Technical Paper

PHOTODECOMPOSABLE BASES: A NOVEL CONCEPT TO STABILIZE CHEMICALLY AMPLIFIED RESISTS

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Standard positive tone chemically amplified resists usually suffer from a latent image instability caused by uncontrolled acid diffusion after their exposure. To improve the delay stability, novel resist additives with both high nucleophilicity and radiation sensitivity have been developed. Typical representatives include onium hydroxides, alkoxides, or carboxylates, which act as strong bases in aqueous media. The compounds decompose into neutral fragments upon exposure but preserve their basic character in the unexposed areas. This enables a selective neutralization of the diffusing acid in areas of intended unexposure. When applied to a chemically amplified resist system the shelf life of the resist solution, the film life stability and the delay time stability are significantly improved, while the photospeed is only marginally deteriorated. Enhanced resolution capability, and improved latitudes are additional benefits.

1. Introduction

Since the late 80's, DUV lithography has developed to a key technology capable of meeting the requirements of quarter micron design rule IC manufacturing, and the immediate demand for production reliable resists has increased considerably. The photoresist industry has res- ponded to these needs and offers a large variety of novel resist materials based on the principle of chemical amplification (CA). Beside a signi- ficantly higher photospeed and thus throughput capability, these materials offer the potential to print critical dimensions down to the subquarter micron region together with practical depth-of-

focus and process latitudes at these pattern dimensions.

However, in order to become production credible materials, several critical performance issues directly linked to the amplification mechanism were to be solved: (1) due to the non-bleaching properties of the resist components, highly transparent materials have to be selected, which make the control of critical dimensions on substrate topography rather difficult unless an antireflective coating layer is employed [1], and (2) most standard positive tone CA materials exhibit a pronounced sensitivity to process interval changes, usually denoted as delay time instability. It is now common knowledge that the photogenerated acid, which induces the differentiation of the latent image in these resist systems may both be trapped by environmental contaminants, and/or evaporate leading to the well known T-topping effect, or may diffuse into unexposed areas to produce time dependant linewidth variations.

Recently, Paniez et al. have found a very elegant solution to solve the latter problem in certain resist systems. They could demonstrate that the major prerequisite for the suppression of interval dependent linewidth changes in chemically amplified resists (CAR) is the elimination of the free resist volume [2]. This may be achieved through the application of a prebake at a temperature equal to, or higher than the glass transi-

tion temperature (T_g) of the respective resist material. As the film softens, the matrix densifies. The resulting solidification of the resist matrix limits the diffusion range of the acid, resulting in a significantly better delay time stable performance.

Although quite efficient, this easy to perform method to stabilize resist lines has some application limits in practical materials: the imaging principle of most chemically amplified resist systems is based on a dissolution rate, and/or a hydrophilicity change due to an acid induced deprotection reaction. Unfortunately, many of the acid labile groups suitable for photoresist applications are also thermally labile. If their thermal decomposition point is lower than, or equal to the glass transition point of the resist mixture, it is not possible to sufficiently reduce the free volume without changing the dissolution rate due to parallel, thermally induced decomposition, or cleavage reactions.

Another method to reduce linewidth variations has been suggested by Roeschert et al. [3]. Their chemistry-based approach uses certain base compounds, typically amines, as resist additives which act as acid scavengers especially for long range diffusing acid molecules. Although this concept improves the delay time stability considerably and offers some additional benefits, as an undesired side effect the resist sensitivity is usually reduced to impractical values thus

lowering the economic throughput advantages characteristic for chemically amplified resists.

Kudo et al. [4] have extended the additive concept to photosensitive compounds. They employed certain basic photosensitive spiropyrane-compounds which rearrange to more acidic derivatives upon irradiation. Although significant improvements of the resist image contrast could be observed, more in-depth investigations revealed that the photochemical quantum yields of acid formation from the spiro-compound were too low to generate the required acid concentration profile.

Furthermore, the use of mixtures of photoacid generators producing acids with different mobilities also resulted in improved resolution and/or depth-of-focus, however, the improvement of the latent image stability was marginal.

Based on the idea of photoinduced, dynamic base consumption an unique concept to reduce the interval-time induced linewidth changes in positive CARs has been developed. It takes advantage of the use of so-called photodecom-

posable bases (PDB), i.e. thermally stable base compounds, which loose their basic properties upon exposure. This paper gives an insight to the chemistry involved and presents its application to a more recently developed positive tone DUV resist system, AZ™ DX 561, indicating the wide applicability and superiority of this concept.

2. Resist Chemistry

The chemistry of Hoechst's three component positive tone chemically amplified resists has been described elsewhere in more detail [5]. As shown in figure 1, the currently developed resist DX 561 contains a PHS-type matrix copolymer, a poly-N,O-acetal as acid sensitive dissolution inhibitor (DI), and a photoacid generator (PAG). The photoacid generator produces a strong sulfonic acid upon exposure, which cleaves the poly-N,O-acetal into its original monomers, namely an alkylsubstiuted benzaldehyde and an aliphatic urethane alcohol. The cleavage reaction leads to the alkali dissolution of the matrix resin
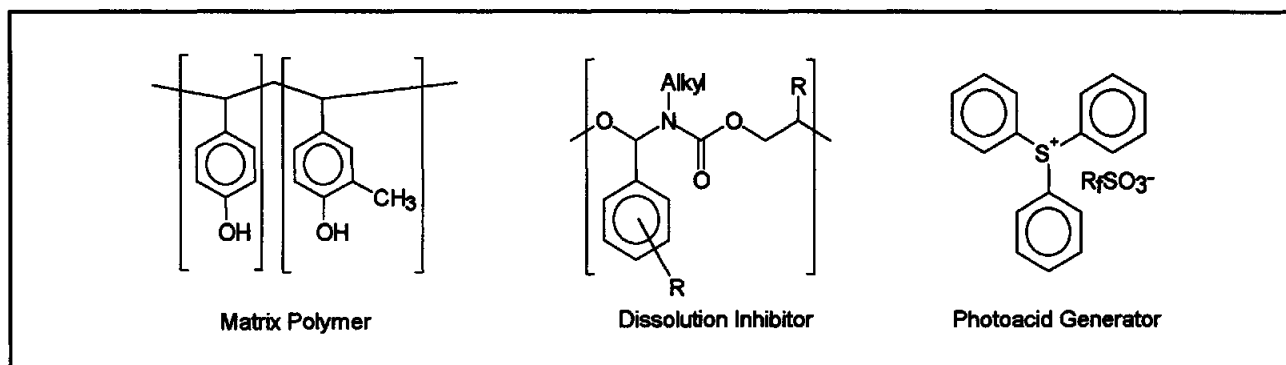

Figure 1: Chemistry of the Acetal Based Resist DX 561

and the cleavage products act as dissolution promoters raising the dissolution rate of the resist from approx. 10 nm/min to more than 15.000 nm/min. The material has been optimized to meet current requirements of the IC manufacturing industry: subquarter micron resolution, adequate depth-of-focus, high photospeed, rectangular pattern profiles and absence of T-tops [6]. However, it was not possible, to implement an adequate delay time stability (> 15 minutes) by sole use of these compounds.

In this particular three component resist system, delay time instability corresponds to higher photosensitivity and linewidth loss with an extended exposure to postexposure bake process interval, and is attributed to uncontrolled acid migration followed by dissolution rate enhancing acetal cleavage reactions. The obvious selection of PAGs generating comparatively bulky, less mobile standard sulphonic acids, such as 2,4,6-triisopropylbenzene sulfonic acid, deteriorated the resist sensitivity and its ultimate resolution capability. The PAG used in DX 561 generates an aliphatic perfluorinated sulfonic acid, which combines high acid strength with reduced mobility. However, irrespective of the size and acid strength of the generated acid significant linewidth changes were observed within few minutes. Therefore, new means to improve the delay time stability were considered. As mentioned before, it was found that the

addition of base compounds, such as amines, to the resist formulation had a positive impact on its delay time stability; as a trade-off, however, a considerable reduction of the photospeed was observed, which made such materials unsuitable for high throughput requirements. A clear breakthrough was achieved, when photodecomposable bases were employed [7]. The photobase concept will be discussed below in more detail.

3. Photobase Concept

The principle idea behind the photobase concept is demonstrated in figure 2. A photodecomposable base, which efficiently decomposes into the corresponding neutral fragments upon exposure, but remains intact in the unexposed areas, is added to the resist formu-
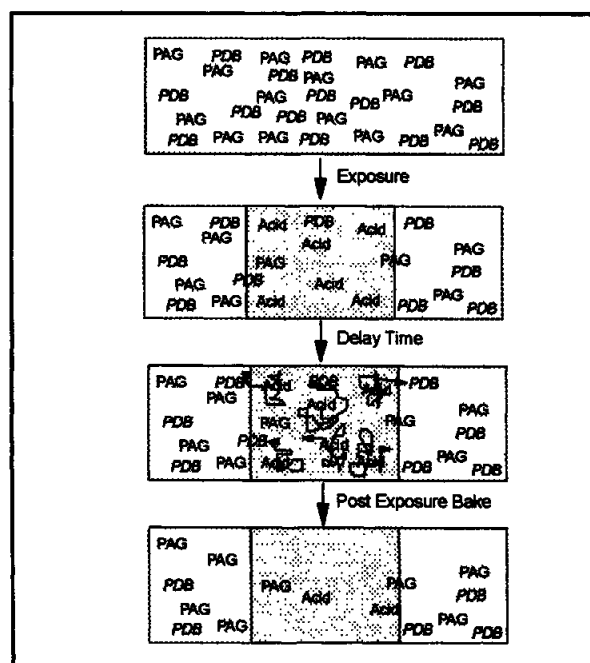

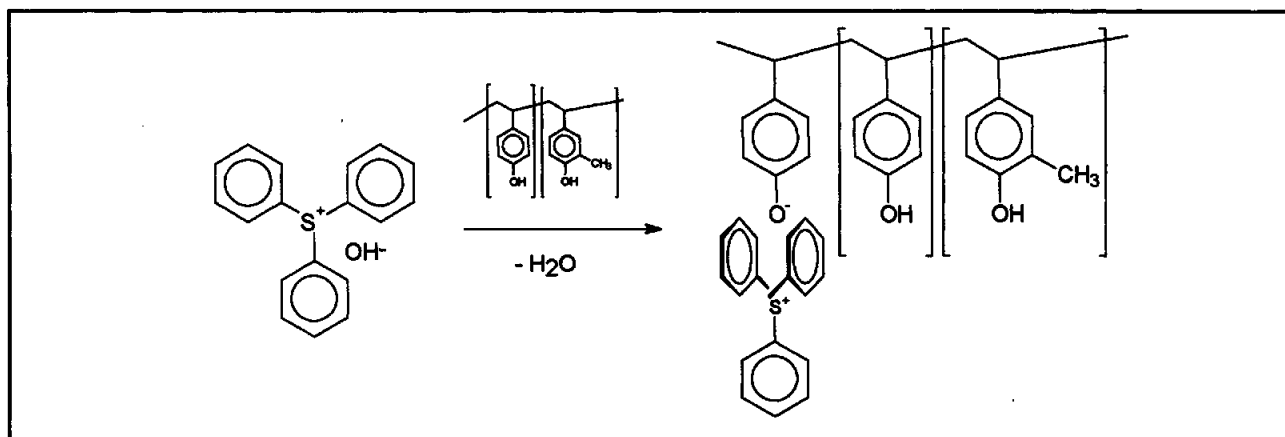**Figure 2**: Schematic Representation of the Photobase Principle

Figure 3: Formation of the Polymeric Photodecomposable Base

lation. The acid released from the PAG in the exposed areas is essentially unaffected, as the base is destroyed. However, when the photo-generated acid molecules diffuse into the unexposed latent image areas, they will be neutralized by the intact base compound.

Although quite a number of suitable PDB materials have been identified and found to be effective, this paper concentrates on the use of a more simple derivative in this series, namely triphenylsulfonium hydroxide (TPSH), as the photodecomposable base. It should be noted, however, that the concept can be easily extended either to substituted sulfonium hydroxides to change the absorption pro-perties, or to other onium compounds, such as iodonium hydroxides, or the like. In addition, a wide variety of anions may find use with similar advantages such as alkoxides, or car-boxylates. The use of sulfonium compounds offer some additional benefits over other

onium compounds, because they are easily prepared, non-hygroscopic and capable to im-prove the lithographic performance of the resist material.

Triphenylsulfonium hydroxide, a strong base, can be synthesized by a metathesis reaction from the corresponding triphenylsulfonium bromide, or sulphonate. The compound is thermally stable, but photochemically highly reactive. When added to the resist solution, TPSH immediately reacts with the active aci-dic hydrogens of the phenolic matrix polymer to form a polymeric ionic photosensitive com-pound, denoted as polymeric photodecom-posable base (PPDB), as shown in figure 3. The fixation of the base moieties to the polymer provides the advantage that this 'in-situ' formed photosensitive base does not migrate within the resist film and base induced diffusion effects are thus negligible. The poly-meric onium compound formed by the
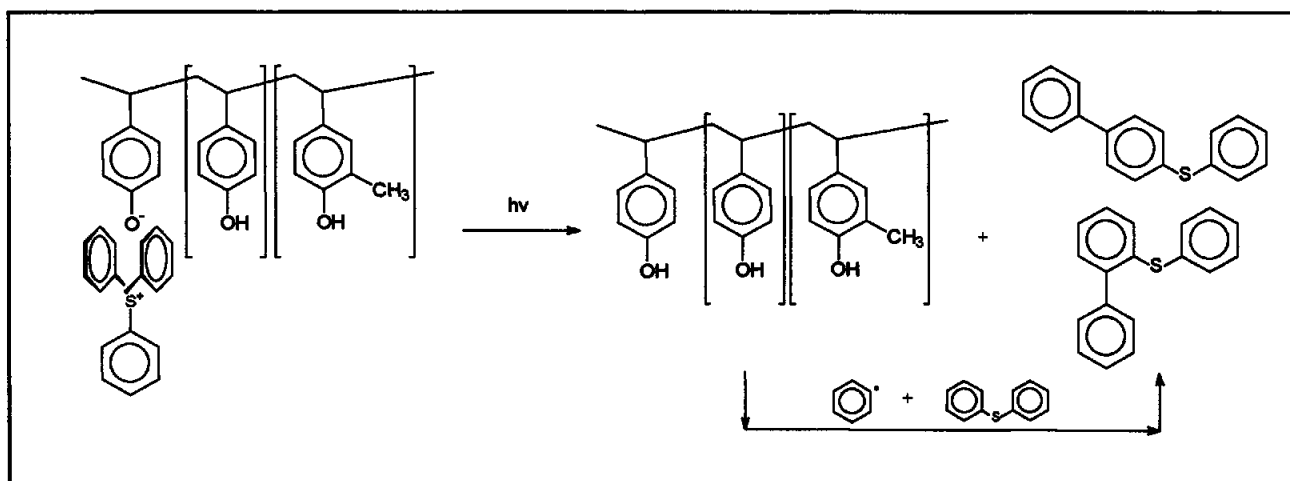
Figure 4: Photoreaction of the Polymeric Photodecomposable Base

reaction with our specific PHS copolymer is stable in standard coating solvents, such as PGMEA, and exhibits excellent film forming properties, as long as less than 5 mol% TPSH are brought to reaction.

In the exposed areas the following mechanism is believed to occur: the PAG produces the respective acid, while the photodecomposable base is fragmented into diphenyl sulfide and a highly reactive phenyl radical (which, according to the literature, may attack the sulfide to form 2- or 4-phenyldiphenyl sulfide), while the

polymeric phenol is regenerated (cf. figure 4). When onium salt based PAGs are employed the photobase destruction and the photoacid generation proceed at almost identical quantum yields. Due to this photochemical synergism high process efficiency even at small base and acid precursor concentrations is guarantied.

In the unexposed areas, no fragmentation of the base polymer occurs, but the acid molecules diffusing from the exposed areas into the unexposed areas are trapped by the PPDB and
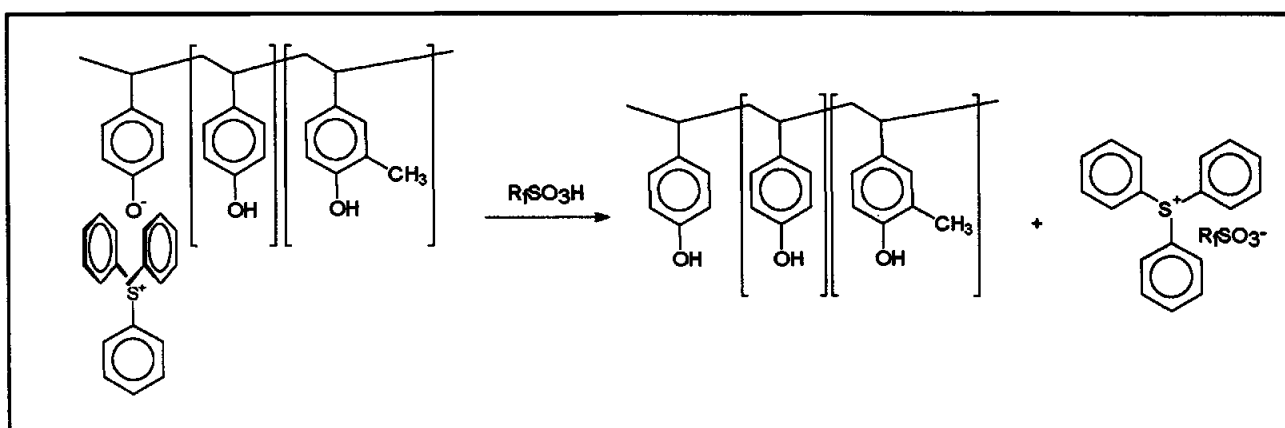

Figure 5: Dark Reaction of the Polymeric Photodecomposable Base

regeneration of the phenolic polymer as well as the respective onium salt occur (figure 5). As net effects, both the catalytic cleavage cycle of acid molecules entering unexposed areas is terminated and the contrast of the resist is enhanced resulting in more delay time stable images and better resolution capability.

To minimize acid loss in the exposed areas and to achieve optimum lithographic performance, the photochemistry of the PAG and the PDB as well as their concentration ratios have to be adjusted; compared to the use of photo inactive amines, the photospeed is much less affected by PDB concentration variations. When other phenolic polymers, e.g. novolaks are used, higher TPSH concentrations may be employed. It should be mentioned that partly protected PHS with acid labile protection groups such as t-BOC-, vinyl alkylether-,

Figure 6: Optical Density (■) and Dissolution Rates (unexposed: ★; exposed 100 mJ/cm²: ◆) of an Experimental Conventional Two Component Resist Based on the PPDB Concept

trimethylsilyl-, tetrahydropyranyl, and t-butyl-acetate, or partly protected carboxylic acid polymers undergo similar reactions without affecting the aforementioned acid-sensitive groups [8].

4. PDB Based Novel Resist Systems

As outlined in the previous chapter, the photodecomposable bases are capable to form polymeric salt-like complexes with phenols which are soluble in standard resist solvents. As mixtures of onium PAGs inhibit phenol type resins [9], it was investigated if the PDB reacted copolymer exhibits a sufficiently high dissolution inhibition towards alkaline developers. Upon exposure, as the main photoproducts the deprotected alkali-soluble resin and onium salt related photoproducts with nearly no dissolution inhibition capability should be formed. Therefore, it was expected that the PDB may act as a photosensitive protecting group in a novel non-chemically amplified positive tone resist system. Figure 6 summarizes the results of our investigation. With the addition of TPSH to the selected resin, a copolymer composed from 66 mol% 3-methyl-4-hydroxystyrene and 34 mol% 4-hydroxystyrene with a dissolution rate of approx. 650 nm/min in 2.38% TMAH, the optical density at 248 nm increases linear from approx. 0.2 μm⁻¹ for the pure polymer to 0.8
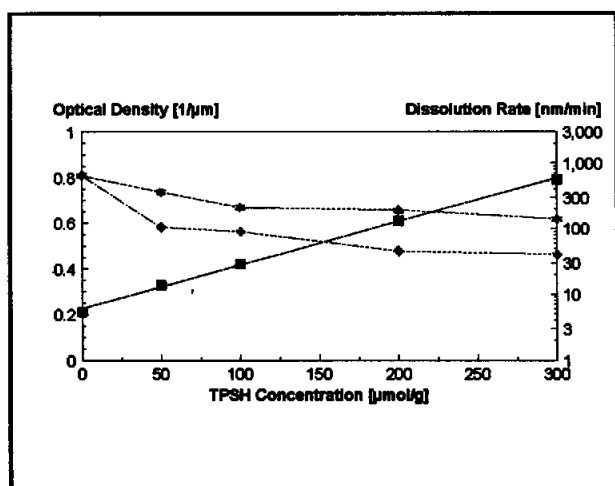
μm^{-1} at a loading of 300 μmol TPSH per g polymer. At the same loading, the dark erosion of the copolymer is decreased to approx. 40 nm/min. When exposed (100 mJ/cm^2), the dissolution rate increases to approx. 105 nm/min. Thus, optical density, dark erosion, dissolution promotion upon exposure, and contrast are insufficient to provide an adequately performing DUV resist on this basis.

With the selection of different polymer types, or through changes of the development conditions, i.e. the application of more diluted developers, some improvements were achieved with respect to the contrast. However, in these cases the high optical density of the resulting films prohibited the formation of high resolution patterns competitive to current state-of-the-art results.

5. Lithographic Performance of DX 561

Figure 7 depicts the calculated and experimental swing curves of DX 561, a CAR which incorporates the features discussed in the previous chapters, for 0.35 μm, 0.30 μm and 0.25 μm lines and spaces. Compared with other DUV resists the swing curve amplitude of DX 561 is rather small (75 nm) suggesting superior linewidth control on reflective and/or topographic substrates. The PAG/PDB ratio is approx. 1:1 in DX 561. The resulting resist
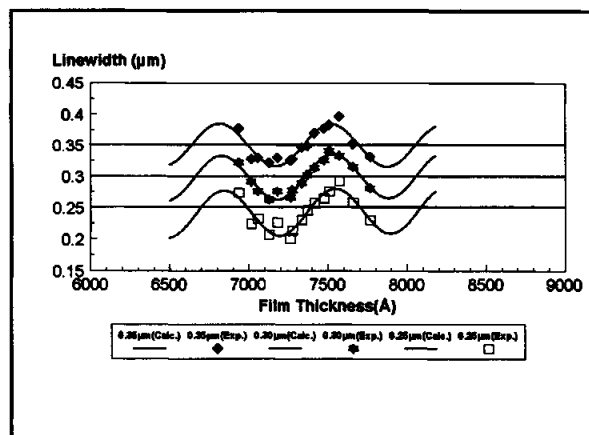

Figure 7: Swing Curve of DX 561. Exposure Dose: 35 mJ/cm^2. Standard Process.

absorbance, which is mainly determined by the PAG/PDB concentration, is in the range approx. 0.39 μm^{-1}. However, the optical density can be varied roughly between 0.25 - 0.55 μm^{-1} by changing the PAG concentration at constant PAG/PDB ratio without detectable deterioration of the photospeed or other relevant lithographic performance properties.

Depending on the PAG/PDB loading, the dark erosion of the resist material is in the range of 6 - 10 nm/min.

The standard processing of DX 561 includes a prebake of 130°C/60 sec, followed by DUV exposure and a post exposure bake at 55°C/90 sec. The low PEB temperature reflects the tendency of the acetal cleavage products, i.e. aromatic aldehydes, to crosslink at higher PEB temperatures. Development is achieved using a standard 2.38% TMAH developer for 60 sec without additive in the puddle mode.

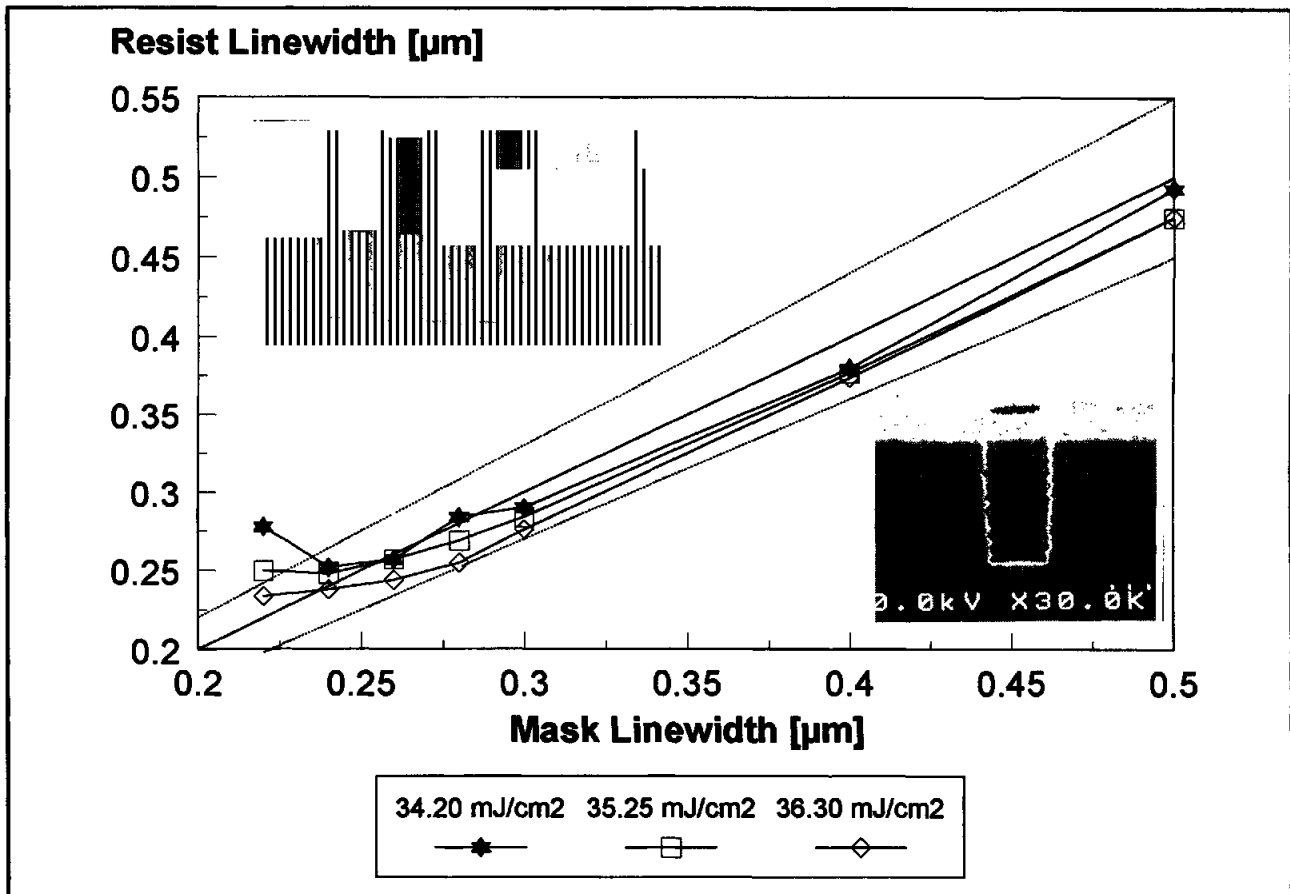Using a dose of approx. 40 mJ/cm^2, an

Figure 8: Linearity Curves of DX 561. SEM Pictures show 0.2 μm L&S (Dose: 40 mJ/cm², left) and 0.3 μm C/H (Dose: 56 mJ/cm², right).

ultimate resolution for long lines & spaces down to 0.2 μm, and for contact holes down to 0.3 μm (NA = 0.55, both minimum feature sizes on the mask) can be achieved at 0.71 μm film thickness (figure 8). The linearity is down to approx. 0.23 - 0.22 μm. Bright field and dark field pattern can be printed at the same dose. For 1.0 μm resist film thickness an ultimate resolution of 0.22 μm has been achieved; due to the high aspect ratio > 4.0 a noticeable line collapse tendency is observed at structures smaller than 0.24 μm.

A quite acceptable DOF of > 1.0 micron at

0.24 μm L&S resolution (NA = 0.55) is obtained on bare silicon at a film thickness of 710 nm, while the 0.3 μm C/H exhibit a DOF of 0.9 μm.

The delay time stability has been improved to > 30 minutes for > 0.22 μm structures (figure 9), indicating that some other effects might also contribute to the delay time instability of this particular resist system.

The thermal tests indicate that pattern rounding and profile deformation of the material occurs above 130°C for both small
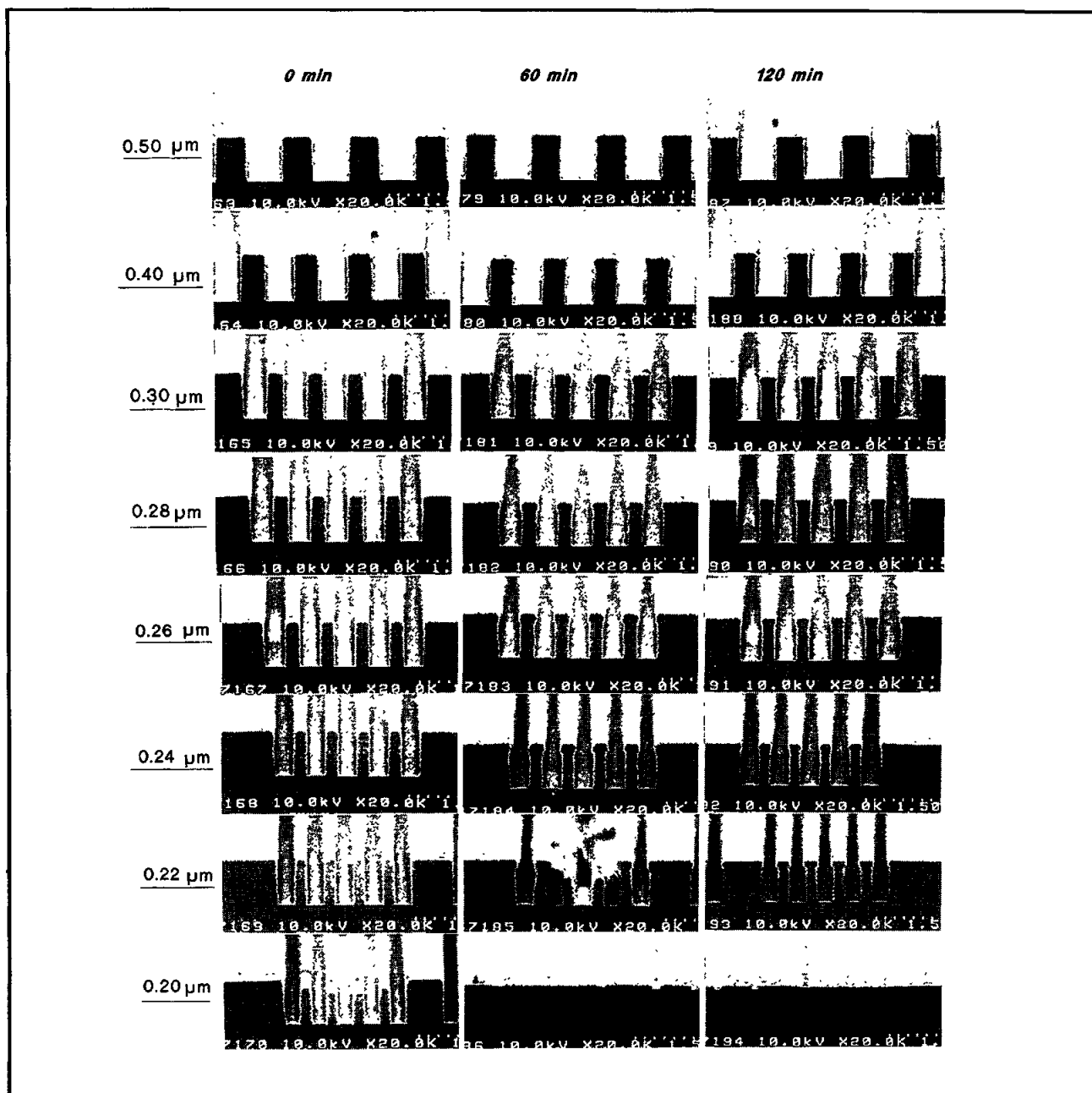
Figure 9: Delay Time Behavior of DX 561.

and large structures. The thermal stability of DX 561 can be further increased through the application of a DUV curing process.

6. Conclusions

The new concept of a photodecomposable base has been incorporated into our three component acetal based deep UV positive resist. The photobase concept is neither restricted to TPSH-type photosensitive bases, nor limited to acetal based resist materials. It is of high universality and utility for

delay time stability and the lithographic performance of the resist material.

7. Bibliography

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