

Direct Measurement of the Reaction Front in Chemically Amplified Photoresists

The semiconductor industry is rapidly approaching the need to fabricate sub-100 nm structures to continue performance increases in integrated circuits. Photolithography remains the enabling technology for the fabrication of integrated circuit patterns. Although industry is able to commercially produce 130 nm features, lithographic materials and processes are not fully available for the production of sub-100 nm structures. New materials must be able to produce structures with dimensional tolerances of 2 nm to 5 nm, dimensions near the size of the polymer chain molecules in the imaging layer.

Current imaging layers, chemically amplified photoresists, are multi-component materials consisting of a polymer resin initially insoluble in an aqueous base developer solution, a photoacid generator (PAG), and other additives. A schematic diagram of the fabrication process and an example structure are shown in Figs. 1 and 2. The patterns are generated in the resist by exposure to UV radiation through a mask. In the exposed areas, the PAG decomposes, forming an acid species. Upon baking, the acid diffuses and catalyzes a deprotection reaction rendering the insoluble resist soluble in a developer. The soluble regions are then removed with the aqueous base developer. Control over this process is dominated by the events in the transitional region between exposed and unexposed areas of the photoresist.

The initial development of chemically amplified photoresists was a key technological breakthrough furthering the continued use of optical photolithography for the

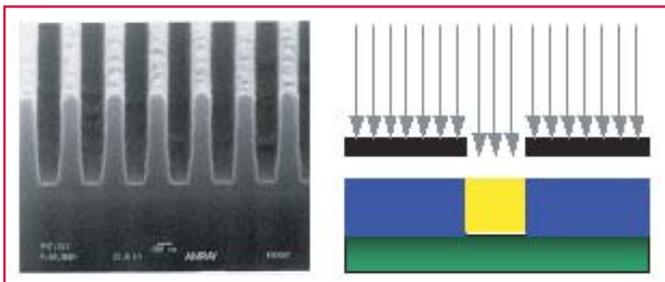


Fig. 1. At left, SEM image of a lithographically fabricated structure with a nominal critical dimension of 150 nm and 300 nm pitch. At right, schematic illustration of patterning through a mask to create the structure.

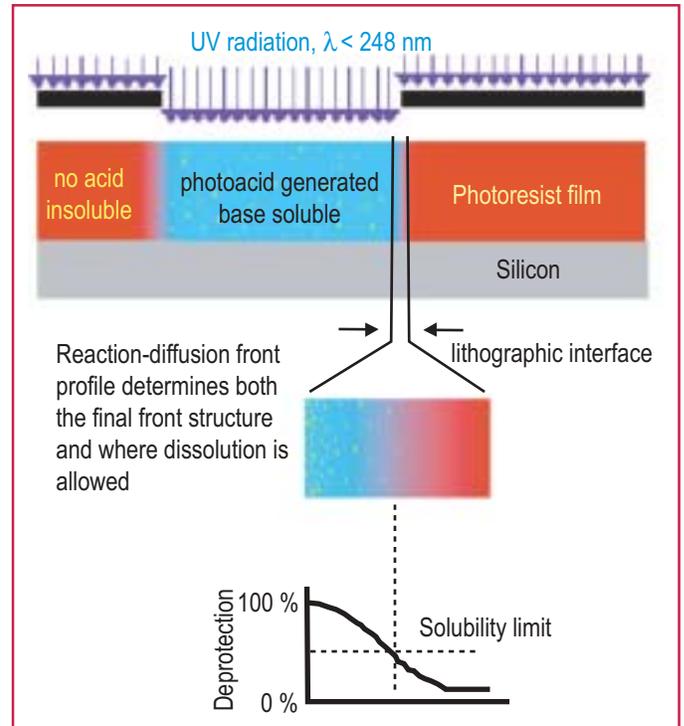


Fig. 2. Schematic diagram of the reaction-diffusion process in chemically amplified photoresists. The transitional region between exposed and unexposed regions is particularly important for critical dimension and roughness control.

fabrication of sub micrometer features. The importance of chemically amplified photoresist concepts is illustrated by the industry-wide use of these materials in the fabrication of state-of-the-art devices today and into the foreseeable future. With the imminent need for sub-100 nm feature

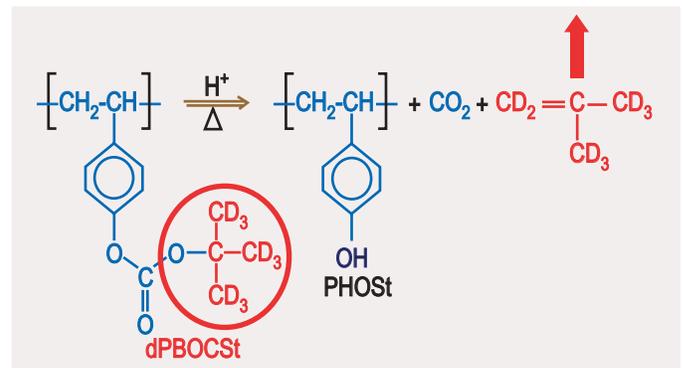


Fig. 3. General deprotection reaction in a chemically amplified photoresist. Deuterated molecular parts with strong contrast to neutrons are shown in red.

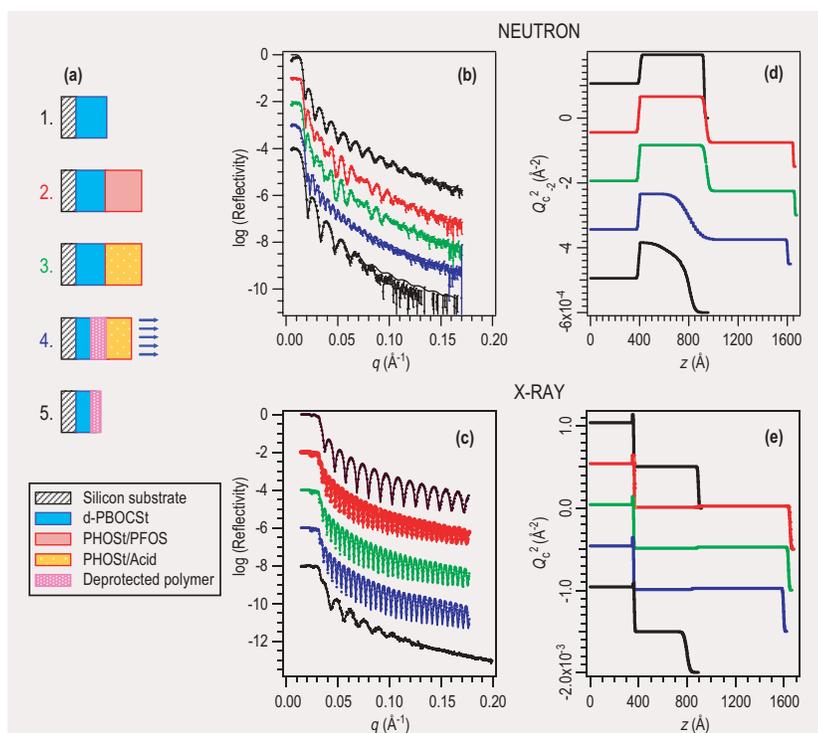


Fig. 4. (a) schematic diagram of the processing steps including the application of each film layer, exposure to UV radiation, a post-exposure bake (PEB) and development. (b) and (d) show the NR data and compositional depth profile and (c) and (e) show the XR data and density depth profiles from each step.

sizes, nanometer level control over the spatial evolution of the deprotection reaction front and the subsequent development steps is needed. The current level of understanding of the acid-catalyzed reaction-diffusion process is not sufficiently detailed to achieve this goal.

To meet the need for spatially detailed data, we have developed, in collaboration with the IBM T. J. Watson Research Center and the University of Texas at Austin, an experimental methodology to directly measure the spatial evolution of the deprotection reaction front through each processing step. By using model photoresist polymers with a deuterated protection group, neutron and x-ray reflectivity (NR, XR) measurements are able to follow the compositional and density profiles of the reaction-diffusion process in an idealized transitional region in a bilayer film stack. Neutron contrast with the reaction is possible because the reaction products involving the deuterated protection group are volatile, as illustrated in Fig. 3.

The NR and XR results from a series of bilayer samples are shown in Fig. 4. NR and XR measurements were taken after each processing step from the spin-coating of each film layer through exposure and bake to the dissolution of the upper layer and any deprotected polymer. The data show that the deprotection reaction front broadens with time within the photoresist. The initial

interfacial width was approximately 4 nm wide whereas the reaction front was nearly 20 nm wide. Upon development, the data show that the developed film remained sharply defined with a surface roughness of approximately 4 nm as well. Although the reaction front was much wider than the final interfacial width, the selectivity of the dissolution process allows for the fabrication of well-defined nanostructures with diffusive transport mechanisms.

The spatial detail afforded by the developed methodology can play an important role in not only the qualitative description of the reaction-diffusion process, but also with the quantitative determination of physical parameters and changes in any physical or chemical properties over the nanometer length scales required for control over the fabrication of sub-100 nm structures. In addition, the strategy developed here is general and can be adapted for the study of candidate photoresist materials being developed for future applications.

“[This work [1]] opens a window of opportunity to construct structure-property relationships between chemical transport mechanisms and ultimate resist resolution. It may also lead to insights into the ultimate, intrinsic resolution limits and critical dimension control of polymer-based imaging materials.” [2]

References:

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