Mean free path of electrons in EUV photoresist in the energy range 20 to 450 eV

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ABSTRACT

The blur caused by the nonzero mean free path of electrons in photoresist during extreme ultraviolet lithography has detrimental consequence on patterning resolution, but its effect is difficult to measure experimentally. In this work, a modified substrate-overlayer technique was used to evaluate the attenuation of the photoemission spectra produced in thin chemically amplified photoresist films. The inelastic mean free path of electrons was found to be between 1 to 2 nm in the entire range of interest for EUV lithography (20 to 100 eV kinetic energy). At higher kinetic energy, the mean free path increased consistently with well-known behavior. The presence of photoacid generator and quencher did not change the mean free path significantly (within experimental error).

Keywords: EUV, resist blur, electron blur, mean free path

1. INTRODUCTION

The distance travelled by secondary electrons generated in photoresists during exposure to extreme ultraviolet light blurs the aerial image and possibly represents an insurmountable limit to high resolution patterning in EUV lithography. The crucial role of electrons in EUV lithography also implies that the path travelled from the initial photoabsorption location to the final thermalization point which might have a detrimental effect on the patterning resolution, as was recognized in early works on X-ray lithography.[1] In general, the distance travelled by electrons in matter is described by an effective attenuation length (EAL) consisting of inelastic (IMFP) and elastic (EMFP) mean free path components. In this study, we measured the MFP of electrons of kinetic energy relevant for EUV lithography and electron microscopy of photoresists. Knowledge of MFP in the energy range between 20 to 450 eV is key to predict photoresist performance and to achieve sub-nm metrology in electron microscopy.

2. EXPERIMENTAL

Samples were prepared in thin films form by spin-coating blends of three basic components of a chemically amplified EUV photoresist (CAR). The first component was a random copolymer of poly hydroxystyrene (CAS 9003-53-6) and tertbutyl methacrylate (CAS 25189-00-8) that serves as backbone for the entire photoresist (Fig. 1a). During exposure to EUV, this copolymer switches solubility when the tertbutyl group is deprotected by direct photoionization and interaction with proton in a mechanism described elsewhere.[2] The second component was triphenyl sulfonium perfluoro-1-butanesufonate (triphenyl sulfonium nonaflate, CAS 144317-44-2, Fig. 1b), a photoacid generator (PAG). In lithography, the PAG catalyzes the deprotection reaction of the copolymer by catalyzing proton generation, which lowers the amount of light needed and increases throughput in manufacturing; it also smooths out line edge roughness of photoresist caused by standing waves and photon shot noise. The third component was trioctylamine (CAS 1116-76-3), an alkaline quencher for the acid generated by the PAG (Fig. 1c).

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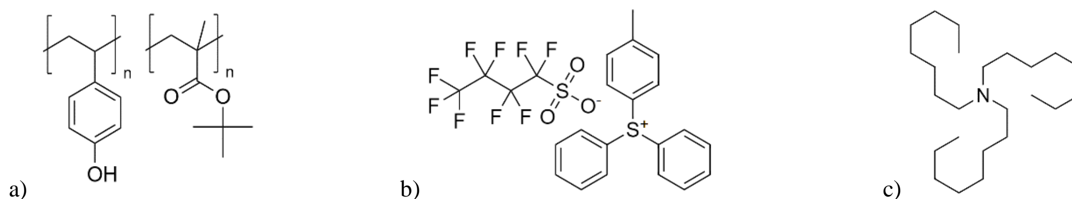

Figure 1. Chemical compounds used in this work: a) random copolymer of poly hydroxystyrene and tertbutyl methacrylate (backbone), b) triphenyl sulfonium perfluoro-1-butanesufonate (photoacid generator), and c) trioctylamine (quencher).

3. RESULTS AND CONCLUSIONS

The mean free path of electron in polymer, polymer and PAG, and polymer with PAG and quencher measured using the overlayer/substrate method in the kinetic energy range 20 to 450 eV ranged from about 2 nm in the EUV lithography-relevant range below 92 eV and up to 4 at higher kinetic energy, as expected per Bethe's theory of fast electrons in solids. Samples containing only polymer showed the lowest uncertainty which we ascribe to the high chemical stability of this compound, the only one among the three which does not contain PAG. To compare with existing literature, lithography-related studies have entirely different approaches to assess electronic processes in photoresists. The thermalization distance of electrons was calculated to be 3.2 ± 0.6 nm in poly hydroxystyrene using Montecarlo simulation[3] and calculations of electron blur from lithographic data yield about 2.5 nm.[4] In these two cases, values were not resolved in energy so it should be assumed they represent electrons of vanishing energy in the conduction band, i.e., EK $\rightarrow$ 0 eV. In sulphonium PAG, the MFP was estimated by electron beam exposures to be 2 nm at 80 eV and increasing up to 5.7 nm at 250 eV.[5] Commercial lithography simulators used photoresist calibration data to estimate a ~80 eV*nm integral total MFP for polystyrene in the range 0-92 eV (EUV), and between 1 and 2 nm MFP below 10 eV.[6]

In summary, our finding that the MFP is approximately constant in the entire range of energy might explain why its effects have been so elusive until today, when the critical dimension of the features is still $\geq$ 14 nm (pitch 28 nm lines/spaces arrays or pitch 32 nm contact holes arrays). Moreover, its effect will play a different role depending on the tonality used (dark field vs. bright field). All photoresists used in EUV will have to deal with the electron blur, even nonchemically amplified ones such as photocondensed metal oxides, polymer scission resists and negative tone crosslinking resists. Electron blur is also unaffected by high-numerical aperture and NILS, which makes it more elusive.

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