

REGIONAL TECHNICAL CONFERENCE

**PHOTOPOLYMERS:  
PRINCIPLES,  
PROCESSES & MATERIALS**

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**"PHOTOPOLYMERS: PRINCIPLES, PROCESSES AND MATERIALS**

**Regional Technical Conference  
Sponsored by the  
Mid-Hudson Section  
Society of Plastics Engineers, Inc.  
October 10, 12, 1979**

# "PHOTOPOLYMERS: PRINCIPLES, PROCESSES AND MATERIALS"

## Regional Technical Conference

Sponsored by the

Society of Plastics Engineers, Inc. Mid-Hudson Section

The Nevele Country Club

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ABSTRACT  
OPTICAL IMAGING FOR SEMICONDUCTOR DEVICE  
FABRICATION : PAST, PRESENT, AND FUTURE

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A brief history of optical imaging for semiconductor fabrication is presented. The technical and economic factors that have helped create today's optical imaging technology are reviewed with respect to their impact on future needs. Projections on the use and direction of optical imaging equipment are made, with special emphasis on economic impact. Major areas discussed are contact, proximity, and projection printing. Various types of equipment are reviewed in terms of their relative contribution to the advancement of optical imaging. More recent developments in step-and-repeat projection and Deep UV projection imaging are explored. The gap between optical and non-optical imaging is discussed again from an economic and technological viewpoint. In this area, X-rays and E-beam technologies will be compared to optical imaging systems, and an attempt to show overlap and specific end use areas will be made.

Conclusions about the future of optical imaging for semiconductor fabrication will be made in the form of five year projections by market segment, percentage usage, system cost and resolution requirements.



# RECENT ADVANCES IN THE PHOTODECOMPOSITION MECHANISMS OF DIAZO-OXIDES\*

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**ABSTRACT:** In 1902, Wölff proposed a mechanism to explain the formation of carboxylic acids from diazo-oxides, Süss in 1944 invoked this same mechanism for the formation of indene carboxylic acid from diazo-oxides. Since these materials are currently used in the well known class of AZ photoresists, the Süss mechanism has been referred to many times to explain the positive working nature of the photoresists. In spite of the widespread use and industrial importance of the AZ resists, the validity of the Süss mechanism had not been unequivocally demonstrated to any degree of satisfaction. For these reasons, photochemical studies were initiated to establish the following:

- 1) Obtain direct spectroscopic evidence for ketene intermediates in the Wölff Rearrangement of diazo-oxides.
- 2) Determine the reactivity of the ketene towards water and hydroxyl containing organic compounds.
- 3) Determine the reactivity of the ketene in the AZ resists.

Fundamental photochemical decomposition mechanisms have been established for the AZ-type photoresists; these and recent theoretical results on the Wölff rearrangement are used to convey the technological implications of the studies.

\*Material presented in part in IBM Journal of Research and Development 23, 42 (1979).



## INTRODUCTION

The use of radiation-sensitive organic monomeric and polymeric compounds (resists) as the imaging layer in the manufacture of high-density electronic circuits has become a standard feature of microlithographic processing in the electronics industry (1). The imaging mechanism results from radiation-induced chemical changes in the resist material, which render the "exposed" resist either more (positive resist) or less (negative resist) soluble than the unexposed resist. The resultant differential solubility then gives rise to image formation when the resist is treated with an appropriate solvent. As is obvious from these remarks, the development of new resist materials requires a basic understanding of the chemical changes that lead to image formation. In this regard, we herein report results on the photodegradation mechanism of the widely used AZ class of photoresists. These positive photoresists consist of mixtures of substituted o-naphthoquinonediazides (diazo-oxides), the photoactive compounds (PAC), in Novolak-type resins. This formulation is the basis for the AZ-1350J (trademark of the Shipley Co., Newton, MA 02162) photoresist, which is composed primarily of the PAC (Structure I) in a phenolic resin (II) as shown in Figure 1.

Imaginary results from UV exposure of the resist in the desired areas to activate a UV-induced transformation of the PAC to a base-soluble material. The base-soluble material has been presumed to be an indenecarboxylic acid that is formed from a reactive ketene intermediate generated by the UV exposure. This mechanism, due to Süss (2), is shown in Figure 2. Süss found that irradiation of the diazo-oxide in acidified

aqueous solution produced 1-indenecarboxylic acid (see Figure 2). On this basis, a ketene intermediate was proposed since the reaction scheme was in accordance with the finding by Wölff (3) that diazo-oxides can undergo ring contractions via ketene intermediates to ultimately form carboxylic acids. The structure proof for the 1-indenecarboxylic acid was based on the synthetic preparation by Weissgerber (4). In addition, Süss found that the acid decarboxylated at the boiling point of water.

Questions concerning the applicability of the Süss mechanism to the action of the o-naphthoquinonediazide as a component of a resist system arise because the compound exists in a much drier, immobile environment (i.e., coated on a Si wafer) as opposed to the acidified aqueous medium used by Süss. Under the drier resist conditions, the reaction of ketene with the phenolic OH group of the resin may compete favorably with the water present, thus yielding ester as well as acid. In addition, the studies of Melera et al. (5) have shown that the preparation of indenecarboxylic acid via the method of Weissgerber produces the 3-indenecarboxylic acid (III) as shown in Figure 3, not the 1-indenecarboxylic acid (IV). Thus, the exact nature of both the initial and final reaction products in the Süss mechanism has not been determined with certainty. However, before discussing the Süss mechanism, it is important to air the salient features of the Wölff rearrangement. This is particularly important here because the Süss mechanism is in essence a Wölff rearrangement.



## THEORETICAL RESULTS ON THE WÖLFF REARRANGEMENT

The simplest case of a photochemical Wölf rearrangement shown in Figure 4, is for the conversion of diazoethanone (V) to ketene (VIII). Large scale CI calculations were initiated by M. Yoshimine (6) in order to investigate the role played by the important formylcarbene (VI) oxirene (VII) intermediates. Their role is clearly demonstrated in Figure 5 where an energy diagram is shown for the Wölf rearrangement on singlet and triplet energy surfaces. Two very important generalizations may be formed as a result of Yoshimine's extensive CI calculations: The first is that the Wölf rearrangement is energetically a downhill, unimpeded process on the singlet energy surface; the second is that due to the very high barrier for the conversion of triplet formylcarbene to triplet ketene, the efficiency of the Wölf rearrangement is dramatically reduced on triplet energy surfaces. As a consequence of the theoretical results presented here, photochemical decomposition of diazo-oxides should always be performed on singlet energy surfaces in order to maximize the yield of ketene. Photochemistry resulting from say the addition of triplet sensitizers decreases the ketene yield because the triplet carbene may undergo other chemistry during the time it takes for it to cross over the large barrier to triplet ketene.

## EXPERIMENTAL SUPPORT FOR THE S<sub>1</sub>S MECHANISM

Low temperature infrared spectroscopic studies (7) were performed in order to establish that a photoactive compound such as PAC (I) photochemically decomposed to form a ketene. In Figure 6 the infrared spectrum of PAC (I) is shown at 77K. The infrared spectrum after exposure

to UV light ( $\lambda > 3600\text{\AA}$ ) given in Figure 7 has been shown (7,8) to be the expected ketene by spectroscopic analysis and by comparison of the spectra and physical properties of the ester formed by trapping the ketene with 2,3,6-trimethyl phenol and methanol.

Subsequently, it was shown (8) that the ketene reacted with water to ultimately form a 3-indenecarboxylic acid. This was accomplished by both spectroscopic analysis (IR,  $C^{13}$  NMR) and by chemical preparation of authentic samples of the 3-indene acid (7). In Figure 8 the infrared spectrum of PAC (I) is shown after complete photo-conversion with UV light ( $\lambda > 3600$ ). The infrared spectrum in Figure 8 is that for the 3-indenecarboxylic acid derivative. Furthermore, exposure of mixtures of PAC (I) and resin (II) to UV light in air always produced a 3-indenecarboxylic acid. Exposure of the same mixtures under high vacuum conditions always produced the infrared spectrum of the phenyl ester of the indenecarboxylic acid (see Figure 9). This latter result is expected because ketenes rapidly react with hydroxyl groups, and as a consequence of this, the presence of a ketene in a reaction is generally tested for by performing exposures in the presence of alcohols to induce ester formation. The unexpected feature for the resist photolysis, as mimicked by the PAC (I), resin (II) exposures, is that the ketene reacts with water to form carboxylic acid rather than the -OH groups of the resin. Recent studies (9) have indicated that the water in the resin is hydrogen bonded to the hydroxyl groups of the resin and thus, difficult to remove. A reasonable, explanation for the difference in the air-vacuum photoproducts for the resist exposures, illustrated in Figure 10, is that water molecules



hydrogen bond to the hydroxyl groups and so protect the resin from reaction with the ketene during irradiations under ambient conditions. The water molecules are removed under high vacuum conditions, and, as a consequence, the ketene has no choice but to react with the hydroxyl groups of the resin.

#### SUMMARY AND TECHNOLOGICAL IMPLICATIONS

The photochemical studies reported thus far reveal that the S<sub>0</sub>S mechanism is indeed operative in AZ-type resists. The theoretical results imply that in order for this mechanism to operate efficiently photochemistry should always be induced on singlet energy surfaces. In other words, exposures that excite singlet energy surfaces maximize the yield of ketene, which in turn produces an indenecarboxylic acid. If we associate, in some manner, the speed of a photoresist with the concentration of the indenecarboxylic acid produced, then faster resists should be obtained by careful design of diazo compounds and control of the conditions of the irradiation, e.g., the removal of triplet sensitizers.

In Figure 11 the results for AZ systems are summarized in three photochemical pathways (circled numbers). The first, not encountered in normal photoresist use, demonstrates that a ketene is the important intermediate in the photoreaction. The ketene does not react with the resin at low temperatures, but does react rapidly with resin to form a carboxylic acid ester when warmed to room temperature under vacuum.

The second and third pathways are very important for photoresist technology. These demonstrate the very important role assumed by the atmosphere during the exposure. Under vacuum, room-temperature irradiation produces an ester via a ketene-phenolic OH reaction. When R contains one or more additional orthonaphthoquinonediazide moieties (as in AZ-1350J photoresist), crosslinking of the resin can occur, and in effect a negative resist is produced.

Irradiation of the resist in air (Pathway 3) produces a 3-indenecarboxylic acid via a ketene-water reaction. The contrast between the two pathways is striking and, in our studies no ester could be detected when exposures were performed in air. The acid formation readily explains the positive working nature of photoresists under these conditions, since the acid can be solubilized as the salt in the basic developer. These exposed regions dissolve at a higher rate than unexposed regions, forming a positive image.

The mechanism in Figure 11 explains not only the usual positive working nature of AZ-1350J resist but also how the resist may function as "both a positive and a negative resist" when the same developer is used. For example, exposures have been performed in vacuum through a mask. This process crosslinks the resin when the PAC contains more than one diazo group. The vacuum exposure is subsequently followed by a flood exposure in air with the mask removed. This process induces acid formation in the previously unexposed areas. The image, a negative one in this case, may



be developed either in an aqueous basic solution, or in an organic solvent, depending on the particular application.

In fact the technological implications of the basic photochemical mechanisms are much broader than described in Figure 11 and, in Figure 12 is a generalization of the photochemical mechanisms that provides a basis and rationale for the synthesis of a large number of materials for lithographic applications. There it is shown that any diazo-oxide, which undergoes a S<sub>is</sub> type mechanism, may be mixed into a polymeric material containing a functional group X. The group X in turn may react with the photochemically generated ketene under vacuum conditions and thus the mixture may function as both a negative and positive resist. The breadth of the generalizations stated in Figure 12 is in part based on the wealth of knowledge on the photochemical Wölff rearrangement (10) and the reactivity of ketenes (11) already present in the literature. In addition, besides our studies on the AZ system presented here, we have shown (12,13) that other polymeric systems containing -OH, -CO<sub>2</sub>H, and -NHR groups also display the type of photochemistry described in Figure 12. In summary, the photochemical studies summarized in Figure 12 provide a basis for the design of lithographic materials with a variety of chemical and physical properties.

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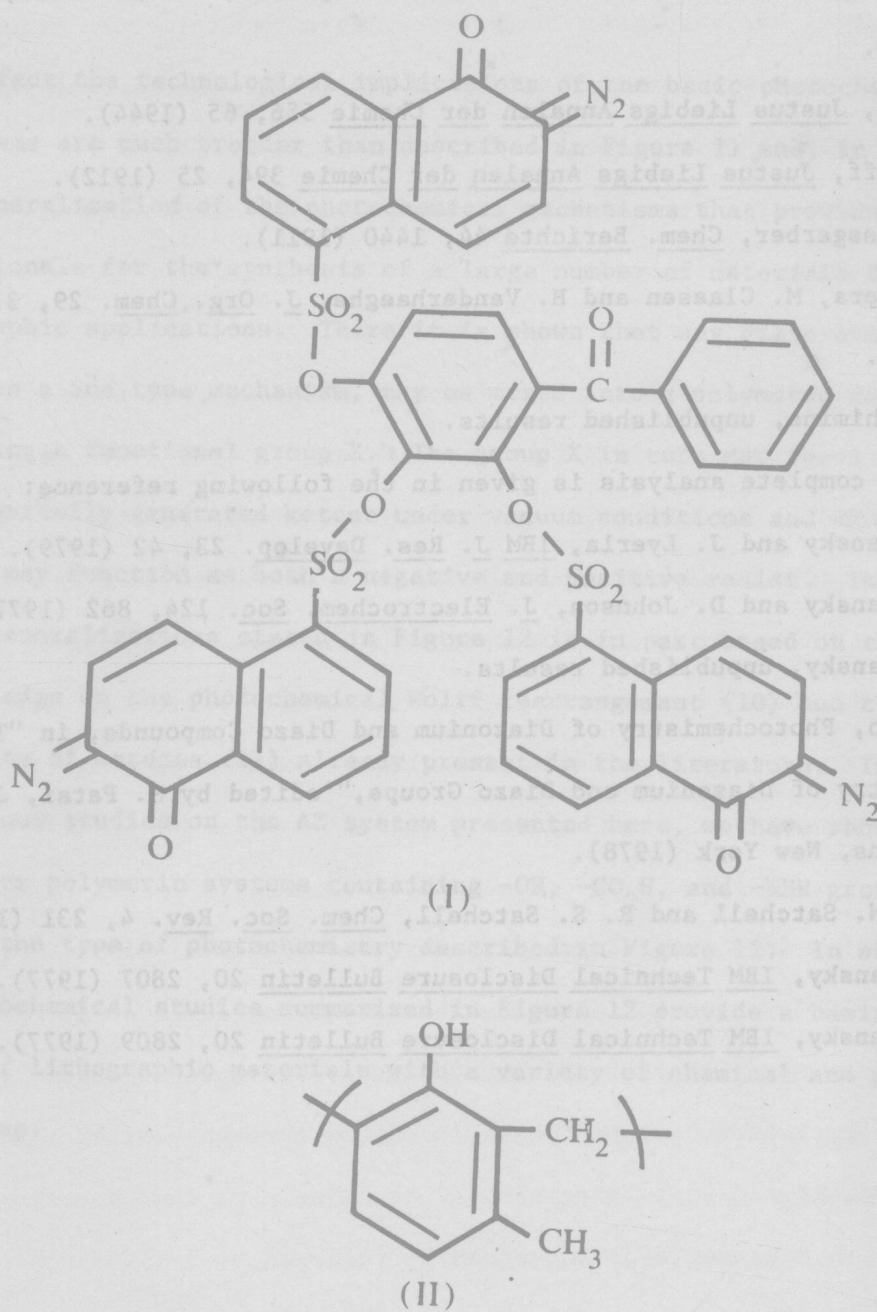


Figure 1. Typical formulation for the AZ-type photoresists. The formulations usually vary for the most part in the structure of the photo-active compound (I).