdot T \cdot I \cdot t} \right) \quad (5)$$

Where ΔP_i is the pressure increase from the base pressure induced inside the chamber by fragments of the species outgassed (i.e. each mass), N_A is Avogadro's number, q_{e^-} is the electron charge, I is the electron beam current, A is the exposed area, D is the dose to size of the resist and t is the exposure time (sampling time).

The sum of partial pressures increase is limited to species that atomic mass unit (amu) is higher than 44. The species included in the 1–44 amu mass range are: dihydrogen H $_2$ (2 amu), water H $_2$ O (16, 17 and 18 amu), nitrogen N $_2$ (14 and 28 amu), dioxygen O $_2$ (16 and 32 amu) and carbon dioxide CO $_2$ (12, 16, 28 and 44 amu) coming mainly from chamber base vacuum. We can notice that all these species do not contain more than one carbon atom. Consequently, they do not contribute significantly to the hydrocarbonaceous contamination growth.

The dose to size considered here was set at $2.5 \cdot D_0$, where D_0 is the dose to clear of each resist determined by resist contrast curve.

Based on the previously published data [11], a measurement result difference of 19–109 times and 1–2 times was obtained by considering resist outgassing rate (molecules cm $^{-2}$ s $^{-1}$) and resist outgassing amount calculations respectively. Thus, in this work, the resist outgassing amount per incident electron was adopted.

3. Experimental

3.1. Materials and sample preparation conditions

We have selected four e-beam resists and one Top Coat (TC) that was cast at two thicknesses, i.e., 10 and 30 nm. Three of these resists are Positive Chemically Amplified Resists (PCAR) while the last one is Non Chemically Amplified Resist (NonCAR). One of the PCARs is a polymer matrix-covalently bonded Photo Acid Generator (PAG) formulation. The e-beam resists and top coat material formulation used in this study are summarized as follows:

Samples name	Type	Polymer matrix type	PAG	Comment
Resist A	PCAR	Acrylate	Yes	Bonded PAG
Resist B	PCAR	Acrylate	Yes	
Resist C	PCAR	PHS	Yes	PHS: Poly Hydroxystyrene
Resist D	NonCAR	PMMA	No	PMMA: Poly Methyl Methacrylate
TC	Top coat	Acrylate	No	

The resists and TC were spin-coated on 100 mm silicon wafers. Spin-coating parameters were set to get 37 nm resist film thickness, excepting for Resist C where a slightly thinner film (32 nm-thick) was obtained. The soft bake temperatures were set at their optimum values for each resist. Each resist was then exposed to its dose to size using the outgassing test tool shown in next section.

3.2. Resist outgassing test tool

Fig. 1 shows a schematic of the experimental setup especially designed and realized at Leti for the purpose of this study. It is basically composed of a vacuum chamber connected to an "ATH1603M" turbomolecular pump that allows to reach ultra-high vacuum conditions. The steady state nominal pressure obtainable was better than $1 \cdot 10^{-6}$ Pa. An "IGM400" ion gauge displays real time value of the pressure inside the chamber. A wafer stage was implemented in order to allow 100 mm silicon wafers moving in two axis. An "EGG-3101" electron gun working at 5 kV bias was used for resists exposure. The raster system implemented on the electron gun was characterized in order to ensure uniform exposure of a square area of $7 \times 7 \text{ cm}^2$ for outgassing measurement tests (after removing mimic support). A "Microvision" QMS is positioned very close to the resist-coated wafer.

Preliminary experiments were conducted to calibrate the e-beam gun and its raster scanning capabilities. Similarly, the effective pumping speed was properly measured according to a well-defined experimental protocol [12] adapted to our set-up.

Before starting the resist outgassing measurements, the stability of the chamber background was evaluated. To do, a clean 100 mm wafer was irradiated with the highest exposure dose and the pressure increase inside the chamber was followed using QMS analysis. 5 clean wafers were tested, each being subjected to 30 scans. The repeatability of the outgassing measurements between each wafer was shown to be better than 0.01 molecule electron $^{-1}$ while standard deviation was found to be equal to 0.03 molecule electron $^{-1}$.

Afterwards, resist coated silicon wafers were introduced inside the chamber. The experimental protocol was the following: The QMS and the electron gun were switched on 15 min before starting resist-coated wafer exposure. The outgassed species spectra were then systematically recorded by the QMS for the exposure duration. The so-exposed wafers were then taken out the chamber, cut to small samples and immediately analyzed by ex situ techniques as explained in the next section.

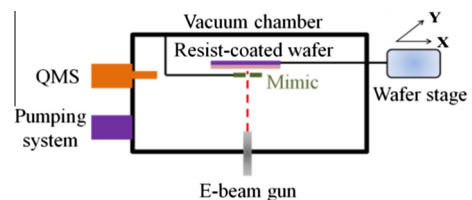


Fig. 1. Schematic of Leti's 5 keV outgassing test tool.

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