Dissociative electron attachment to pentafluorophenyl triflate: quenched acid generation in neutral ester PAGs for EUV lithography

Reza Tafrishi[a,*], Mónica Mendes[b], Pedro Guerra[b], Fabian Holzmeier[c], Oddur Ingólfsson[a], Filipe Ferreira da Silva[b]

[a] Department of Chemistry, University of Iceland, Science Institute, Dunhagi 3, 107 Reykjavík, Iceland;
[b] CEFITEC, Department of Physics, NOVA University Lisbon, School of Science and Technology, 2829-516 Caparica, Portugal;
[c] IMEC, Kapeldreef 75, 3001 Leuven, Belgium

From the physical and chemical point of view the introduction of extreme ultraviolet lithography into high volume manufacturing of computer chips constitutes a transition from non-ionizing to ionizing radiation, and respectively, a transition from photochemistry to electron driven chemistry in the solubility switching of the resist materials.[1-3] With most manufacturing facilities being tailored to processing chemically amplified resists (CARs) this calls for a closer look at the electron induced chemistry within these materials and eventually modification and adaption of their composition to improved response to EUV radiation. Furthermore, both the quantum yield and photon count is low in EUVL as compared to the conventional DUVL scanners and sensitivity is an important parameter in adapting CARs to EUVL.

An attractive way to increased sensitivity of CARs is to formulate these with higher load of "photo"-acid generators (PAGs), the critical component in initiating the chemistry behind solubility switching up on exposure. However, with the commonly used ionic PAGs, phase separation poses a limitation to the practically applicable load. In this context neutral aryl ester PAGs have been considered, among them pentafluorophenyl triflate; CF_3SO_2-O-C_6F_5, for which homolytic ester cleavage leads to formation of the radical precursor of the very strong triflic acid.[4,5]

Here we present a combined experimental and theoretical study on electron induced fragmentation of this compound through dissociative electron attachment (DEA). We find that the yield is dominated by the formation of $CF_3SO_3^-$ (m/z 149), i.e., the pH neutral complementary base to the triflic acid. while $C_6F_5^-$ (m/z 67), the complementary ion to the triflic radical (the targeted pre-acid), is only observed with marginal intensities.[6]

The prerequisite for pentafluorophenyl triflate to act as acid generator in EUVL CARs, is the electron induced generation of the CF_3SO_3 radical as a precursor for the respective acid formation. The dominating formation of the closed shell, pH neutral complimentary base to the triflic acid ($CF_3SO_3^-$), however, shows clearly that DEA to pentafluorophenyl triflate rather quinces than promotes acid generation. Moreover, from the observed ion yields and computed MO structures and thermochemistry, we arguue that this may be expected to be general for DEA to asymmetric neutral ester PSGs.

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References

[1] Kazazis D et al Nat Rev Methods Primers 4 84 (2024)
[2] Kostko O et al J. Micro/Nanopatterning Mater. Metrol. 23(1), 014602 (2024)
[3] Kozawa, T., and Tagawa, S. Jpn. J. Appl. Phys. *49*, 30001 (2024)
[4] Manouras, T., and Argitis, P. Nanomater. (Basel, Switzerland) 10 (2020).
[5] Martin, C.J., et al.. J. Photochem. Photobiol. C Photochem. Rev. 34, 41–51 (2018).
[6] Fallica R et al J. Photopolymer Sci. Technol. 34(1), 99-103 (2021)
[7] M. Dapor et a. J. Electron Spectrosc. Relat. Phenom. 222 95–105 (2018)
[8] M. Mendes, R. Tafrishi, P. Guerra, F. Holzmeier, O. Ingólfsson, F. Ferreira da Silva, iScience 28, 114020 (2025)

* Corresponding author: ret1@hi.is; phone +354-7874564