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# Photolithography at the Limits of Optical Resolution

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**Abstract.** The continuous miniaturization in microelectronics requires advanced materials and processes that allow millions of electronic components to be integrated on a single chip of less than 1 cm<sup>2</sup>. The resolution of structures in the half and even quarter micron region is performed by the photolithographic process, *i.e.* the patternwise exposure of light-sensitive photoresist layers that alter solubility in developers when exposed to light. A recently developed bilayer photoresist consists of specifically functionalized anhydride-containing polymers and photoactive dissolution inhibitors. Within the CARL (Chemical Amplification of Resist Lines) process, the anhydride moieties in the resist enable room-temperature silylation with bisamino-siloxanes in aqueous based solvents that enhances oxygen-plasma etch resistance and creates widened structures. Thus, the resolution capability of optical exposure tools can be used to the full extent, and even structures beyond the optical resolution limit become accessible. Copolymerization of maleic anhydride with Boc-maleimide or *tert*-butyl methacrylate yields polymers for highly sensitive acid-catalyzed deep UV resists.

## 1. Introduction

Optical lithography is a key technology for manufacturing microelectronic components, *e.g.* Dynamic Random Access Memories (DRAMs) or Application-Specific Integrated Circuits (ASICs). It creates a steady demand for equipment, materials, and processes that permit the economic production of even finer, and thus more, transistors, capacitors, *etc.* on a single chip. The pace of development thereby is mainly ruled by the current resolution capability of the photolithographic process, *i.e.* the minimum size of an object that can be printed by projection exposure onto a light-sensitive photoresist layer and subsequent development [1][2]. The resist patterns obtained serve as etch resistant masks in wet chemical and plasma etching processes for pattern transfer into different substrates.

According to Eqn. 1, a steady enhancement of Resolution Capability (RC) has been achieved hitherto by continuously reducing the exposure wavelength ( $\lambda$ ) and increasing the Numerical Aperture (NA) of the projection lens system [3][4].

$$RC = \frac{\lambda}{2 NA} \quad (1)$$

$$DOF = \frac{\lambda}{(NA)^2} \quad (2)$$

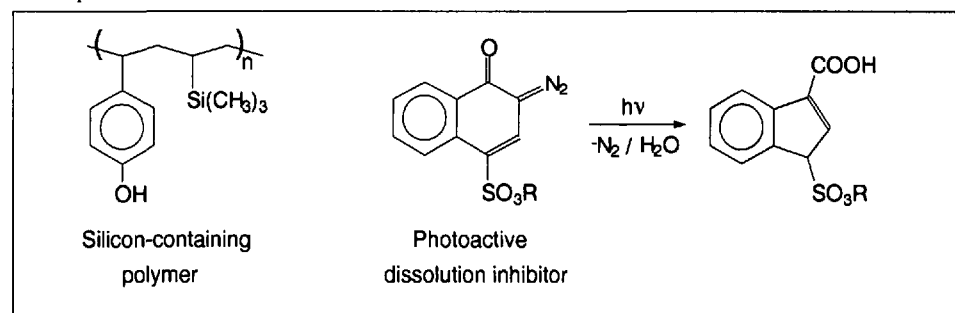
Nowadays, half-micron resolution can be achieved with the use of the 436-nm or 365-nm wavelength ('near-UV'), optics

substrate topography. Additional factors like light-scattering at reflective substrate steps and interference effects during the exposure step also prevent utilization of the full resolution capability of the exposure tool [7][8].

## 2. Bilayer Resist Technique

Among other complex processes that have been developed so far [9] the bilayer resist technique promised to solve these problems by first covering the substrate with a thick opaque organic layer (*e.g.* hardbaked novolac) that planarizes steps and prevents light being reflected from the substrate surface [10][11]. Ideal preconditions are thus created for projection exposure of a thin imaging resist layer ('top resist'). After alkaline development, the resulting highly resolved top resist image is transferred anisotropically into the planarizing layer with Reactive Ion Etching (RIE) in oxygen plasma. Completely new types of resist polymers have to be

Scheme 1. Example of the Composition of a Positive Tone Top Resist Layer [12] Consisting of an Alkaline-Soluble Silicon-Containing Polymer and an Alkaline-Insoluble Photoactive Dissolution Inhibitor. In the presence of environmental humidity, the dissolution inhibitor is converted into indenecarboxylic acid, thus enabling exposed areas to be washed out selectively by an alkaline developer.



with high numerical apertures (NA = 0.5–0.6) and highly advanced, fine-tuned photoresists for microlithography that have been based on novolak resins and diazonaphthoquinone-dissolution inhibitors for some twenty years [5][6]. However, with an increasing resolution capability of the exposure tool the Depth Of Focus (DOF) vanishes in accordance with the laws of physics (Eqn. 2). The new KrF-excimer laser steppers ( $\lambda = 248$  nm, NA = *ca.* 0.5), *e.g.*, allow optical resolution even in the quarter micron domain on the one hand but, on the other hand, they suffer from the small DOF available (*ca.* 1  $\mu$ m). In combination with other disturbing effects, like wafer distortion or field curvature, the *utilizable* depth of focus will be far below 1  $\mu$ m. This prevents a sharply defined and precise optical projection into a photoresist layer, which has to be >1  $\mu$ m due to the erosion of the resist structures during etching processes and due to the

developed for those top resists, which have to contain silicon (Scheme 1). During the etch process, top resist structures are converted to resistant SiO<sub>2</sub> at their surface and thus act as a protective mask. However, a constant reduction of the lateral dimensions of the top resist, and, therefore, also the bottom resist structures, cannot be avoided during the transfer process of the patterns due to sputter attack in the aggressive oxygen plasma [11][12].

## 3. CARL Bilayer Resist Technique

The Chemical Amplification of Resist Lines (CARL) process [13–15] is an in-

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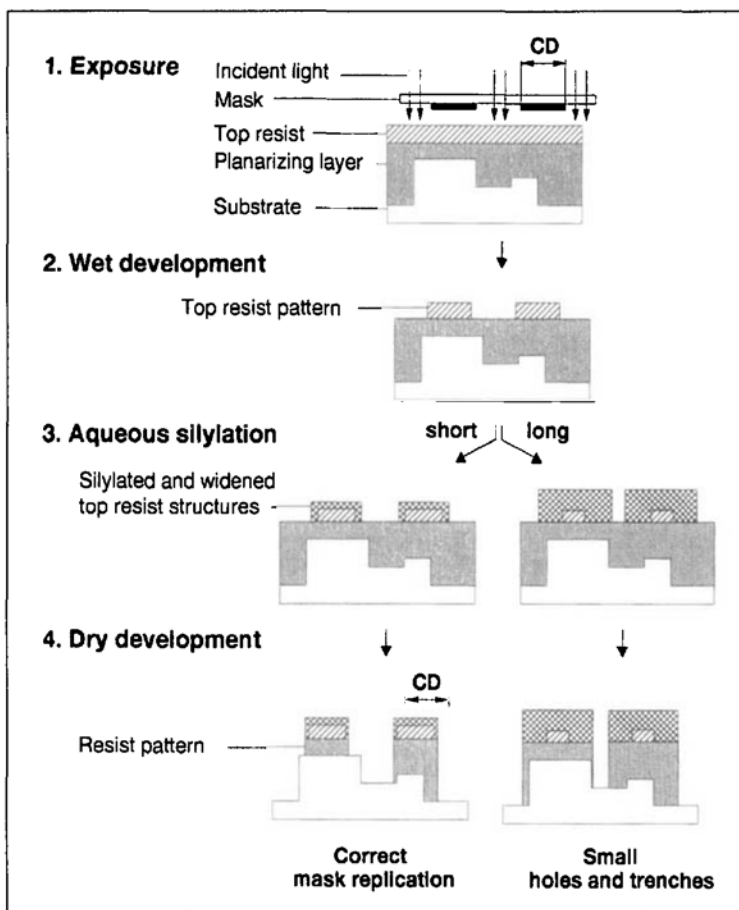
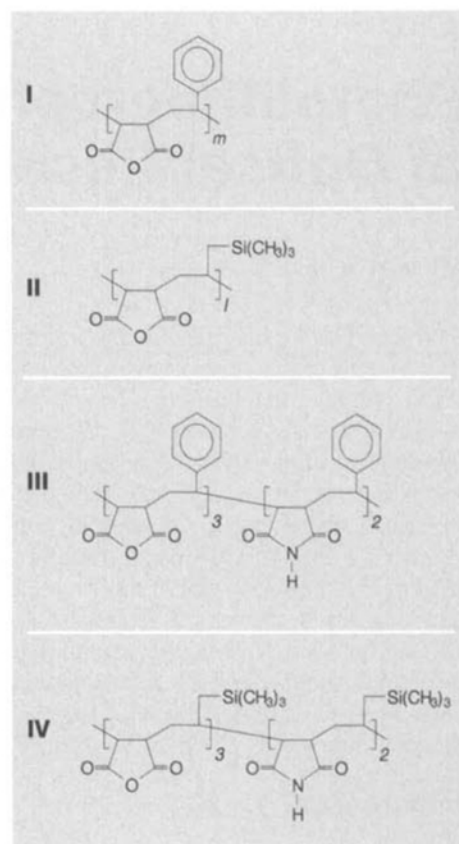


Fig. 1. CARL bilayer resist processing steps. Steps 2 and 3 are performed on a standard puddle development track at room temperature and environmental humidity. Depending on exposure dose and silylation conditions, equal lines and spaces and small isolated trenches can be achieved.

Table. Anhydride-containing Polymers as used in Near UV Top Resists for the CARL Process

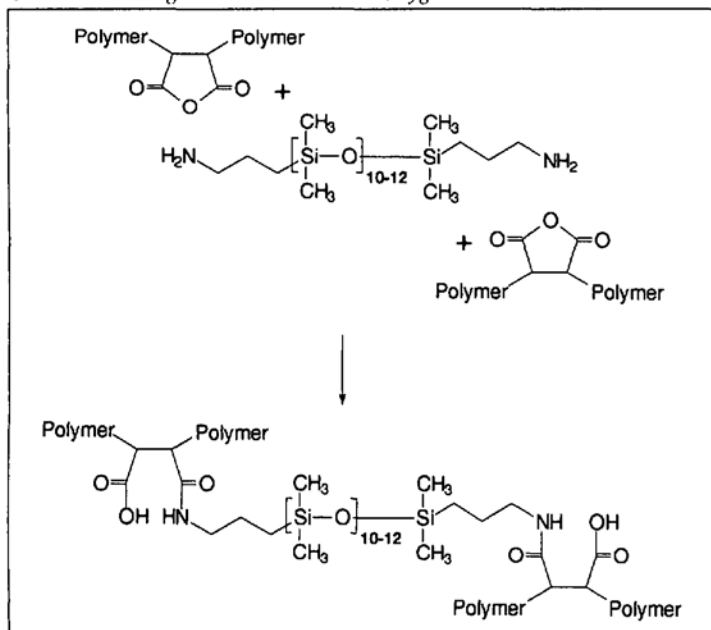


teresting variant of the bilayer resist technique (Fig. 1). In this technique, the resist polymer does not necessarily have to contain silicon. Instead, the alkaline development of top resist patterns is followed by a treatment with a silylating reagent. This causes incorporation of siloxane units into structures necessary for etch resistance to the oxygen plasma and the build-up of a

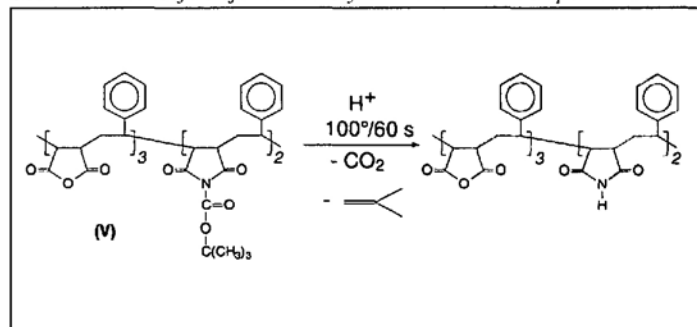
linewidth bias, i.e. the structures are 'chemically expanded'. The latter is needed for compensating the linewidth loss mentioned above and thus enables true-to-size replication of the mask pattern in the planarizing layer. Moreover, this process offers the possibility of narrowing the resist trenches and holes below the resolution limit of the optical equipment used.

The chemistry of the process is based on anhydride-containing resist polymers that provide spontaneous reactivity with primary (and secondary) amines at room temperature. The  $\gamma,\gamma'$ -bis(aminopropyl)-oligodimethylsiloxane that is used as the silylating reagent in aq. alcoholic solution diffuses rapidly into the solid top resist structures and crosslinks polymer chains

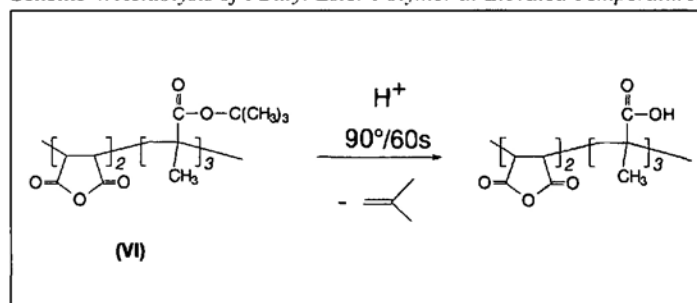
Scheme 2. Reaction of Each Anhydride Group of the Resist Polymer with One Amino Group of  $\gamma,\gamma'$ -Bis(aminopropyl)oligodimethyl-siloxane to an Amide Linkage Results in a Cross-Linked Polymer Matrix with High Silicon Contents and High Etch Resistance to Oxygen Plasma



Scheme 3. Acidolysis of N-Boc-Polymer at Elevated Temperatures



Scheme 4. Acidolysis of t-Butyl Ester Polymer at Elevated Temperatures



during the silylation step (Scheme 2). Thus, highly oxygen-plasma resistant siloxane units are incorporated into the structures, and silicon contents between 19 and 28 wt-% are achieved, depending on the monomeric composition of the anhydride-containing polymer used.

Although the well-known copolymer of maleic anhydride with styrene was applied for first investigations, the selection of other comonomers, e.g. trimethylallylsilane or maleimide, enables polymer properties to be improved with regard to transparency in deep UV, etch resistance, alkaline solubility, and adhesion aspects. Several anhydride-containing polymers (Table), prepared by simple radical copolymerization with azoisobutyronitrile as the starter, were used in resist formulations together with diazonaphthoquinone or  $\alpha$ -diazo- $\beta$ -keto esters as dissolution inhibitors. All of them form clear films on semiconductor substrates and exhibit good performance in near-UV and deep-UV lithography.

A crucial point in the development of a photoresist is its photospeed, since this controls the time that is needed to expose the resist film and thus limits throughput in a production line. Modern KrF-excimer laser exposure tools use the 248-nm deep-UV wavelength and offer high resolution capability. On the other hand, however, they suffer from the small light intensity that reaches the photoresist surface. A reasonable throughput, therefore, requires resists with high deep-UV sensitivity, i.e. exposure doses below 20 mJ/cm<sup>2</sup>.

In order to enhance the deep-UV sensitivity of CARL top resists, the principle of *Chemical Amplification*, that was reported by Ito and Willson [16], was taken as a basis for the design of new polymers bearing not only anhydride moieties but also acid-cleavable groups. After a preparation method for the monomer *N*-Boc-maleimide had been developed [17], it was possible to replace all of the *N*-bound acidic hydrogen in polymer III by Boc groups and thus to produce the completely alkaline insoluble polymer V (Scheme 3). If a resist layer made from this polymer and an *Onium Salt* [18] is patternwise exposed with deep-UV light, a strong acid is formed photochemically from the onium salt in the exposed areas. At elevated temperatures (> 100°), only a small amount of protons is necessary to cleave a multitude of the *N*-bound Boc groups to imide groups in a catalyzed reaction (Scheme 3). Thus, the exposed areas of the resist film become alkaline soluble at a very low exposure dose and a pattern can be generated by alkaline development. According to the results of Ito and Ueda [19], who described the acidolysis of different meth-

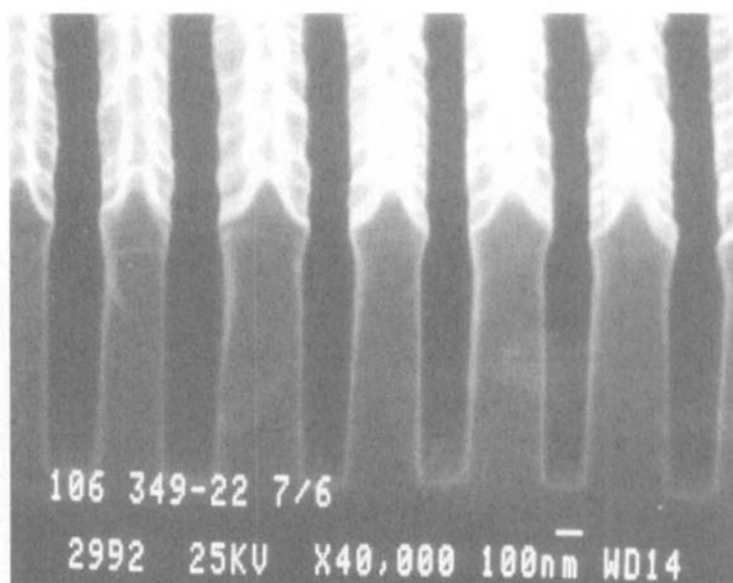


Fig. 2. Resolution of 0.25- $\mu$ m lines and spaces with the use of an acid-catalyzed top resist in the CARL process. The theoretical resolution capability of the exposure tool was 0.33  $\mu$ m.

acrylates, polymer VI (Scheme 4) was prepared from maleic anhydride and *tert*-butyl methac and used for acid-catalyzed imaging resists in the CARL process. Similar to polymer V, this polymer also cleaves at elevated temperatures (> 90°) in the presence of strong acids to form alkaline soluble co-(maleic anhydride/methacrylic acid) (Scheme 4).

For lithographic investigations on a KrF-excimer laser stepper ( $\lambda = 248$  nm; NA=0.37), triphenylsulfonium trifluoromethanesulfonate was used as photoactive acid generator in top resist formulations for the CARL process. As demonstrated in Fig. 2, the theoretical resolution limit of the exposure tool (= 0.33  $\mu$ m, see Eqn. 1) was exceeded with the resolution of 0.25- $\mu$ m line and space patterns.

#### 4. Conclusions

Anhydride-containing polymers are useful as base resins in near-UV- and deep-UV-sensitive top resist layers with high-resolution capability. Aqueous based silylation of resist structures in the CARL process allows simple process integration and offers accurate transfer of the mask pattern into the planarizing layer. The property of maleic anhydride to copolymerize with a variety of comonomers enables easy optimization of the polymer design and thus resist performance. For example, acid-catalyzed and highly deep-UV-sensitive top resists for the CARL process are obtainable by incorporating Boc and *t*-butyl ester groups into the anhydride-containing resist polymers. Thus, highly resolved patterns can be generated at and even beyond the theoretical resolution limit at exposure doses that satisfy future production requirements.

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