Novel Fast Etch Rate BARC for ArF Implant Layer Lithography

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As the pattern size for the implantation process decreases, KrF lithography has reached its limit in the implementation of micropatterns, calling for the switch to ArF lithography. The change in wavelength for better resolution has led to the development of patterning materials. As a result, the development of a new bottom anti-refractive coatings (BARC) for implant layer patterning with ArF lithography became necessary. In addition to required chromophores for controlling optical properties with ArF lithography, the new BARC system requires a fast etch rate to reduce etch bias during BARC-opening process with plasma. Designing of fast-etch material could be accomplished with utilization of the widely-used model of Ohnishi parameters (O.P.), while designed material revealed the trade-off between etch rate and solubility in organic solvents. In this paper, the design of the material as well as the problem-solving process to address and resolve the trade-off between the desired properties as BARC and the accompanying problems.

Keywords: 193 nm, Etch rate, BARC, Anti-reflective, Implant, Lithography

1. Introduction

Organic Bottom Anti-reflective Coatings (BARCs) are widely used in microlithography to improve process latitudes by controlling reflection from substrate [1]. Despite the flexibility of fab and low cost of KrF lithography, KrF lithography has begun to be replaced by ArF lithography because of decrease in size and increase in complexity of patterns in implantation processes [2]. One of the key requirements of the ArF BARC systems to be developed is a fast etch rate to minimize the substrate damage and etching bias during the BARC opening process with plasma, as shown with Fig. 1, in addition to other properties as BARC [3].

Ohnishi parameter (O.P.) is a theoretical model which can be used to predict etch rate based on the chemical structure of the material. According to the model, the etching rate of the material can be increased by reducing the number of carbons while increasing the number of heteroatoms such as oxygens (O) and nitrogens (N) [4]. Fortunately, change from KrF to ArF lithography allowed elimination of previously required carbon-rich aromatic chromophores.

Increase in heteroatoms consequently gave rise to another problem of increased polarity of developed material and reduced solubility in organic solvents. We attempted to address this issue in the initial designing stage by incorporation of the Hansen Solubility Parameter (HSP) of the monomers of the resin.

This paper will describe how appropriate theoretical models were applied in the designing of materials with desired properties as well as evaluation result of the developed material to address the needs from the industry.

Fig. 1. Advantages of fast etch BARC.
2. Experimental

2.1. Polymer resin
Polymers were synthesized following general synthetic methods with pre-screened monomer through Ohnishi and Hansen solubility parameter calculations, described in the following section.

2.2. BARC formulation
BARC formulations were prepared with polymers, cross-linkers, thermal acid generators (TAG) and solvents. BARC films were prepared by spin-coating on bare silicon wafers followed by baking at 150-215 °C for 60 seconds.

2.3. Solubility measurement
BARC polymers were dissolved in 2-hydroxyisobutyrate (HBM) in 10 wt% and shaken for 4 hours. The mixtures were filtered through 0.45 μm PTFE syringe filters, and the filtrates were measured with HACH turbidimeter.

2.4. Film thickness measurement
Thickness of BARC films were measured by Thermawave (Opti-probe) after following steps outlined in 2.2.

2.5. Etch rate measurement
The determination of etch characteristics was carried out at SEMES Korea. An ICP-type oxide dry etcher was used to expose all samples to N₂/H₂ gas mixture for specific time. Thickness change after the etch process was measured by Thermawave (Opti-probe), and the difference in film thickness caused by etch process was used to determine etch properties of samples.

2.6. Optical properties
BARC samples were prepared by procedure outlined in section 2.2 to achieve 60-80 nm of film thickness. Optical constants, the refractive index (n) and the extinction coefficient (k), were measured at wavelengths ranging from 170 to 900 nm by J. A. Woolam’s VUV-VASE ellipsometer.

2.7. Strip loss measurement
The strip test was performed by dispensing the testing solvent onto the prepared BARC films. The strip loss was calculated by taking the difference between the film thickness measurements before and after the dispense and soft-bake to remove the testing solvent.

2.8. Contact angle measurement
The wafer was prepared following the procedure outlined in 2.2. The contact angle measurements were made using goniometer (DSA-100). 3 μL of water was dropped onto the prepared wafer and the water contact angle at 9 points throughout the wafer were measured with each point averaging of 20 consecutive measurements.

2.9. Lithography test conditions
PTD lithography was performed with TEL LITHIUS i+ coater/developer Nikon S610C immersion scanner. Prepared BARC materials were first coated onto Silicon wafers, then selected immersion photoresist was coated onto the BARC. For the exposure, binary mask under annular illumination with 1.35 NA, 0.835 outer sigma, 0.589 inner sigma without polarization was used. The pattern size was 80 nm trench 700 nm pitch and the depth of focus margin was evaluated.

3. Results and discussion

3.1. Polymer design
As described in the introduction, the objective of this study was to develop a novel BARC system with high etch rate and good solubility while balancing the trade-off between increased polarity and decreased solubility in organic solvents.

First, Ohnishi parameter (O. P.) model described earlier in the introduction is well known to have good overall correlation at dry etch rate. Specifically, the O. P. is calculated following equation 1 below. Maximization of O. P. can be achieved by reducing the number of carbon atoms and/or increasing the number of oxygen or nitrogen atoms present in the substance.

\[ O.P. = \frac{N_{total}}{N_c - N_O - N_H} \propto \text{Etch rate (In reducing gas)} \] (1)

However, materials with high O. P. are likely to be very polar due to increase in heteroatoms, unfortunately leading to decreased solubility in organic solvents present in the process. Hansen solubility parameter (HSP) model quantifies the solubility of materials in targeting solvents by measuring the distance between two. In the calculation, the dispersion forces (d), polarity (p), and hydrogen bond (h) are considered as described by Eq. 2 below [5]. Shorter distance in
the three-dimensional coordinate system between
the solute and solvent predicts good solubility of
solute in designated solvent.

\[
(R_a)^2 = 4(\delta_{\text{d}2} - \delta_{\text{d}1})^2 + (\delta_{\text{p}2} - \delta_{\text{p}1})^2 + (\delta_{\text{h}2} - \delta_{\text{h}1})^2
\]

Ra : Distance between molecules

The objective of achieving both fast etch rate
and good solubility in formulating solvents can be
translated into development of substance having a
high O. P. and a short distance from an organic
solvent. Figure 2 lists monomers considered for
the design of target material. Most of selected
high O. P. monomers were far from process
solvents A and B compared to low O. P.
monomers, which was expected. Per contra, the
monomer \( g \) in Fig. 2 were located within the short
distance of both formulating solvents A and B
when compared to other high O.P. monomers
such as \( a, b \) and \( f \).

Fig. 2. Monomer’s O. P. and HSP distances.

While monomer \( g \) was chosen as the new
monomer to be included in the resin, other
monomers also should be selected with discretion
so that the developed BARC system would fulfill
the general requirements in performance. Other
monomers to be included in the polymeric system
are chromophore with absorbance at 193 nm (for
ArF lithography), a unit for crosslinking to
prevent intermixing with photoresist above, and a
monomer for forming a hard film. Various
copolymers were synthesized using monomers
with desired properties, and the overall design
scheme is illustrated in Fig. 3.

3.2. O. P. versus etch rate

The Ohnishi parameters of the synthesized
polymers were calculated using their \(^{13}\text{C} \) NMR
composition. The calculated value of O. P. was
increased up to 65% compared to Reference 2 in
Fig. 4, with the actual measured etch rate increase
by 55%. The slight difference between theoretical
predictions and experimental results could be
attributed to the inadequacy of NMR composition
for factors effecting the etch rate such as exact
quantification of monomers and detailed
description of polymeric structure.

Fig. 3. Polymer design concept.

3.3. Polymer solubility

Previously described decreased solubility of
resin with high O. P. could provoke serious defect
sources during reduced resist consumption (RRC)
or edge bead remover (EBR) processes using
organic solvents. Such sources must be eradicated
so that developed systems could be applied
without any problem and function as BARC. The
compatibility of developed polymers with two
process solvents were investigated via
turbidimetry. As shown in Fig. 5, the turbidity of
mixtures of polymers of interest and solvents was
below the baseline of being transparent when
visually examined. The relatively high turbidity
value of polymer 1 could be attributed to higher
molecular weight of polymer compared to other two.

3.4. Strip test
Complete crosslinking of BARC during the bake step is necessary to minimize its intermixing with photoresist. Developed fast etch rate BARCs (FER BARC), formulated with polymers 1, 2 and 3, showed similar strip loss compared to references as shown in Fig. 6.

3.5. Contact angle results
The incompatibility between photoresist and BARC can cause distortion of resist profiles such as footing, undercut or pattern collapse [1]. Ergo, BARC surface properties were inspected by contact angle measurement. Contact angles of fast etch rate (FER) BARCs were lower than that of the reference. This could be associated to aforementioned increased polarity of polymers coming from higher contents of heteroatoms to maximize etch rate. As shown in Fig. 7, the Polymer 3 with fastest etch rate has lowest contact angle compared to others; nevertheless, such difference is within acceptable range of BARC application based on our experience.

3.6. Lithography performance
Evaluation of lithography performance was carried out as described in section 2.9 (Fig. 8). FER BARC 3, which showed fastest etch rate, showed comparable depth-of-focus (DoF) margin with conventional implant BARC.

4. Conclusion
We have developed the novel BARC system with high etching rate without sacrificing solubility. Two theoretical models of Ohnishi and Hansen solubility parameters were integrated for designing of targeting material – specifically, for pre-screening and selection of monomers. Among developed materials, Polymer 3 showed a faster etch rate by 55% when compared to the conventional KrF implant BARC polymer while retaining its solubility in process solvents. Formulation with selected polymer, FER BARC 3, showed comparable lithography performance to that of conventional KrF implant BARC despite decreased contact angle due to higher polarity. In conclusion, we have developed a novel fast etch rate BARC applicable to ArF lithography. We further expect it to be widely used in advanced node implantation processes.
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