

Ultrasensitive Non-Chemically Amplified Negative-Tone Electron Beam Lithography Resist

V. Canalejas-Tejero,¹ S. Carrasco,² F. Navarro-Villoslada², M.C. Capel-Sánchez³, J.L. García Fierro³,
M.C. Moreno-Bondi^{2*}, C.A. Barrios¹

¹ *Instituto de Sistemas Optoelectrónicos y Microtecnología (ISOM), ETSI Telecomunicación, Universidad Politécnica de Madrid, CEI-Moncloa, 28040 Madrid, Spain.*

² *Optochemical Sensors and Applied Photochemistry Group (GSOLFA). Department of Analytical Chemistry, Faculty of Chemistry, Universidad Complutense, CEI-Moncloa, 28040 Madrid, Spain.*

³ *Grupo de Energía y Química Sostenibles (EQS). Instituto de Catálisis y Petroleoquímica (ICP-CSIC). C/ Marie Curie 2, Cantoblanco, 28049 Madrid, Spain.*

* carlos.angulo.barrios@upm.es; mcmbondi@quim.ucm.es

Abstract

Electron-beam lithography¹ (EBL) is a well-known and powerful technique for top-down nanofabrication approaches². However, EBL has some disadvantages for mass production like a low processing speed. Highly sensitive EBL resists are therefore desirable as they reduce the writing time considerably.

We have developed and characterized a new negative-tone EBL resist with an extremely high sensitivity. The resist is based on the dual copolymer mixture poly(2-hydroxyethyl methacrylate-co-2-methacrylamidoethyl methacrylate) (poly(HEMA-co-MAAEMA)) and has been synthesized using free radical polymerization of 2-hydroxyethyl methacrylate and 2-aminoethyl methacrylate (9:1 monomer feed ratio) with further methacryloylation of the amine side-chain groups.

The poly(HEMA-co-MAAEMA) resist exhibits a crosslinking threshold dose as low as 0.5 $\mu\text{C}/\text{cm}^2$ (Fig. 1), which is one order of magnitude smaller than those of commercially-available EBL negative resists. Unlike the latter, the high sensitivity of our copolymer mixture does not arise from a chemical amplification process induced by a photoacid generator, but caused by the presence of a large proportion of double bonds (~10%) into the resist composition, which increases the probability of electron-induced bond breakage significantly.

The copolymer mixture has been analyzed by ¹H NMR (Fig. 2). In addition, exposed and non-exposed resist films have been characterized by X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy to study the polymerized species.

Our resist possesses a contrast value as low as 1.2 (Fig. 1), making it particularly suitable for achieving grey (3D) lithography³, and a half-pitch resolution of 100 nm. Dual-tone behaviour occurs at high electronic doses; in particular, the polymeric resist becomes positive for doses in the range of 5 – 10 mC/cm^2 .

Exposed resist patterns show good adherence to silicon substrates without the assistance of adhesion promoters or thermal treatments, and have been shown to be adequate for use as a mask for both wet (HF+HNO₃+AcOH solution) and dry (SiF₆-based Reactive Ion Etching) etching of Si.

The presented resist is highly transparent in the visible, which, along with its aforementioned 3D fabrication capability, makes it suitable as a structural material for the implementation of micro- and nano-optical components, such as microlenses (see Fig. 3).

Acknowledgements: The authors gratefully acknowledge financial support from MICINN (TEC2010-10804-E, CTQ2009-14565-C03-03 and TEC2008-06574-C03-03), and the Moncloa Campus of International Excellence (CEI).

References

- [1] R. Fabian Pease and Stephen Y. Chou, Proceedings of the IEEE, **96**, 2 (2008), 248-270.
- [2] George M. Whitesides, Small, **2**, 1 (2005), 172-179.
- [3] Chen J-K, Ko F-H, Chen H-K and Chou C-T, J. Vac. Sci., Technol. B, **22** (2004), 492-500.

Figures

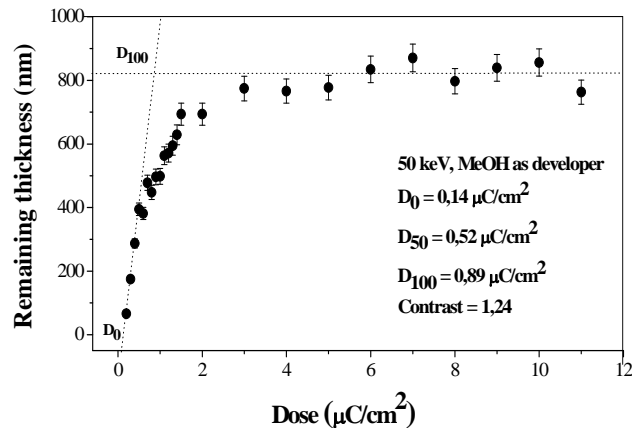


Fig. 1. Contrast curve for the poly(HEMA-co-MAAEMA) resist exposed at 50 keV and developed by methanol at room temperature.

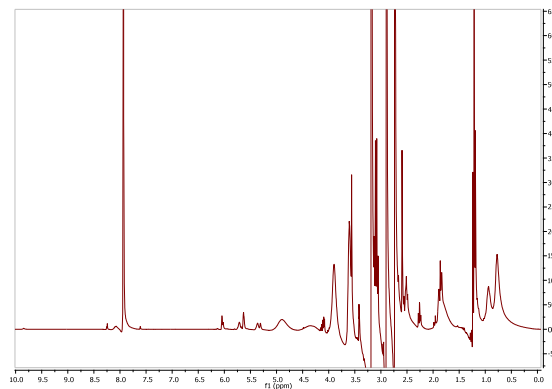


Fig. 2. ^1H NMR spectra of the poly(HEMA-co-MAAEMA) copolymer.

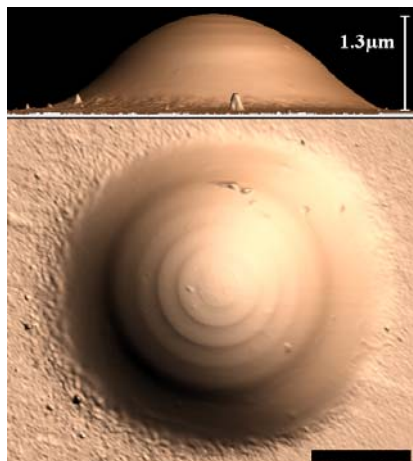


Fig. 3. poly(HEMA-co-MAAEMA) resist dome fabricated by exposing concentric circles with gradual doses from 0.5 to 50 $\mu\text{C}/\text{cm}^2$. Dome height: 1.3 μm . Horizontal scale bar equals 10 μm .