Molecular roughness analysis of developed resist by LER method

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Abstract

In this paper, line edge roughness (LER) analysis on top–down images acquired by means of a scanning electron microscope is here proposed as a powerful and non-invasive technique to map the molecular aggregate distribution in a chemically amplified resist: in particular the periodicity of the aggregates themselves is determined via power spectral density method (PSD). The roughness of two resist developers with different chemical composition will be compared on the base of 1D power spectral density function: in case of SEM acquisition, the profile to be analyzed is extracted from a top–down acquisition, while atomic force microscope (AFM) inspection of surface topography allows to calculate PSD along a user-defined line. The two approaches confirm a reduced surface roughness in case of development with smaller molecule.

Keywords: Line edge roughness; Power spectral density method; Molecular aggregate distribution

1. Introduction

Miniaturization of photonic components, in the quest for nanoscale regime, is a quite demanding issue. In particular, when nanolithography is concerned, simple and non-invasive methods to determine the molecular distribution in resists are appealing. Actually the resist roughness is strongly determined by the distribution of its molecular aggregates. Besides, as device size gets lower and lower, roughness increasingly affects performances in terms of optical propagation losses. The critical dimension of a pattern exposed in a polymeric resin is fastly going below the 157 nm-technological node: therefore the profile roughness is progressively becoming an important part of the tolerance budget on a designed feature size.

Line edge roughness (LER) is the term used to identify the amount of spatial irregularities along the sidewalls of micrometric and sub-micrometric structures. LER is affected by many factors, including the chemical composition of the resist itself and the lithographic process conditions, mainly the development step.

In the present work, LER analysis on a waveguide top–down scanning electron microscope (SEM) image [1–3] is successfully exploited to determine the molecular aggregate periodicity of a developed chemically amplified resist (CAR) by means of the power spectral density approach; the roughness of the resist itself is compared via atomic force microscope (AFM) inspection, in the two cases of typical metal-ion free tetramethylammonium hydroxide (TMAH) – based development and a potassium hydroxide (KOH) solution development. It is shown that the latter approach can improve the roughness statistical parameters, standard deviation above all.

2. LER analysis by power spectral density approach

It is well known that LER can be statistically described in a complete way by using a triplet of parameters: standard deviation takes into account the “vertical” distribution of a real profile, while correlation length and Hurst coefficient are related to the spatial complexity of the profile itself. These parameters can be quantified in the
hypothesis of self-affine profile via two different approaches: the height-to-height correlation function and the power spectral density. In both cases the three parameters can be determined, but PSD function can also offer quite precise information about the profile spatial periodicity, as it is related to its Fourier transform (Fig. 1).

In this paper PSD function of a real waveguide profile obtained after lithographic process will be calculated both by LER analysis of a top-down microscope image and AFM analysis of surface topography. The standard deviation and profile periodicity will be found out in both cases, leading to prefer the SEM-based method as a faster and non-invasive technique.

3. Experimental results

The resist is Sumitomo HN-432, spun on a silicon substrate at 4000 rpm with a 135 nm resulting thickness: it is exposed by means of a 266 nm-direct writing laser with a typical clearing dose of 50 mJ/cm². The post exposure bake step is performed at 96 °C for 60 s, followed by development either in TMAH 2.38% for 35 s or in a 1:2 AZ400K (KOH-based)/DI water solution for 10 s. The structures are straight lines, exposed with half the optimal dose in the samples for AFM inspection (i.e. 25 mJ/cm²) [4]: in such way it is possible to perform the analysis via AFM on the top of the structure instead than on sidewalls, which would require a not so easy and destructive cleaving step.

LER analysis of top-down SEM acquisitions can be usefully exploited to detect and quantify the molecular aggregate distribution in the resist: through pre-processing, quantization and thresholding of a number of acquired images, the distance vectors between real (Fig. 2a, black line) and fitted profile are calculated. The statistical analysis is led on an average distance vector, which represents the systematic contribution. In particular the evaluation of the PSD function (discrete Fourier transform of autocorrelation vector) reveals the existence of periodicities in the real profile. In Fig. 2b, solid curve is related to TMAH case, showing a marked periodicity with a first harmonic spatial frequency $f_1$ at $10^{-1.59}$ nm$^{-1}$ (around 40 nm), while dashed curves are related to KOH development, where only a small overelongation is present. The TMAH curve itself clearly shows also second ($f_2 = 10^{-1.32}$ nm$^{-1}$ ) and...
third harmonic \(f_3 = 10^{-1.08} \text{nm}^{-1}\) related peaks. This characterization confirms the better performance of KOH due to the fact that its low-weight molecule (56.11 g/mol) with a single bond can more easily penetrate into the resist molecular aggregates, breaking their bonds and thus reducing roughness with respect to TMAH. Its molecule is centrosymmetric and its size and weight (91 g/mol) do not allow breaking the resist molecular bonds, leaving a post-development rough surface.

An AFM inspection is usefully exploited to confirm standard deviation values obtained via LER analysis for TMAH developed samples: besides it suggests the presence of similar peaks in PSD function evaluated on a single line of 2D image (Fig. 3).

The AFM acquisitions related to TMAH development (Fig. 4) and KOH one (Fig. 5) validate the stronger roughness in the TMAH case.

The statistical parameters of roughness distribution are reported in Table 1: the performances of both developers are compared with the one of unexposed sample. The standard deviation (Rq) of the distribution is worse after development than in the pre-exposure case (virtually smooth surface, roughness comparable with instrument limits \(1 \text{Å}\)), but TMAH sample roughness is around 3 nm, a factor of three greater than KOH one and confirming the standard deviation values obtained with LER analysis.

4. Conclusions

In this paper roughness analysis of a real waveguide profile in chemically amplified resist has been performed: LER on a top-down scanning electron microscope acquisition showed to be as precise as classical AFM surface investigation, in order to determine standard deviation and profile periodicity. Besides, the use of resist developers with different molecule size, tetramethylammonium hydroxide and potassium hydroxide, helped to bind the origin of the PSD peaks to the periodicity of molecular aggregates in resist: the lighter and smaller molecules of the latter developer can lead to substantially reduced resist roughness in a nanometric regime.

The achieved results point out the role of LER analysis on SEM images as a powerful and non-invasive technique.
to characterize roughness in developed resist on a molecular scale.

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References


Table 1
Roughness statistical parameters before resist-exposure and after TMAH/KOH development

<table>
<thead>
<tr>
<th></th>
<th>Min (nm)</th>
<th>Max (nm)</th>
<th>Mean (nm)</th>
<th>Rpv (nm)</th>
<th>Rq (nm)</th>
<th>Ra (nm)</th>
<th>Rsk (nm)</th>
<th>Rku (nm)</th>
</tr>
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<tbody>
<tr>
<td>Pre exp</td>
<td>1.456</td>
<td>2.33</td>
<td>1.848</td>
<td>0.87</td>
<td>0.17</td>
<td>0.13</td>
<td>−0.01</td>
<td>0.09</td>
</tr>
<tr>
<td>TMAH dev</td>
<td>3.84</td>
<td>17.42</td>
<td>10.50</td>
<td>13.54</td>
<td>3.36</td>
<td>2.85</td>
<td>−0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>KOH dev</td>
<td>2.02</td>
<td>7.09</td>
<td>4.63</td>
<td>5.07</td>
<td>1.18</td>
<td>0.97</td>
<td>0.00</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Rpv = peak-to-valley, Rq = standard deviation of the height value, Ra = average, Rsk = skewness, Rku = kurtosis.