Metal-containing Materials as Turning Point of EUV Lithography

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Limitations on current performances of the chemically amplified resists (CAR), as well as the productivity driven low exposure dose requirements (below 20 mJ/cm²), have brought the researchers to look at a novel class of materials as possible alternative to the CA resists to simultaneously achieve resolution, line-width roughness (LWR) and sensitivity. In 2014, imec has started a new project to look into novel materials for EUV lithography with particular attention to metal containing materials (MCR) to explore alternative approaches that can offer superior characteristics in photoresist imaging: improved LWR and line collapse, high sensitivity and high etch resistance. In this paper we report the first assessment on the enablers of the MCRs from a manufacturing compatibility prospective, as metal cross-contamination and outgassing, to a device integration prospective through the patterning on the ASML NXE:3300 full field scanner exposure tool, the etch performances and new litho-etch integration scheme for 1x nm technology and below. The results obtained are highly promising and give a clear indication that other chemical paths in novel resist formulations are possible in advanced EUV lithography.

Keywords: EUV lithography, EUVL, EUV resist, metal containing resist

1. Introduction

Today the shortening wavelength trend of exposure tools is continuing with the aim of achieving < 1x nm resolution mass production by the deployment of the extreme ultraviolet lithography (EUVL) at 13.5 nm wavelength. EUVL requires highly sensitive resists for the reduction of the development cost of high-power exposure sources and although in general a conventional CA resist can have a good Sensitivity (S), its drawbacks are Resolution (R) and Line-Width-Roughness (LWR) that are not simultaneously satisfied (RLS trade-off). The resolution of EUV CA resist is also strongly affected by pattern collapse, which becomes increasingly important as feature sizes move into the nm size range. Recently further efforts have been done on the development of CA resists in order push its lithographic performances. Although the resolving resolution of these CA resist on the 0.33NA ASML NXE:3300 EUV tool has reached today 13nm line-space features, the dose remains higher than 20 mJ/cm² with the LWR higher than 20% of the printed critical dimension (CD) line.

Even if these exceptional patterning performances have been obtained, the current RLS performances with CA resists still indicate the limitations of CA resist that are intimately tied to the nature of the resist chemical amplification imaging mechanism, the thin-film confinement effects and the polymer molecular properties. It is in this frame that imec has started a new project [1] in 2014 to look into novel materials for EUV lithography and explore alternative approaches that potentially can offer benefits...
in terms of resolution and LWR, patterning image fidelity, line collapse and etch resistance.

In this paper the imec exploratory work on novel EUV materials is introduced describing the lab-to-fab concept as resist path to enable pipeline between risky exploratory research and fab process enablement. The metal containing resists (MCR) are explored within this work aiming to enable such a resist for its future usage in a manufacturing environment. The first reported results are from the metal contamination and outgassing tests as initial results for the manufacturing compatibility checks. Because of the positive output from the initial manufacturing compatibility studies, the EUV lithographic performances and the etch resistance properties of such a MCR were afterwards investigated. Their initial results are reported with a look on potential new litho-etch schemes for 1x nm technology and below.

In the next two paragraphs, the motivations of such research are shortly illustrated describing the limits of CA resists and the potential benefits of MC resist in EUV regime.

1.1. Chemically amplified resist and its limitations in EUV lithography

**Mechanism of chemical amplification**

Chemical amplification is based on the generation of a chemically stable catalytic compound in the areas that are exposed to a source of energy such as UV light. The initial resist irradiation produces a catalyst (i.e. the photoacid), initiates a chain reaction that render surrounding polymer soluble in developer. The concept of chemical amplification has made a great impact on photo resist designs because the sensitivity of a resist based on chemical amplification can be as high as two orders of magnitude greater than those of resist systems that consume at least one photon for every functional conversion. While maximizing the sensitivity of CA resists, it is fundamental to control the photoacid diffusion in order to mitigate the resolution-loss issue of chemical amplification resists, particularly as the feature geometries approach a few multiples of the radius of gyration of the resist polymer. In fact, one of the major limitation of CAR resists, especially in the EUV context, is the blur effect [2], where the catalyst generated on the exposed regions can diffuse into unexposed regions causing blurring of the latent image with consequent impact on resolution. It is possible to reduce catalyst migration by increasing the size of the catalyst or by reducing the temperature of the post-exposure bake (PEB) step or by incorporating base additives onto the resist formulation. All these approaches that reduce acid catalyst migration, generally reduce the catalyst efficiency of each photoproduct and therefore increase the total dose of exposure energy with consequent throughput reduction at the expenses of the exposure dose.

**Near-atom scale resolution**

Two major issues of CARs are to be considered when going at nanometer size scale: first, the low mechanical strength that limits the amount of stress a CA resist can withstand during development and drying. Pattern collapse [3] of small resist features is driven by the very high capillary forces that are generated in the developed feature during drying, particularly in the common case of a final de-ionized water rinse. The high capillary forces will be an issue for all small features, but this problem is exasperated by the fact that these types of resist materials show dramatically reduced modulus [4] at sub-50 nm features sizes due to high surface to volume ratio effects; second, the resist homogeneity which is of critical importance in patterning features on the order of 10 nm in size since the features themselves are only roughly an order of magnitude larger than their constituent molecules in many cases and can be critically impacted by micro-phase separation.

**Stochastic effects**

With the shortening of exposure wavelength, the photon energy increases from 5eV at 248nm wavelength to 6eV at 193nm wavelength and then to 92.5eV at 13.5nm wavelength and low dose of high-energy photons causes the number of photons to fall low enough to cause the statistical variations [5]. This photon randomness leads to random deprotection reactions of protecting groups in chemically amplified resist and inevitably will
cause the line width roughness (LWR) to increase beyond an acceptable limit. In turn, higher LWR can lead to random defects as bridging and scumming.

1.2. The light-matter interaction in EUV and the introduction to metal containing resist (MCR)

**Light-matter interaction in EUV**

The EUV radiation chemistry uses high energy photons and the resist exposure mechanism is driven by the ionization of the resist material that generate photoelectrons which in turn generate secondary electrons. The primary high energy EUV photons do not expose resists (i.e. do not cause a chemical reaction in the resist), but they generate secondary electrons on account of their interaction with resist material and which in turn expose the resist. The efficiency with which the primary beam interacts with the resist film to produce secondary electrons depends only on the resist capacity to absorb EUV light radiation. Differently from DUV light-matter interaction, the energy absorption is not associated with particular chromophores at molecular level, but occurs at random in the resist material at atomic level.

**Toward metal containing resist**

Looking at the current CAR limitations and the light-matter interaction in EUV it is clear that possible viable solutions to improve the patterning definition in EUV lithography are the identification of alternative resist with different solubility switching mechanisms able to suppress the blur effects and hybrid organic-inorganic resist systems able to capture more productive photons and offer better sensitivity. In order to minimize the resist blur effect the switching on solubility should happen in a short distance from the ionization point where the photoelectrons are generated with a short mean free path of the secondary electrons. Such a switching mechanism would suggest a mechanism without chemical amplification.

In order to make the resist capture more EUV photons, the resist should contain atomic elements able to absorb the EUV light and improve their absorbance capacity more than a traditional organic resist. The introduction of atom metals [6, 7] into the formulations should be able to improve the EUV light absorption, capturing more productive photons and making more productive use of secondary electrons. Further, the high EUV light absorption resist should maintain patterning fidelity and mitigate shot noise with higher resist sensitivity and a better tradeoff between sensitivity and LWR.

Further, if the metal is appropriately selected, other benefits can be obtained from its introduction into the resist formulation. For instance the thin films used in EUV lithography can significantly limit the ability to transfer the pattern to the substrate during the etch steps. To obviate the need for a hard-mask layer and thus the increasing of the process costs, the improvement of the resist etch resistance by using a MCR can be a reasonable approach to fix this issue.

**Metal containing resist challenges in manufacturing environment**

A possible introduction of MCRs in the line of a device high volume manufacturing (HVM) flow open new scenarios about the management of the wafers and tools at contamination and process level [8]. First MCRs have to demonstrate a high capacity to compete with traditional organic materials showing no risk of cross metal contamination and no risk of high levels of outgassing when exposed on EUV tools. Second, MCRs have to demonstrate high and stable EUV patterning performances able to compete with organic resists breaking the current barrier of the RLS trade-off and offer superior lithographic-etching process schemes integrable in real devices at nanometer scale.

2. The imec exploratory work and the introduction to the Lab-to-Fab concept

Imec is exploring novel EUV materials such as new photoresist platforms (non-chemically amplified resists, inorganic or hybrid organic-inorganic resists, molecular resists,..) and novel ancillary materials to enable the current EUV CAR resists (post processing materials for LWR mitigation, topcoat for out-of-band suppression..) with the intention to find alternative solutions that offer higher performances in EUV lithography with respect to the conventional existing CA resist in an HVM environment. The approach
that imec is following is described in Figure 1.

![Diagram](image)

**Fig. 1 Novel material path finding: imec’s role**

Basically imec’s objective is to bring novel valuable material concepts that are at an early development stage in their research centers to a higher level of maturity with the ultimate goal of integrating such a novel material into device modules and propose them as potential alternative materials for nano scaling device in advanced semiconductor technology. The transition between the initial stage to the ultimate stage is called the Lab-to-Fab cross over. The experimental results reported in this paper on MCR are produced within this frame.

### 3. Experimental

As a starting point, two different MC resists have been considered to check their metal trace level at liquid level. The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has been used to analyze those samples. After that, a cross contamination test has been performed focused on the key metal species of the resist to check the potential risk of cross metal contamination at tool level. A manufacturing 300mm track tool has been used for such an experiment. Two runs have been performed in “dry mode” i.e. without dispense of chemicals using witness wafers: the first run before the MCR coating process and the second one after the MCR coating process. Clean monitor wafers for advanced lithography have been used as witness wafer and analyzed by Vapor Phase Decomposition (VPD) in combination with ICP-MS tool to quantify the contamination level of the samples depending on the metal type. Outgas of the resists has been evaluated and quantified using EUV infrastructure at imec.

Exposures have been carried out on the EUV ASML NXE:3300B full field EUV scanner tool. Line-space patterning was exposed with dipole illumination. CD and LWR have been measured on HITACHI CG-5000 scanning electron microscope. Etch selectivity studies have been carried out on a LAM tool with wafers coated on a SOKUDO DUO track. All the resist samples were coated on bare silicon wafers. Process window was analyzed by PWA Software from Synopsys based on CD measurements and top-down quality image check.

### 4. Results and Discussion

#### 4.1. Metal trace analysis

Two MCRs have been evaluated including their casting solvent to check the metal trace of the liquid sample. Both materials are at the early stage development. The cumulated metal trace pareto is reported in Figure 2 including the metal trace from their casting solvent. Excluding the key metal specie involved in the formulation the metal trace level is quite acceptable considering that both materials are at the early stage development. Most of the metals are in the order of tens of ppb except three metal types, Calcium, Sodium and Magnesium that showed up in these analyses as main undesired elements. This experimental evidence has been addressed to the respective material suppliers. The root-cause has been identified and actions have been taken in order to fix the issue for potential future scaling up of the material.

![Graph](image)

**Fig. 2 ICP-MS analysis results on two MC resists, sample A and sample B with their respective casting solvent. The output of the metal trace has been normalized to have a better view of the pareto. Calcium and Sodium are the main elements detected at the highest concentration.**

#### 4.2. Cross contamination test

In order to investigate the MCR and its potential risk in cross contamination the resist with the highest concentration in the key metal species in the formulation was selected. 24 wafers were processed as depicted in Figure 3 and explained in the experimental paragraph,
then all the witness samples were sent to the VPD-ICP-MS analysis. The results of the detected contamination are reported in Figure 4. The total concentration of the key metal species on each wafer (front-side and back-side of witness wafers and front-side of control wafer) is reported as atoms/cm². Detection limit of the ICP tool and the imec spec warning limit are also reported in the same chart. The results are good showing that after coating of 25 wafers with the MCR the risk of cross contamination is very low with a metal concentration one order of magnitude below the spec warning limit (1E10 at/cm²). This result has opened the path to move forward to the next step, i.e. the MCR outgas evaluation. The comparison of results obtained on witness wafers before and after wafer coating with MCR suggests also that extra explorations are needed in order to assess the cross contamination when working at high volume manufacturing levels. Further tests are planned in this direction including process and material optimization.

![Basic process working flow](image)

**Fig. 3 Basic process working flow for cross contamination studies of MC resists.**

![Cross contamination results](image)

**Fig. 4 Cross contamination results from ICP-MS analysis on MCR pre and post coating of 24 wafers on track. Metal trace of the key metal species is reported for each witness sample pre MCR coating and post MCR coating at front-side and back-side level. Contamination level of the control wafer is also reported. All the metal concentrations detected on the witness wafers are below the imec warning limit spec (1E10 at/cm²).**

### 4.3. Outgas test

Standard procedure in place at imec and in line with ASML NXE scanner requirements has been applied to investigate the outgas of MC resists looking at cleanable and non-cleanable contamination levels.

![Outgas detection](image)

**Fig. 5 Resist outgas process flow test at imec.**

**Contamination growth (CG)**

Description of the process steps are reported in Figure 5. Several MC resists have been tested at imec in conventional outgas tests and compared to traditional CAR. Residual gas analyzer (RGA) has been used to detect the outgassed species from the resist and the results put in correlation with the contamination growth [9]. The operational description of the RGA and CG measurement output is depicted in Figure 6. Looking at the outgas results for the MCR plot reported in Figure 7 there is a different offset in relationship between outgassing and cleanable contamination compared to traditional CAR.

![Operational description of RGA and CG measurement](image)

**Fig. 6 The operational description of the RGA and CG measurement output.**

![Outgas detection by RGA vs. CG](image)

**Fig. 7 Outgas detection by RGA vs. CG of CA resists and MC resists. CG of MCRs have similar order of magnitude as for CARs.**

Cleanable contamination of MCRs have similar order of magnitude as for CAR, in
some cases even much smaller. Further, no clear non-cleanables have been detected either by RGA analysis or by X-ray photoelectron spectroscopy surface (XPS). The results produced so far are very promising. A continuative activity is now in place at imec to explore different platform of MC resists.

4.4. Patterning

The positive results obtained on the contamination studies on MCRs have led us to have a waiver from ASML to start the patterning exploration on the EUV NXE full field exposure scanner tool. The initial exposures have been done using 0.33NA and dipole 90 degree as illumination mode targeting 22nm dense line-space. The selected MC resist for the patterning exploration was a non-chemically amplified resist and its nominal film thickness was 26 nm. The results on the process window (PW) analysis, considering a CD specification of ±10%, gave a maximum exposure latitude (EL) of 15% and a Depth of Focus (DoF) of 180nm at 10% EL. Dose to size was 58nm mJ/cm². Mask error enhancement factor (MEEF) and LWR were also evaluated. The top-down image of 22nm HP, LWR and MEEF curves are reported in Figure 8, 9 and 10 respectively.

In general the obtained initial patterning performances of this MCR were very promising with excellent MEEF and large PW. LWR value at the 22nm line was found to be 5.3nm and it is higher than the LWR target calculated as 20% of the line CD target (4.4nm) and to the CAR LWR reference which gave a value of 4.8nm.

The patterning performances of such a MCR have been explored looking more at the ultimate patterning resolution. For this purpose a thinner version of the resist (20nm) and a 60 degree dipole illumination were used to expose the material on the NXE3300 EUV scanner tool. The evaluated MCR has shown high patterning resolution reaching the ultimate resolution of 26nm pitch on 1:1 line-space features. Even if the dose-to-size is around 55mJ/cm², this result is an impressive achievement for such a novel metal containing resist not only for the tight resolved pitch, but also because resolution results are comparable to the current state-of-the art of advanced chemically amplified resists (Figure 11). The next challenges for such a MCR is to improve its sensitivity with the goal of 25mJ/cm² and reduce the LWR to 3.2nm at 32nm pitch dense line-space features.

4.5. Etching

The use of a MCR can improve the ability to transfer the pattern to the substrate during the etch steps. Because of the presence of the metal the resist itself can work as a photo patternable hard mask having higher etch resistance with respect to traditional organic films. In order to understand the potentiality of a such MC resist on the etching process, etch tests have been carried out to determine the etch rate of MCR at different types of etch chemistry when used to open different
materials: 193nm conventional anti-reflective coating (BARC), EUV underlayer (UL), spin-on-carbon (SOC) and spin-on-glass (SOG).

Fig. 11 A comparison on the ultimate patterning resolution on EUV NX3300 with dipole illumination between a metal containing (non-chemically amplified) resist and a chemically amplified resist. Both resists show the ultimate resolution of 26nm pitch on dense line-space features.

The same tests have been done on EUV CA resist in order to have a 1:1 comparison between both resists.

Figure 12 shows the results of the calculated etch rate determined experimentally using the appropriate gas etching chemistry listed in Table 1 for each type of material taken into account.

Fig. 12 Etch rate of EUV MCR and EUV CAR resist for four different etch chemistry conditions.

Table 1 The chemistry used for each type of etch process step to determine the etch rate of the EUV CA and MC resists.

| Etch step type | Etch chemistry     |
|----------------|--------------------|
| BARC Open      | Cl2/O2             |
| UL Open        | CF4/O2/CH2F2       |
| SOG Open       | Cl2/O2/N2          |
| SOC Open       | SF6/N2/CH2F2/He    |

Results indicate that a large advantage can be taken when using a MCR to transfer the patterning to the substrate underneath with respect to organic resist. For instance, the etch selectivity of MCR vs SOC is 1:40, so a potentially simplified litho-etch process scheme can be designed to integrate MCR on advanced process modules of new technology devices where cost-of-ownership reduction is requested. An example of a simplified process scheme is reported in Figure 13 where a traditional tri-layer system for a CA resist is compared to a simplified stack when using a MC resist directly on top of a spin-on-carbon.

Fig. 13 MC resists can enable new process schemes. An example of MC resist directly on top of a spin-on-carbon is depicted and compared to a traditional tri-layer system where more organic layers are used for pattern transfer.

5. Conclusion and outlook

Novel EUV materials are under evaluation at imec aiming to find suitable materials for EUV lithography that can accomplish EUV RLS targets and improve the current process margin with high resist image contrast, no pattern collapse and high etch resistance. New concepts are under investigation trying to move beyond the chemically amplified mechanism and to incorporate metal atoms into the resist formulation. Within this frame a novel class of metal containing photoresist has been considered as a solution for advanced EUV patterning for 1x nm technology and below. Metal containing resists are now under evaluation at different levels from manufacturing compatibility to device integration point of view. The data produced so far on metal contamination levels look promising, but even further challenges on process and material optimization are needed to guarantee a smooth transition into a HVM environment without metal contamination risk at wafer and tool level. From a patterning perspective excellent performances have been demonstrated with the use of a MC resist not chemically amplified reaching the ultimate resolution of...
13nm half-pitch on dense line-space features on 0.33NA ASML NXE:3300 full field exposure tool. Resist sensitivity improvement and LWR reduction are the next challenges for such a MC resist. Initial etch tests have demonstrated excellent capability on etch selectivity versus organic layers when compared to a traditional CA resist. Next challenges is to demonstrate the ability of MCR to realize a full pattern transfer on stacked wafer and use it as a smart solution for dedicated device applications in EUV lithography.

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