



HAL
open science

Water-soluble bio-sourced resists for DUV lithography in a 200/300 mm pilot line environment

Isabelle Servin, Alexandre Teolis, Arnaud Bazin, Paule Durin, Olha Sysova,
Corinne Gablin, Benoît Saudet, Didier Leonard, Olivier Soppera, Jean -Louis
Leclercq, et al.

► To cite this version:

Isabelle Servin, Alexandre Teolis, Arnaud Bazin, Paule Durin, Olha Sysova, et al.. Water-soluble bio-sourced resists for DUV lithography in a 200/300 mm pilot line environment. *Micro and Nano Engineering*, 2023, 19, pp.100202. 10.1016/j.mne.2023.100202 . hal-04265241

HAL Id: hal-04265241

<https://hal.science/hal-04265241>

Submitted on 30 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Water-soluble bio-sourced resists for DUV lithography in a 200/300 mm pilot line environment

Isabelle Servin^{a,*}, Alexandre Teolis^b, Arnaud Bazin^a, Paule Durin^{c,d}, Olha Sysova^{e,f}, Corinne Gablin^d, Benoît Saudet^a,
Didier Leonard^d, Olivier Soppera^{e,f}, Jean-Louis Leclercq^c, Yann Chevolut^c, Raluca Tiron^a, Thierry Delair^b and
Stéphane Trombotto^b

^a Univ. Grenoble Alpes, CEA, LETI, Grenoble F-38000, France

^b Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Ingénierie des Matériaux Polymères, IMP UMR 5223, F-69622 Villeurbanne Cedex, France

^c Univ Lyon, CNRS, INSA Lyon, Ecole Centrale de Lyon, Université Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, F-69134 Ecully, France

^d Univ. Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences Analytiques, UMR 5280, 5, rue de la Doua, F-69100 Villeurbanne, France,

^e Univ. de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France,

^f Univ. de Strasbourg, F-67000 Strasbourg, France

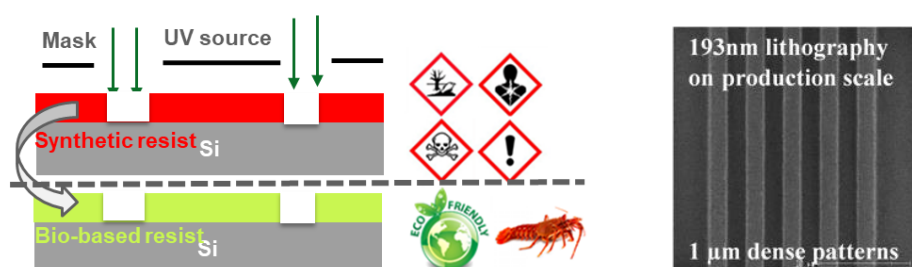
*Corresponding author: isabelle.servin@cea.fr

Tel: +33 438 782 364

ABSTRACT

Water-based bio-sourced resists are promising candidates as alternatives for deep ultraviolet (DUV) lithography by replacing current photoresists issued from petro-chemistry for microelectronics application. Chitosan films produced from seafood industry wastes enable patterning processes free of organic solvent and alkali-based developers, by substitution with water. After demonstrating high-resolution patterning at lab-scale after transfer into silica 10 mm wafer, we investigate here the industrial pre-transfer chitosan-based photoresist on the 300 mm pilot line scale at CEA-Leti for 193 nm DUV lithography.

Graphical abstract



Highlights

- First industrial pre-transfer from R&D to production scale for photopatterning
- DUV lithography patterning with chitosan films on 300 mm Silicon wafer size
- Fully covered film on Si substrate by spin-coating with thickness uniformity ± 9 nm
- Well-resolved features down to 1 μ m after 193 nm DUV exposure

Keywords: Lithography, photoresist, chitosan, water-based, semiconductor, industrial pre-transfer, sustainability

1 Introduction

Environmental sustainability and user-toxicity have become a critical concern in the semiconductor industry [1, 2]. Photolithography, as the major process of transferring patterns for the nanofabrication, requires the use of high volume of organic solvents and alkali-based solutions as developers, hazardous for health and environment. Environmentally friendly water-based bio-sourced resists may constitute improved alternatives to current synthetic

petroleum-derived photoresists for deep ultraviolet (DUV) lithography [3-5].

Among bio-sourced materials, chitosan is a promising candidate as photoresist. Chitosan is a natural polysaccharide derived from chitin, which is the second most abundant natural biopolymer on earth behind cellulose and mostly provided by seafood industry wastes [6]. Its high versatility thanks to its non-toxicity, biodegradability, film-forming properties and UV sensitivity permits to address a wide range of applications. In our previous works, it was shown that chitosan films allow patterning processes free of organic

solvent and alkali-based developers, by substitution with a green solvent (deionized (DI) water). High-resolution patterning with 100-nm thick chitosan films was obtained at lab-scale down to 50 nm lines by writing with a 30 kV electron beam system after transfer into silicon wafer [7] and 5 μm by exposing on DUV lithography tool [8].

Here, the lithographic process with chitosan films was firstly investigated at production scale on the 300 mm pilot line scale at CEA-Leti. Finally, we started to quantify the environmental impacts of the photolithography process based on water-soluble bio-sourced resists using the life cycle analysis (LCA) methodology for assessing its environmental relevance compared to current processes using synthetic petroleum-derived resists.

2 Experimental

2.1 Materials

The conventional resist, soluble in organic solvent was spin-coated on Si wafer followed by resist rinsing with PGMEA to clean both edge and back-side of the wafer and developed after exposure with alkaline solution TMAH 2.38% and finally rinsed with DI water. The bio-sourced resist differs from conventional one by the compositions, by substituting the solvent by DI water for dissolution and development (Table 1).

Composition	Conventional resist	Bio-sourced resist
Photoresist	Petrochemical industry Polyacrylates, polystyrenic...	Polysaccharides extracted from natural sources
Solvent	Organic solvents PGMEA, Ethyl Lactate, PGME...	De-ionized water Acetic acid
Developer	Alkaline solution TMAH 2.38%	De-ionized water

Table 1. Photoresist composition comparison: conventional organic resist vs bio-sourced resist

Chitosan resist is a positive-tone water developable bio-sourced resist directly coated on the substrate (Si) for photolithography by modifying its intrinsic properties. The photosensitive thin layer has a 100 nm-thickness.

Chitosan obtained from squid pens was provided by Mahtani Chitosan from batch type 114 with a degree of acetylation (DA) of 2 % determined by ^1H NMR, a mass-average molar mass (M_w) of 619 kg/mol and a dispersity (\mathcal{D}) of 1.6 determined by size-exclusion chromatography. Chitosan was acetylated at 0.5 % (w/v) in a hydroalcoholic mixture of 1, 2-propanediol and AcOH (50/50 v/v). An amount of acetic anhydride was added stoichiometrically to D-glucosamine (GlcN) unit of chitosan and mixed for 18 h under vigorous mechanical stirring to reach the targeted DA. Chitosan solution was then filtered through cellulose membranes with decreasing pore sizes from 3 μm to 0.45 μm . Acetylated chitosan was finally precipitated with NH_4OH , washed with deionized water and freeze-dried. Acetylated chitosan with a DA of 35 %, a M_w of 693 kDa and a dispersity of 1.8 was obtained.

Chitosan films (DA 35 %, M_w 693 kDa) were obtained by spin-coating of a 0.5 % (w/w) solution of acetylated chitosan. Chitosan was solubilized with AcOH aqueous solution (stoichiometry to GlcN unit) for 18 h. Solution was

then filtered through 0.45 μm cellulose membranes prior using.

2.2 Lithography process & equipment

The lithographic process consists of three main steps: (a) chitosan film coating, (b) DUV exposure on scanner, (c) development step to reveal binary patterns (Figure 1).

Following spin-coating of high M_w chitosan film, the DUV exposure induces depolymerization of chitosan by scission of glycosidic linkages, decreasing M_w then revealing patterns by resist removal into DI water during the development step.

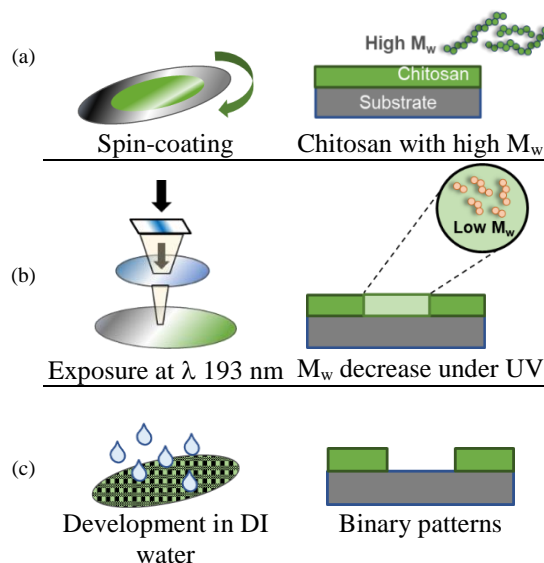


Figure 1. Lithographic process steps with chitosan films. (a) Spin-coating of chitosan film (b) Exposure at 193 nm (c) Development step with DI water.

Resist was spin-coated on a SOKUDO DUO coat and develop track from SCREEN in a dedicated aqueous spin-coat unit. The resist was then exposed on a 193 nm dry scanner NIKON NSR 307E with an NA 0.85 and using a binary mask with multiple patterns (lines, trenches, contact, plots) with varying Critical Dimension (CD) and pitch. Finally, the wafer was developed in a standard develop unit

2.3 Characterization methods

The degree of acetylation (DA) of chitosan was determined by ^1H NMR spectroscopy (AVANCE III 400 MHz, Bruker) according to the Hirai *et al.* method [9].

The averages molar masses (M_w , M_n) and the dispersity \mathcal{D} were determined by size exclusion chromatography (SEC) using a differential refractometer (Optilab T-rex, Wyatt) coupled online with a MALLS detector (Dawn Heleos II, Wyatt). The refractive index increment (dn/dc) was adjusted according to Schatz results [10].

Chitosan film thicknesses on Silicon bare wafers were controlled with a KLA-Tencor ellipsometer using a Cauchy model.

Post-lithography imaging and CD of the patterns were measured with a HITACHI CG4000 top-view CD-SEM, with an acceleration voltage of 300 V.

The profiles were carried out with a Bruker InSight 3D AFM (Atomic Force Microscopy), a non-destructive technique.

3 Lab-scale results

At lab-scale, we have previously demonstrated high-resolution sub-micron patterning with chitosan resists (DA 2%) down to 50 nm lines by writing with a 30 kV electron beam system or 300 nm with 248 nm DUV tool [7]. Features of 5 μm lines exposed on 193 nm DUV lithography tool were transferred by plasma etching into Silica substrate preserving pattern fidelity [8] as shown in **Figure 2**.

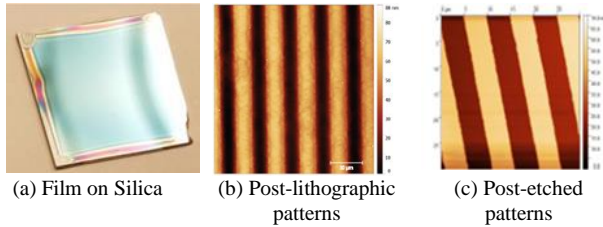


Figure 2. Patterning of chitosan at lab-scale. (a) Film deposition on Silica "coupons" 10*10 mm - AFM images of 5 μm lines patterns (b) after 193 nm DUV exposure (c) after plasma etch transfer into silica. Adapted from [8]

4 Pilot line results

4.1 Scale-up challenges

Chitosan solutions at the state-of-the-art have been designed and tuned to meet the microelectronics specifications (clean room rules, thickness target, adhesion...).

Nevertheless, the scalability from small coupons to large scale on 300 mm Si wafer size remains challenging. The industrial pre-transfer of chitosan resist requires to control and fit several key performance criteria listed in **Table 2**.

Key parameters	
Clean room rules	Contamination control (metallic, particles)
Compatibility on substrate	Adhesion, film coating on Si
Lithography step	Thickness uniformity, profiles patterns after development
Performances	Resolution, sensitivity, LWR
Etch transfer capability	Profiles preservation, resist budget, resist stripping
Material in solution	Shelf life, purity, viscosity

Table 2. Key parameters of new resist qualification in semiconductor.

4.2 Clean room controls

The introduction of new material as chitosan requires a strict control of sources of contamination (metallic and particles) to fit the cleanroom specifications defined by the manufacturing of integrated circuits (IC). Metallic contamination analyzed with Total reflection X-Ray Fluorescence (TXRF) technique reveals that all metal contaminants measured on back-side wafer are below the defined limits authorized in clean room (**Table 3**).

Metal	(At/cm^2)
Al	$< 5^{12}$
Co, Cr, Cu, Fe, Mn, Ni, V	$< 1^{11}$
Ca, K, Mg, Na	$< 1^{12}$
Ti, Zn	$< 5^{11}$

Table 3. Metallic contaminants control.

Particles control measured with Unpatterned Surface Inspection System from KLA-Tencor SP3 tool shows equivalent particles number on back-side wafer before and after film spin-coating of bio-sourced chitosan film compared to a process of reference (wafer without chemistry).

Thus, contamination controls show the compatibility of chitosan with the clean room rules for both metallic and particles contaminants. Moreover, the Edge Bead Removal (EBR) and back-side (BS) chemical cleaning with DI water reveals to be efficient with a complete edge bead elimination and a back-side substrate without resist residues.

4.3 Spin-coating optimization

Chitosan films of 100 nm thickness were prepared onto 300 mm silicon wafers by resist spin-coating in manual dispense mode in a dedicated aqueous-based unit. Commonly, adhesion promoters are used prior process steps to promote wetting and adhesion of the photoresist onto the surface. This step is unnecessary with chitosan resist due to its high affinity with silanol groups on the surface wafer [11]. Amine, hydroxyl and carbonyl groups of chitosan form hydrogen bonds with the surface providing a strong adhesion onto the substrate.

Despite its great affinity with Si surface, chitosan resist difficultly spreads onto the wafer. The high viscosity (~ 0.5 Pa.s) of the resist caused by the high molecular weight chitosan requires optimizing the spin-coating process. A slightly acidic solution was firstly spread on the surface to promote the full coverage of the resist.

Here, a two-step dispense of the solution was performed according to the method proposed by Young *et al* [12]. The method applied for chitosan resists consisted of a first dispense of the solution (200 RPM, 10 s). The spinning of the wafer was stopped and a second volume was dispensed. The wafer was then spun up at the rotational speed of 1000 RPM during 120 s for final thickness adjustment. The 300 mm wafer was fully covered without defects (**Figure 3a**). A soft-bake at 150 $^{\circ}\text{C}$ for 5 min was finally applied to remove residual solvent and densify the film. The resulting coating had a thickness of 94 nm with a uniformity of ± 9 nm (**Figure 3b**). The thickness uniformity should be improved to aim the same target as conventional resists ($3\sigma < 1\text{nm}$). Here, no surfactants were added to the resist for the smoothing of the film. Formulation with additives for modifying the surface tension could be considered to get better uniformity. On other hand, the automatic dispense of the resist could greatly improve the uniformity thickness and should be envisioned in future works.

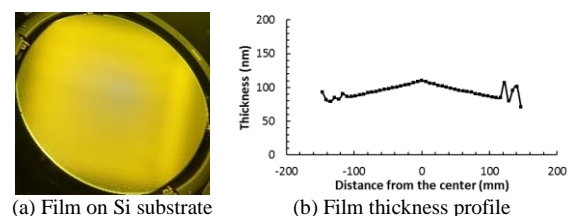


Figure 3. (a) Chitosan film deposited by spin-coating on a 300 mm Si wafer. (b) Associated film thickness profile along the wafer.

4.4 DUV exposures: patterning

DUV exposures have been carried out using the 193 nm dry scanner to pattern ~ 100 -nm thick chitosan films.

Irradiation doses from 600 to 900 mJ/cm² through a binary mask with multiples features were applied on chitosan films, acting as a positive resist under DUV irradiation by chain depolymerisation. Investigations by SEC of 100-nm thick chitosan films showed a strong decrease of the M_w down to 14 kg/mol with a Đ of 2.0 after an irradiation at 600 mJ/cm². Low molecular weight chitosan chains lead to an increase of the film solubility and are removed during the development step in deionized water (pH ~ 6,5 – 7) while unexposed areas are not diluted and remain [13, 14].

Thus, the binary patterns revealed after development show a good quality imaging down to 1 μm line/space (L/S) patterns (**Figure 4**). The optimal dose is between 600 and 700 mJ/cm², which is greater than conventional resists (< 100 mJ/cm²). Photosensitivity enhancement will be required prior to its industrial implementation. Addition of PhotoAcid Generators (PAG) may improve the lithographic performances of chitosan-based resists. Chitosan solubility for higher molecular weight chains increases in acidic environments [15]. The generation of acid species from PAG under UV exposure should promote the dissolution of longer-molecular-weight chitosan chains, and consequently permits a full-pattern opening at lower doses.

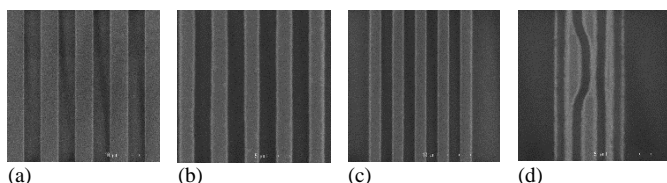


Figure 3. Top-view CD-SEM images with chitosan dense trenches patterns Half-pitch (HP) (a) HP 5 μm (b) HP 2 μm (c) HP 1 μm (d) HP 0.7 μm after DUV exposures at 700 mJ/cm².

The 2 μm L/S pattern profile analyzed by 3D-AFM shows fully opened features with no remaining chitosan between lines (**Figure 5**). A dose of 700 mJ/cm² gives a height pattern of 70 nm. The thickness loss in the non-irradiated area is about 25 % corresponding to the dark erosion effect. Below 1 μm resolution, the patterns were not fully opened or are deformed. This lack of resolution of the resist may be due to surface tension during development step inducing resist deformation. Further improvements should be performed to obtain the maximum photoresist contrast.

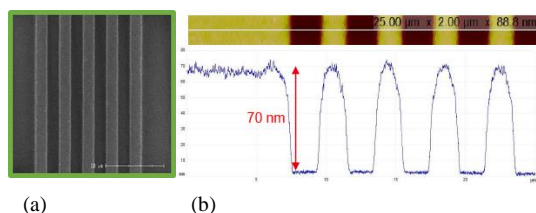


Figure 4. Patterning with chitosan resist. (a) Top-view CD-SEM image of 2 μm dense trenches. (b) 3D-AFM profile of 2 μm patterns.

5 Environmental impacts

This Life Cycle Analysis (LCA) aims to compare the environmental impacts of the lithographic process using a chitosan-based bio-resist compared to a conventional process using a petro-sourced resist. The functional unit of our system is referred to a batch of 25 Silicon 300 mm wafers size with equivalent DUV lithographic performances as standard one.

The LCA is based on ISO 14040 standard [16] and the impact assessment method recommended by the European Commission (PEF): EF 3.0 Method (adapted). The software used is Simapro version 9.3.0.3 coupled with the Ecoinvent 3.8 database. The LCA carried out is attributional and only uses "cut-off" data.

The LCA boundaries extends from the extraction of the raw materials till the end of lithographic process step for the two systems, by excluding some common steps, namely Silicon wafer production or energy consumptions and materials required to operate cleanroom infrastructure. Data collection listed for all the inputs and outputs included the energy, the resources and the materials, required for Life Cycle Inventory (LCI) phase come from on-site process, tools parameters, from publications [17], patents, or data provided by manufacturers for raw materials synthesis.

The LCA unique score of the two processes has revealed the same six main impact factors among 16, whose the sum is at least equal to 80%, namely depletion of fossil fuels, climate change, ecotoxicity in fresh water, ionizing radiation, depletion of mineral and metallic resources and water use.

The LCA comparison shows that the environmental impact of the chitosan process is on average 10% less polluting than the classic one on trilayer stack (**Figure 6**). The impact is lower for all the indicators except that of ionizing radiation due to high electricity consumption during the synthesis of the chitosan, resulting from the use of nuclear energy in France. However, this indicator is certainly overestimated as chitosan preparation is performed in R&D laboratory and not at an industrial scale.

For processes using chitosan resist, the need of underlayers (SOC-Si-ARC) [18] are not yet been proved. In this case, their removal would contribute to a drastic reduction down to 81% in the overall environmental impact, due to the preponderant role of the organic solvent (PGMEA) which serves to dilute the underlayers/resist, and wafer cleaning operations.

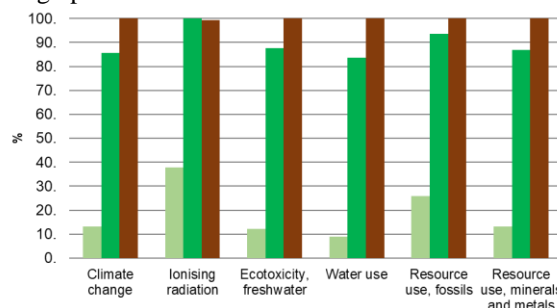


Figure 5. LCA comparison based on a batch of 25 wafers ● Conventional resist on trilayer stack ● Chitosan on trilayer stack ● Chitosan on Si substrate.

6 Conclusion

The lithographic process based on water-soluble chitosan resist was developed on a 300 mm pilot line. The industrial pre-transfer of chitosan films on 300 mm Si wafer for DUV lithography has been successfully proved. The essential key points were highlighted:

- Clean room controls within IC industry
- Solution ready-to-use for spin coating on 300 mm track using a dedicated aqueous-based unit
- Spin-coating of a film with thickness of ~ 100 nm ± 9 nm without defects

- Photopatterning capability with 193 nm DUV lithography down to 1 μm with preserved patterns profile.
- Reduce the environmental footprint by using a bio-sourced resist and replacing PGMEA and TMAH organic products by DI water.

The latest achievements are very encouraging to consider eco-friendly chitosan-based resists for lithography process. Prior to its implementation, it requires improving sensitivity and resolution with formulation with added PAGs. Etch plasma transfer in silicon and resist stripping are under investigation on 300 mm industrial tool.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors gratefully acknowledge the financial support from the French National Research Agency (ANR) within the ANR-19-CE43-0009 'LITHOGREEN' project.

The authors will acknowledge Ahmed Gharbi, Rémi Cocquand (CEA-Leti) and Agnès Crépet (CNRS-IMP)

References

- [1] P.T. Anastas et al., *Acc. Chem. Res.*, 35(9), 686–694 (2002)
- [2] E. Mullen et al., *Nanomaterials*, 11, 1085 (2021)
- [3] Y. Liao, J. H. Liu, *J. Applied Polymer Science*, 109, 3849 – 3858 (2008)
- [4] S. Takei et al., *Japanese Journal of Applied Physics*, 53, 116505 (2014).
- [5] A. Grebenko et al., *Advanced Functional Materials*, 31, 2101533 (2021)
- [6] M. Rinaudo, *J. Progress in Polymer Science*, 31, 603 – 632, (2006)
- [7] M. Caillaud et al., *Proc. of SPIE Advanced Lithography*, Vol. 10587105870S, (2018)
- [8] O. Sysova et al., *ACS Applied Polymer Materials*, 4 (6) (2022)
- [9] A. Hirai et al., *Polymer Bulletin*, 26, 87-94. (1991)
- [10] C. Schatz et al., *Biomacromolecules*, 4, 641-648 (2003)
- [11] D. W. Lee et al., *Langmuir*, 29, 14222 – 14229 (2013)
- [12] B. Young et al., *US Patent 2002/0127878 (A1)*, 1-5 (2002)
- [13] L. Minhyung et al., *Pharmaceutical research*, 18, 427-431 (2001)
- [14] F. Tao et al., *European Food Research and Technology*, 225, 133-138 (2006)
- [15] K. Vårum et al., *Carbohydrate Polymers*, 25, 65-70 (1994)
- [16] M. Finkbeiner et al., *The International Journal of Life Cycle Assessment*, 11, 80–85 (2006)
- [17] I. Muñoz I. et al., *The International Journal of Life Cycle Assessment*, 23(5), 1151–1160 (2018)
- [18] Y. Wei et al., *Proc. of SPIE Advanced Lithography*, vol. 7972, 79722L (2011)