Recent Progress of Negative-tone Imaging Process and Materials with EUV Exposure

Toru Fujimori, Toru Tsuchihashi and Toshiro Itani

EUVL Infrastructure Development Center, Inc. (EIDEC)
16-1 Onogawa, Tsukuba-shi, Ibaraki 307-8569, Japan
toru.fujimori@eidec.co.jp

This study describes the recent progress of negative-tone imaging with EUV exposure (EUV-NTI) compared with positive-tone development (PTD). NTI uses organic solvent-based developer to provide low swelling and smooth-dissolving behavior. Therefore, EUV-NTI is expected to offer several advantages in terms of performance, especially for improving line-width roughness (LWR), which is expected to resolve the resolution, LWR, and sensitivity (RLS) trade-off. Herein, novel chemical amplified resist materials for EUV-NTI are investigated to improve LWR and sensitivity. Results indicate that the EUV-NTI has better performance than PTD, while maintaining the LWR performance. The novel high sensitivity formulation, with ‘single digit mJ/cm² photo speed’, resolved 22-nm half pitch using NXE3100 scanner. Furthermore, EUV-NTI processing such as the pre-applied bake (PAB) temperature, post-exposure bake (PEB) temperature, development procedure, and rinse procedure are very effective for improving the lithographic performance. In addition, the lithographic performance with NXE3100 scanner is also reported.

Keywords: EUV, negative-tone imaging (NTI), organic solvent development, resist

1. Introduction

Extreme ultraviolet (EUV) lithography is considered to be the most effective strategy for realize sub-10 nm manufacturing and beyond [1]. A key factor for the realization of EUV lithography is the choice of EUV resist material that is capable of resolving below 20-nm half pitch with high sensitivity without the issue of outgassing. Recently, some researchers have reported concerns on the limitations in the performance of chemically amplified resist (CAR) [2-3]. This implies that there is often a trade-off between resolution, sensitivity and line-width roughness (LWR). Consequently, there is a critical need for new chemistry and development of new resist materials. Nevertheless, CAR continues to remain as a potential candidates for realize sub-10 nm using EUV lithography.

Typically, CAR is developed using water-based alkaline developer such as 2.38% tetramethylammonium hydroxide (TMAH) by a process called positive-tone development (PTD). It is especially useful for semiconductor industry, given that TMAH is a standard developer used in almost every lithographic process. However, the issue associated with such water-based developers is the swelling of resist film, which often leads to poor LWR performance and pattern collapse. It is almost practically impossible to resolve these issues associated with the water-based alkaline developer system.

Upon EUV exposure, protected co-polymers in CAR materials release carboxylic acid as a result of the reaction with the generated acid from the phot acid generator (PAG). The released carboxylic acid dissolves in the alkaline solution, which is otherwise insoluble in organic solvent. On the other hand, protected co-polymers can be readily dissolved in organic solvent to form the negative-tone pattern. Negative-tone imaging (NTI), which uses organic solvent-based
developer, results in low swelling and smooth-dissolving behavior. Accordingly, NTI with EUV exposure (EUV-NTI) is considered to have several advantages in terms of performance, especially for improving LWR [4-8]. This, in turn, expected to resolve the RLS trade-off. Moreover, the NTI system has already been used in manufacturing with ArF exposure [9].

![Fig. 1. Overview of the NTI process using organic solvent developer compared PTD using water-based alkaline developer.](image)

![Fig. 2. Development behavior of NTI compared with PTD, as observed using in situ high-speed atomic force microscope. NTI shows no swelling and dissolve smoothly.](image)
2. Experimental

2.1. Materials

Protected co-polymers were synthesized according to the conventional polymerization methods [10]. Photoresist formulations were prepared by blending the protected co-polymers with optimized amounts of PAG and organic amine as a quencher in organic solution. The resulting photoresist solution was filtered using 0.02 \( \mu \)m polyethylene filter before lithographic performance evaluation.

2.2. Lithographic performance evaluation

The photoresist solution was filtered and spin-coated onto a Si wafer, which was treated with an under layer, followed by pre-applied baking at the appropriate temperature for 60 s to give a specific film thickness for each patterning feature. Subsequently, the Si wafer was exposed to EUV light (13.5nm) using ASML NXE3100 scanner (NA = 0.25), small-field exposure tool (SFET) (NA = 0.30) at EIDEC, or EB lithography tool using ELIONIX ELS-F125 (Vac = 125keV) at the National Institute for Materials Science (NIMS). After exposure, the Si wafer was baked (post-exposure baking) at the appropriate temperature for 60 s followed by a stream or paddle development for 30 s using n-butyl acetate for NTI. As a reference, 2.38% TMAH aqueous solution was used as developer for PTD. The Si wafer was evaluated for resolution, LWR, sensitivity and pattern profile using CD-SEM (Hitachi CG4000) and SEM (Hitachi S4800).

3. Results and Discussion

3.1. Advantages of EUV-NTI lithography

Studies have reported novel chemical amplified resist materials for EUV-NTI, with an aim to improve the LWR and sensitivity. To study the LWR performance, the EUV-NTI resist performance shows 80% better LWR performance than PTD resist under same conditions of sensitivity owing to their smooth-dissolving behavior and non-swelling properties. Furthermore, use of other novel chemical amplified resist materials A1 for EUV-NTI with NXE3100 scanner (NA = 0.25) exposure resulted in significant improvement in the sensitivity. The sensitivity of the novel EUV-NTI resist material A1 was 13 mJ/cm\(^2\), which was 60% better than conventional PTD resist under same LWR conditions at 24-nm half pitch.

![Fig. 3. Typical examples comparing lithographic performance between NTI and PTD.](image1)

![Fig. 4. Improvements in the sensitivity of EUV-NTI resist material A1 compared with PTD resist material.](image2)

3.2. Resolution performance and resolution capability of EUV-NTI

The resolution performance of EUV-NTI was observed using NXE3100 scanner (NA = 0.25). The resist with lower sensitivity formulation, with 33 mJ/cm\(^2\) photo speed, exhibited good LWR performance of 3.0 nm and 3.8 nm at 24-nm and 22-nm half pitch, respectively. Even the resist with high sensitivity formulation, with 9 mJ/cm\(^2\) photo speed, resolved 24-nm half pitch and 22-nm half pitch with an LWR 4.9 nm and 5.4 nm, respectively. It was helpful to use sub-10 nm generation with this EUV scanner because of its low energy power source.

The resolution capability of EUV-NTI was examined using electron beam lithography. As
Fig. 5. Resolution performance of EUV-NTI

Fig. 6. Resolution capability of EUV-NTI observed using EB lithography

Fig. 6. shows, the line and space of 14-nm half pitch could be clearly resolved, indicating the high possibility of EUV-NTI for use in sub-10 nm generation and beyond.

4. Conclusion
This study shows the recent progress of EUV-NTI compared with PTD. In particular, EUV-NTI offers several advantages in terms of lithographic performance including sensitivity and LWR. The study suggests a great promise for the use of EUV NTI for sub-10 nm manufacturing. Novel chemical amplified resist materials for EUV-NTI exhibit 80% higher sensitivity or 60% better LWR performance than conventional PTD. The novel high sensitivity formulation, 9 ml/cm² photo speed, resolved 24-nm half pitch and 22-nm half pitch with 4.9 nm and 5.4 nm LWR, respectively. In particular, the novel high sensitivity formulation could be used for sub-10 nm generation with EUV scanner, which has a low energy power source.

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References
1. ITRS, The international Technology Roadmap for Semiconductors (2013).
2. A. Yen, International Symposium on Extreme Ultraviolet Lithography (2014).
3. M. A. Goethals, D. De Simone, Ph. Foubert, F. Van Roey, and E. Hendricks, International Symposium on Extreme Ultraviolet Lithography (2014).
4. S. Tarutani, W. Nihashi, S. Hirano, and N. Yokokawa, Proc. SPIE, 8682 (2013) 868241.
5. T. Fujimori, H. Tsubaki, W. Nihashi, S. Tarutani, H. Takizawa, T. Goto, International Symposium on Extreme Ultraviolet Lithography (2014).
6. H. Tsubaki, S. Tarutani, T. Fujimori, H. Takizawa, T. Goto, Proc. SPIE, 9048, (2014) 90481E.
7. T. Fujimori, J. J. Santillan, T. Takahashi, E. Shiobara, T. Itani and S. Inoue, International Symposium on Extreme Ultraviolet Lithography (2014).
8. T. Fujimori and T. Itani, International Symposium on Semiconductor Manufacturing, PO-O-042 (2014).
9. S. Tarutani, H. Tsubaki, S. Kamimura, Proc. SPIE, 7273 (2009) 72730C.
10. G. Odian, “Principles of polymerization”, John Wiley (2004).