Sub-Millisecond Post Exposure Bake of Chemically Amplified Photoresists by CO$_2$ Laser Spike Annealing

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Abstract:
Pattern formation in a chemically amplified photoresist requires a post-exposure bake (PEB) to catalytically deprotect the polymer. Excessive diffusion of the photogenerated acid results in the loss of line edge definition, blurring of latent images, and changes in the line edge roughness. To optimize the process, we have explored sub-millisecond PEB using a CO$_2$ laser-based scanned annealing system. Several polymer and photoacid generator resist systems were studied under 500 µs laser spike annealing (LSA) at estimated temperatures between 120 and 240°C. All the resist systems exhibit remarkable stability in this time/temperature regime, with the maximum useful temperature limited by thermal deprotection and/or decomposition of the polymer backbone. At lower laser power (temperature), high resolution patterns with sub-100-nm features are formed, comparable to hot plate reference samples. Resist sensitivity is improved significantly for several resist systems (dose to clear is lowered), while other systems exhibit little change in photosensitivity.

Summary of Research:
Chemically amplified resists (CARs) are the current workhorse in lithography for semiconductor device manufacturing because of their high sensitivity and excellent patterning performance. In 1982, Ito, et al., proposed the concept of chemical amplification [1], where irradiation activates photoacid generators and the generated photoacids subsequently catalyze numerous reactions in a resist film before being trapped or quenched. In CARs, acids must be mobile enough within the resist matrix to deprotect sufficient acid-labile protecting groups to achieve the solubility switch in the developing media, but excessive acid diffusion can lead to image blur and loss of resolution. This chemistry occurs during the post-exposure bake, normally done on a hot plate at a temperature of 90-150°C for 30-120 s.

In this work, an alternative post exposure bake (PEB) approach involving higher temperatures for dramatically shorter times has been investigated [2].

Figure 1 displays the chemical structures of resist copolymers and photoacid generators used in this study.

Figure 1: Chemical structures of resist copolymers and photoacid generators used in this study.

With LSA PEB, under DUV exposure at 235-260 nm, up to 3.5 times sensitivity enhancement was achieved for the P(MAdMA-co-GBLMA)/NI-Tf resist system, 0.67 times for ESCAP/NI-Tf, and 3 times for ESCAP/THS, compared to hot plate results. Under 405 nm exposure, up to 5.3 times sensitivity enhancement was achieved for the P(MAdMA-co-GBLMA)/NI-Tf resist system, 3 times for ESCAP/NI-Tf,
and 4.2 times for ESCAP/THS. LSA PEB showed imaging capabilities comparable to hot plate PEB.

In contrast, the commercially available TOK-EUVR P1123 ME resist was also tested at DUV exposure wavelengths. Over a wide range of annealing conditions, the dose to clear showed only small changes and, generally, slightly less sensitivity than hot plate PEB. The sensitivity change in LSA post exposure baked photoresists may be linked to the extremely high thermal ramp rate of LSA (10⁶ K/s, compared to 10 K/s for hot plate) and the extremely short PEB time of LSA (500 µs, compared to 60 sec for hot plate) that can affect the reaction and diffusion kinetics in the photoresists.

To assess the potential for high resolution patterns, electron-beam lithography was done on the TOK resist using Leica VB6. 80 nm 1:1 line/space patterns were achieved for both hot plate (e-beam dose: 17.4 µC/cm²) and LSA PEB (e-beam dose: 43.1 µC/cm²), as shown in Figure 3.

We have demonstrated sub-millisecond LSA as an alternative approach for PEB annealing. In future work, the impact of varying laser anneal dwell time and resist/PAG architecture will be explored. The quantitative determination of acid diffusion rates and activation energies is being carried out using a resist bilayer system (PAG loaded/PAG-free) [3]. Higher resolution imaging and line edge roughness measurement will also be undertaken.

References: