

# PROCEEDINGS

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Volume 771

## **Advances in Resist Technology and Processing IV**

**Murrae J. Bowden**  
Chair/Editor

*Sponsored by*  
SPIE—The International Society for Optical Engineering

**2-3 March 1987**  
**Santa Clara, California**

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Volume 771

# Advances in Resist Technology and Processing IV

Murrae J. Bowden  
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*ADVANCES IN RESIST TECHNOLOGY AND PROCESSING IV*

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## INTRODUCTION

This issue of the proceedings contains all but one of the papers presented at the conference on Advances in Resist Technology and Processing, held 2–3 March as part of SPIE's 1987 Santa Clara Symposium on Microlithography, 1–6 March 1987. This conference is the fourth in the highly successful series of annual conferences on this subject. The principal themes of this meeting were chemistry and physics of resist processing; new resist materials for photo, electron-beam, x-ray, and ion-beam lithography; materials and processes for multilayer resist technology; and exposure and development modeling. These themes were presented in four oral sessions dealing with resist materials, resist processing from both the chemical and processing points of view, and advanced materials and processes. The conference concluded with a poster session covering all themes.

We are approaching the dawn of submicron device lithography, and this places numerous constraints on hardware design, resist chemistry, and processing technology. The purpose of this conference is to emphasize recent advances in the science and engineering of high-resolution resist materials and processing. It is interesting, in this regard, that the bulk of the papers presented deal with "old" technology, namely, positive photoresist chemistry and processing based on the dissolution inhibition of novolac matrices by naphthoquinone diazides. In spite of the fact that resists based on this chemistry have been used for over 30 years, we are only just now learning to design them at the molecular level, thereby gaining insight into their mode of operation. The trend toward multilayer processing continues and several papers deal with organometallic resist systems specifically designed to withstand reactive-ion etching. There is considerable interest, for example, in gas-phase silylation as a means of achieving all-dry processing. Interestingly, in spite of rapid advances in the development of laser systems for deep-UV lithography, only one paper was presented that revealed a novel resist structure specifically designed for 250-nm exposure.

Judging from the attendance at the meeting and the uniform high quality of the papers in both the oral and poster sessions, the conference was extremely successful. For this, I sincerely acknowledge the capable assistance of my cochairs, Daryl Ann Doane (DAD Technologies, Inc.), Scott A. MacDonald (IBM/Almaden Research Center), Toshiaki Tamamura (NTT Corp.), and S. Richard Turner (Eastman Kodak Co.) in soliciting papers and serving on the program selection committee. I would also like to thank Lois Damick of Bell Communications Research for handling many of the administrative tasks associated with organizing the technical program. Finally, I would like to thank the staff of SPIE, without whose dedication this conference would not have taken place.

**Murrae J. Bowden**

Bell Communications Research, Inc.

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*ADVANCES IN RESIST TECHNOLOGY AND PROCESSING IV*

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**Session 1**

**Resist Materials**

*Chair*

**Murrae J. Bowden**

Bell Communications Research, Inc.



# NEW DIAZOKETONE DISSOLUTION INHIBITORS FOR DEEP U.V. PHOTOLITHOGRAPHY

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## Abstract

The results of studies directed toward the design of diazoketone dissolution inhibitors for deep U.V. photolithography are described. This work has identified a useful chromophore, the 1,3-diacyl-2-diazo linkage which has the requisite spectral characteristics for use in the deep UV. Incorporation of appropriate hetero-atoms into the structure has allowed synthesis of analogs that survive common processing sequences. A detailed study of the photochemistry of these analogs led to an understanding of the importance of the stability of the ketene photoproduct on resist contrast. Imaging results are presented for a trilayer application and for excimer laser projection printing.

## Introduction

The continuing drive toward higher circuit density in microelectronic devices has led to a quickening interest in exposure technology based on short wavelength or deep U.V., ultraviolet radiation. This interest derives from the fact that for a given lens system, the resolution is directly proportional to the exposure wavelength. Several manufacturers have made<sup>1</sup> or will soon make available sophisticated aligners designed to provide deep UV (248 nm) radiation at the resist surface. Most of these systems are based on the use of excimer laser light sources and refracting optics. The performance of these tools is currently resist limited<sup>1</sup> since the diazoquinone/novolac (DQN) materials available for general use were designed for exposure at longer wavelength. These DQN materials have a high initial absorbance in the deep UV and do not bleach adequately upon exposure. The consequence of the unbleachable, strong absorbance is to produce sloping resist side walls. This performance degradation was predicted by modeling studies<sup>2</sup> and has now been documented by experimentation.<sup>1</sup>

## Results and Discussion

For some time, we have been working toward the design of a deep UV resist system that would mimic the familiar and attractive processing characteristics of the DQN systems yet function properly in the deep UV such that the potential for improved resolution that these new exposure systems offer might be realized. Our goal was to design a two component system analogous to the DQN system using a base soluble matrix resin analogous to novolac and a dissolution inhibitor analogous to the diazoquinones. To date, our efforts have focussed mainly on the chemistry of the dissolution inhibitor.

The ideal deep UV dissolution inhibitor should

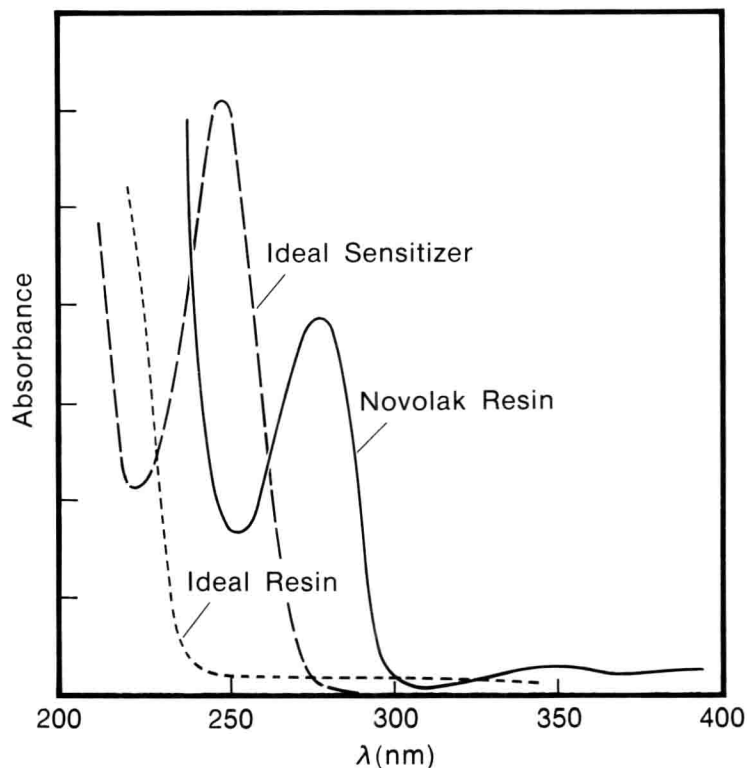
- 1) have significant absorbance in the deep UV
- 2) have photo products that are transparent in the deep UV
- 3) act as a dissolution inhibitor for base soluble resins
- 4) provide a photoproduct that is not a dissolution inhibitor
- 5) have thermal stability consistent with normal processing
- 6) have solubility in common casting solvents.

We have imposed a 7th less critical requirement for "self-filtering." That is, the chromophore should absorb in the deep UV but not in the near UV such that low transmission, narrow band-pass filters in the condenser system are not required to achieve high resolution imaging. (Figure I.) This requirement is not essential to excimer laser powered systems but is important for systems such as the Perkin Elmer Micralign 500 which have deep UV compatible optics but use a broad band, mercury discharge lamp as the light source and are thus flux limited.

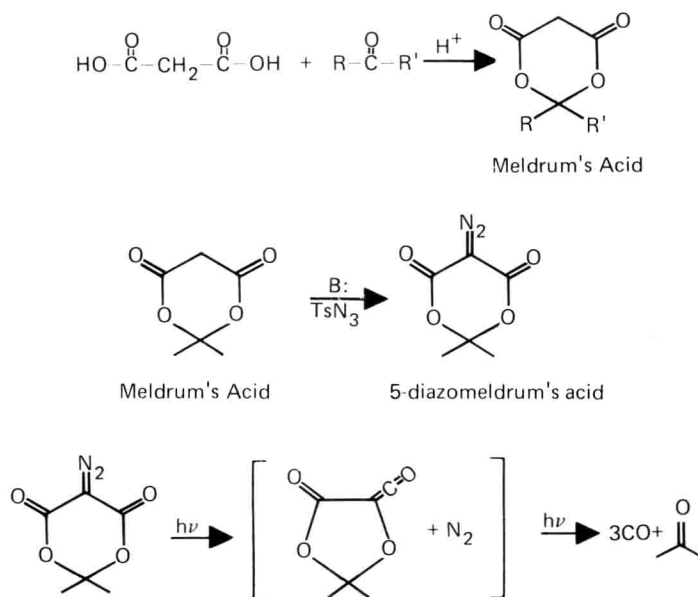
5-diazo Meldrum's acid, 2,2-dimethyl-4,6-dioxo-5-diazo-1,3-dioxolane (Figure II) fulfills all of the requirements described above. Our detailed study of this interesting material<sup>2</sup> however, revealed that though it functions as desired, the parent compound is evolved (sublimed) from the matrix resin to a significant extent during the baking cycle that is required to remove casting solvent after spin coating. All attempts to modify the structure of Meldrum's diazo led to either materials that were virtually insoluble in common casting solvents or materials that like the parent compound, sublimed during baking.<sup>2</sup>

During the course of continued analog studies we prepared the diazo pyrazolidinedione derivative, 1,2-diphenyl-4-diazo-pyrazolidine-3,5-dione (DPD) (Figure III). This compound has spectral characteristics that are essentially the same as Meldrum's diazo. However, upon casting films in novolac, unlike Meldrum's diazo and its soluble analogs, DPD is not evolved from the film during baking (Figure IV). DPD functions as a dissolution inhibitor for novolac and we have successfully imaged resist formulations based on DPD albeit, with rather low contrast. The photochemistry of DPD is different from Meldrum's diazo in that some acid is formed from the insipient ketene through reaction with water but the ketene also undergoes decarbonylation in a sequence of steps that ultimately produce a stable photoproduct that is, its self, a dissolution inhibitor.<sup>3</sup> Hence, though bleaching occurs, to the extent that material is lost to the decarbonylation

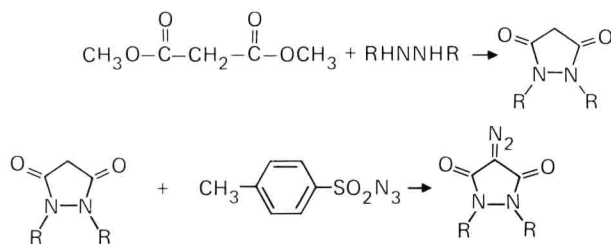
pathway the chemical changes that result from photolysis are not particularly efficient in generating solubility rate changes. The important discovery that emerged from analysis of DPD was that incorporation of the lactam linkage provided stability against volatilization during the baking process.



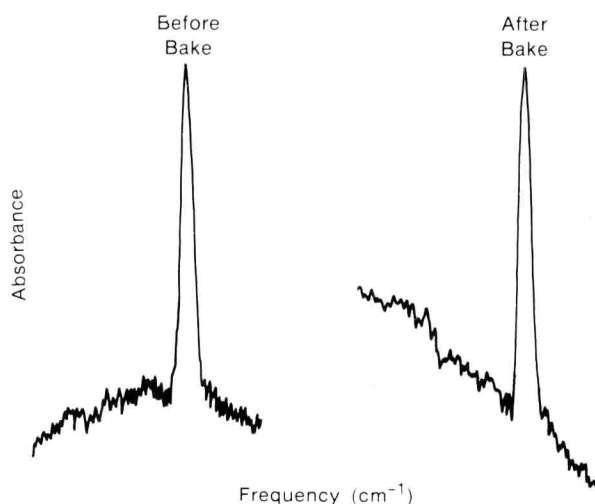
**Figure 1.** Absorbance curves for ideal deep U.V. resist components. The absorbance spectrum of a typical novolac resin is provided for reference.



**Figure 2.** Synthesis and photochemistry of Meldrum's diazo. Note that the photolysis yields all volatile products.



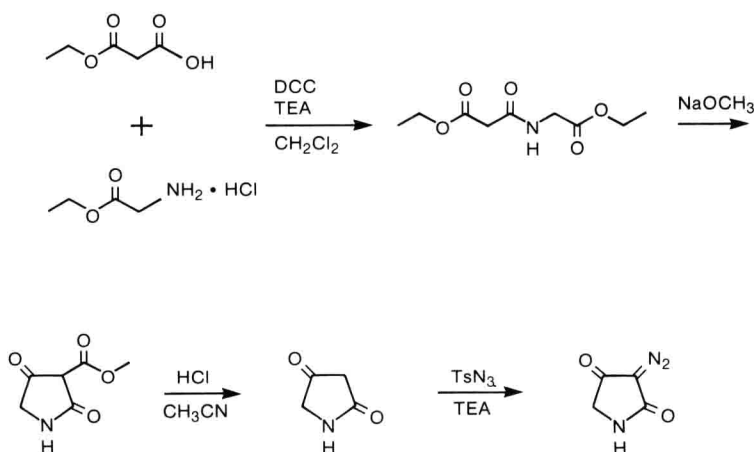
**Figure 3.** Synthesis of diazopyrazolidinedione dissolution inhibitor.



**Figure 4.** Diazo stretching absorbance in the infrared for 1 micron thick film of diazopyrazolidinedione in novolak before and after baking at 105°C for 30 minutes. No material loss occurs during this bake.

The experiments with Meldrum's diazo and DPD have provided two important general, structural principles to guide further work. The first is that the 1,3-diacyl-2-diazo chromophore is perfectly matched to our spectral requirements. The second is that the lactone linkage is not effective toward minimizing material loss through sublimation during baking but the lactam linkage is. This latter observation is presumably the result of improved hydrogen bonding interactions between the inhibitor and the weakly acidic resin.

Based on these general principles, we designed new sensitizers based on the tetramic acid and homotetramic acid (piperdinedione) ring systems. (Figures V and VI). These materials have the two requisite structural features and they have an acylcarbon-carbon bond available for insertion of the photogenerated carbene. This insertion is favored over insertion into the lactam linkage during the Wolff rearrangement. It was reasoned that this improved reactivity would maximize the desired pathway to the keto-ketene and ultimately to the keto-acid derived through nucleophilic addition of water. In fact, the Wolff rearrangement proceeds essentially 100% via carbon carbon bond insertion to give a single keto-ketene. The ring contracted keto-ketenes thus generated are extremely stable to subsequent irradiation under low temperature, matrix isolation conditions in novolac resin.



**Figure 5.** Synthesis of diazotetramic acid.

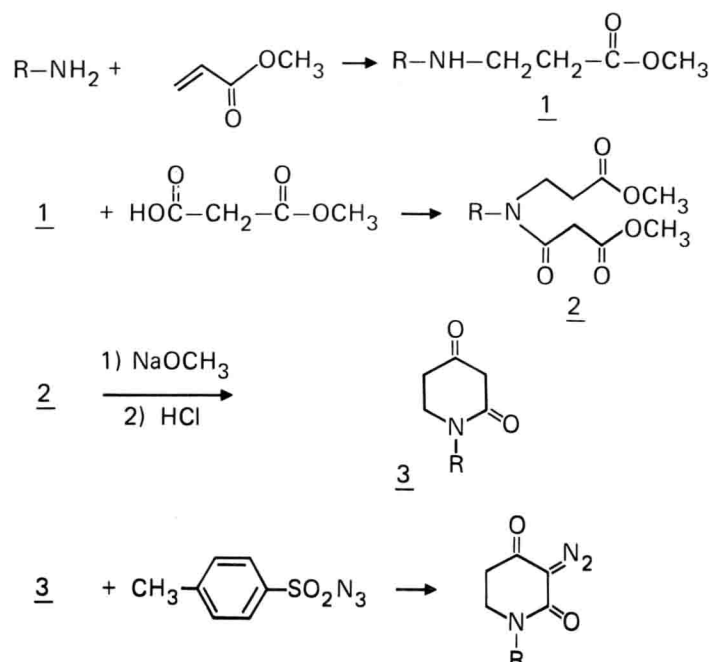


Figure 6. Synthesis of diazopiperdinedione.

Resist formulated from analogs of diazotetramic acid and diazopiperdinedione provides useable function in deep UV imaging albeit with less than desirable contrast (Figure VII). We have exercised analogs of these materials in novolac of various isomeric composition, in styrene-maleimide copolymers, in polyglutarimide, poly(p-hydroxystyrene) and other base soluble, matrix resin materials with reasonable optical transmission at 248 nm. In all cases, the sensitivity of the systems is about 100 mJ/cm<sup>2</sup> but the contrast is low compared to diazoquinone sensitizers in the same matrix resin. The low contrast is manifested in sloping resist side walls (Figure VIII). Interestingly, excimer laser projection printing of these materials seems to provide improved performance. Figure IX shows the improvement in image quality achieved by projection printing in a full wafer scanning tool using an excimer laser source.<sup>4</sup> One possible explanation for this observation is involvement of multiphoton chemistry. We are exploring this hypothesis and measuring the reciprocity response of these interesting materials.

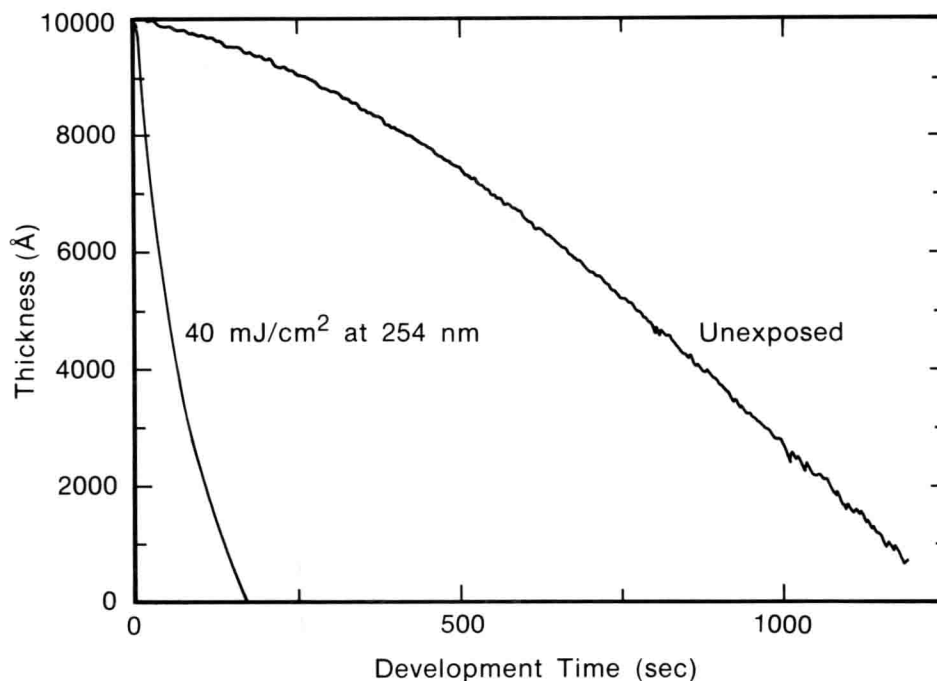
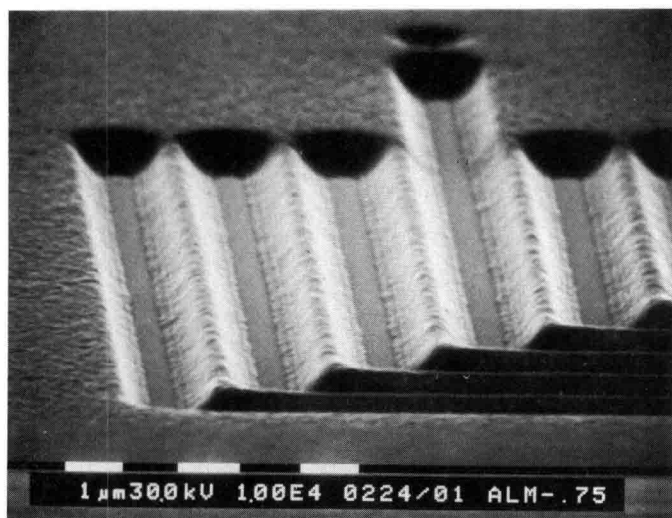
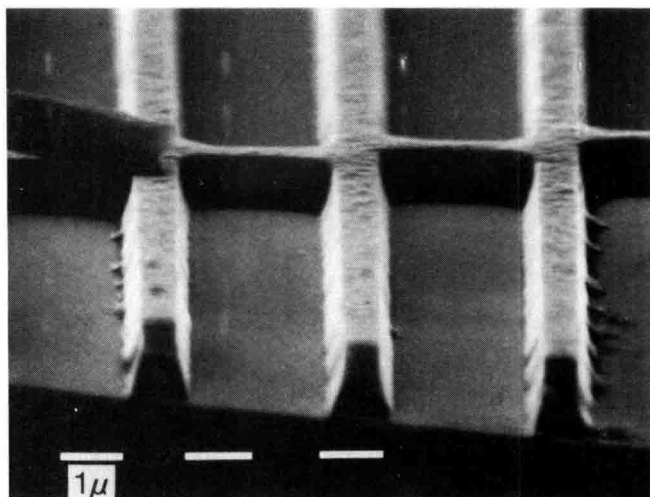


Figure 7. Thickness versus time plot for exposed and unexposed resist formulate from novolac and diazopiperdinedione. The developer is AZ2401: water 1:4.5.



**Figure 8.** Scanning electron micrograph of images printed on Micralign 500 in U.V.-2 using diazopiperdinedione resist. Note the sloping sidewalls.

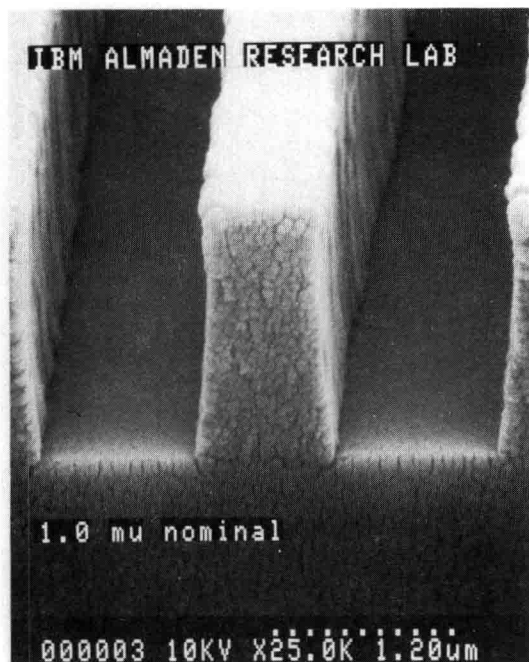


**Figure 9.** Scanning electron micrograph of images printed in diazopiperdinedione resist using 248 nm, full wafer scanning tool with excimer laser light source.

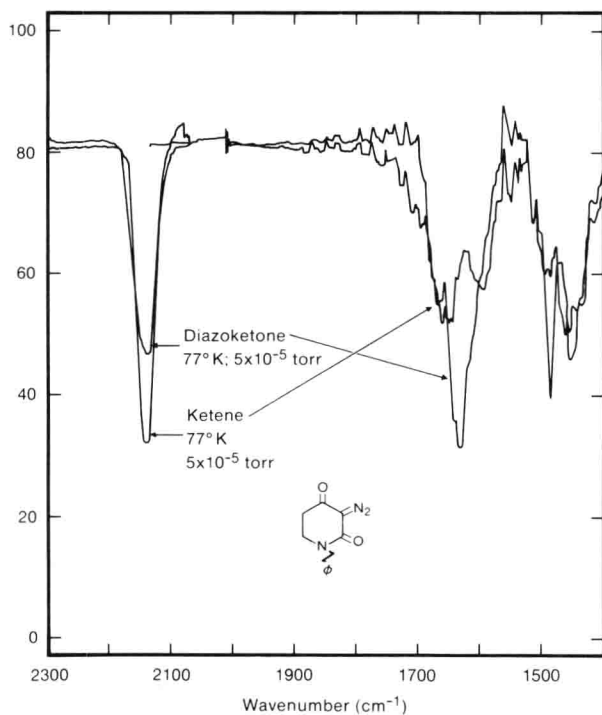
Though the sloping resist side walls are not useful for device manufacturing directly because of the difficulty in controlling critical dimensions over topography, such images can be used in trilayer application. In trilayer application, the resist is imaged over a planarizing layer. Hence, the effect of sloping side walls on critical dimension control is reduced. We have exercised these resists in such a process. Hard baked photoresist was used as the planarizing layer. We studied both commercial "spin on glass" and polysilane,<sup>5,6</sup> as the barrier layer. Image transfer was accomplished by  $\text{CF}_4$ -RIE of the barrier layer followed by low pressure  $\text{O}_2$ -RIE for image transfer through the planarizing layer. One micron dimensions were printed with this process on a Perkin Elmer Micralign 500 in the UV-2 mode (Figure X).

One explanation for the poor contrast of resist systems based on analogs of diazotetramic acid and diazopiperdinedione emerged from matrix isolation infrared studies of the photoactive component of DQN photoresists, substituted sulfonate esters of the 2-diazo-1-naphthalenone chromophore. To examine the thermal stability of the ketenes produced photochemically from these sensitizers in novolac resins under vacuum, samples were irradiated using a Pyrex filter. The IR spectrum of the bis-ketene produced by irradiation of a typical bifunctional diazo-5-sulfonate ester of an aliphatic diol is shown in Figure XI. The ketene derivative thus produced is relatively stable in the hostile matrix environment under vacuum even at temperatures of  $0^\circ\text{C}$  or above. If the vacuum is released during the warmup, the ketene band at  $2130\text{ cm}^{-1}$  disappears immediately due to rapid reaction with water in the air. When the sample is maintained under vacuum the ketene disappears very slowly through reaction with the phenolic hydroxyl groups of the resin to form resin sulfonate esters. Although the thermal stability of the ketene derivatives of this type varied somewhat with the nature and position of the substituents, all were relatively stable below  $0^\circ\text{C}$ . The relative stability of the ketenes in novolac resins coupled with their high reactivity with water is of course important to the utility of the diazonaphthoquinones as sensitizers in positive resist formulations.

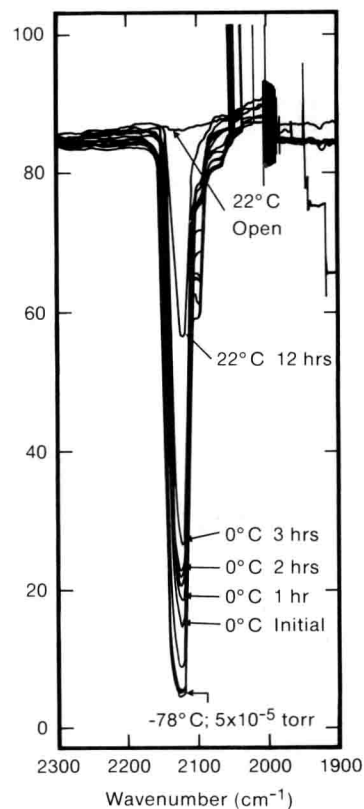
The difference in the matrix stability of the ketenes generated from the classical diazonaphthoquinones and those produced from the diazohomotetramic acids is striking. In this regard, irradiation at 254 nm of a typical derivative, N-( $\beta$ -phenethyl)-3-diazopiperdine-2,4-dione, in a novolac resin at  $77^\circ\text{K}$  rapidly produces the corresponding ketene derivative as suggested by the observation of a strong ketene band at  $2140\text{ cm}^{-1}$  (Figure XII). The structure of the proposed ketene was assured by irradiation the same material in a 1:1 ethanol-dioxane solution at room temperature and the isolation of the corresponding ethyl ester in  $>90\%$  yield. The structure of the ethyl ester was confirmed by its analytical and spectral data. The ketenes derived from diazotetramic acid and diazopiperdinedione are, however, quite unstable in the resin even at low temperatures as evidenced by the rapid disappearance of the ketene band as the temperature of the matrix is raised from  $77^\circ\text{K}$  where the irradiation was performed to  $-78^\circ\text{C}$  (Figure XIII). Interestingly, however, the product from the photo decomposition of the diazopiperdinediones at  $-78^\circ\text{C}$  is not the expected ketoamide as evidenced from the appearance of a strong carbonyl band concurrent with the disappearance of the ketene band at  $1630\text{ cm}^{-1}$  which is consistent with the direct formation of the enol (Figure XIV). The absorption at  $1630\text{ cm}^{-1}$  decreases upon standing at room temperature with the formation of new bands at  $1740\text{ cm}^{-1}$  and  $1690\text{ cm}^{-1}$  characteristic of the ester-amide structure (Figure XV). We attribute this behavior to the addition of the phenolic hydroxyl group of the resin to the ketene via a cyclic six-membered transition state. This curious behavior presumably results from the rigid cisoid conformation of the  $\alpha$ -ketenyl lactam enforced by the peripheral carbocyclic skeleton. This would suggest that the instability of these ketene derivatives is due in part to the cisoid conformation of the reactive functionality. consistent with this hypothesis, preliminary studies on ketene derivatives derived from acyclic diazo- $\beta$ -ketoamides suggest that the corresponding ketenes are considerably more stable in the novolac matrix presumably due to availability of a number of non-cisoid conformations for the ketene intermediates.



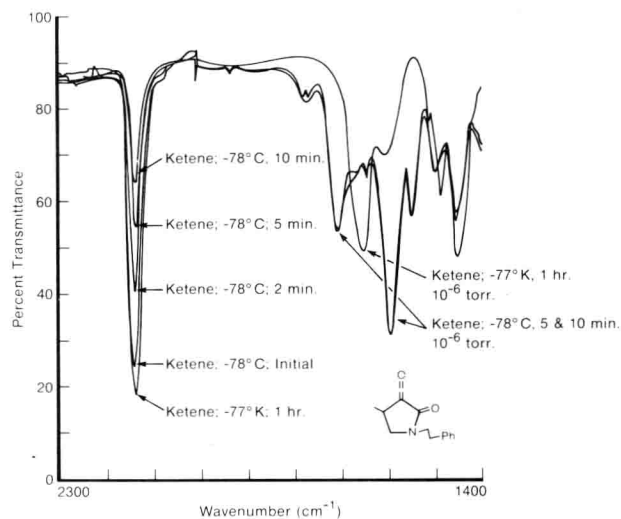
**Figure 10.** Scanning electron micrograph of trilayer structure using diazopiperdinedione resist as the imaging layer.



**Figure 12.** Changes in the infrared spectrum following low temperature photolysis of diazopiperdinedione to generate the corresponding keto-ketene.

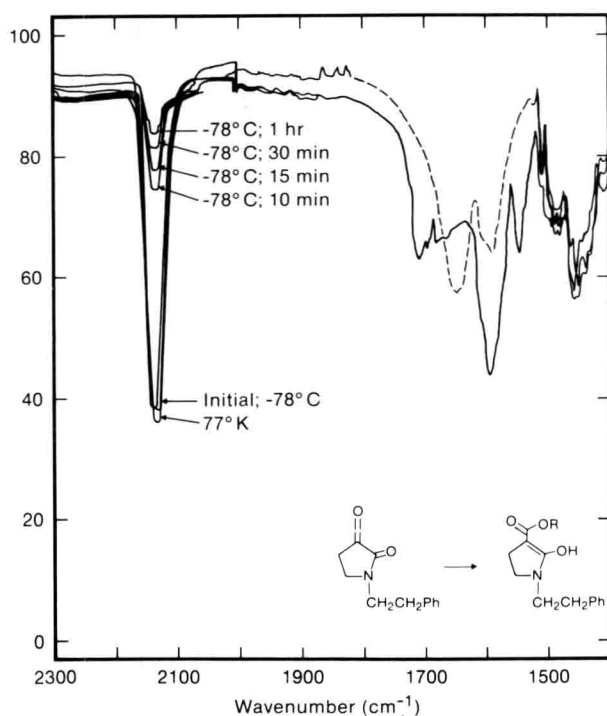


**Figure 11.** Matrix isolation study of ketene stability. Photolysis of bis-diazonaphthoquinone at  $-78^{\circ}\text{C}$  followed by warming to  $0^{\circ}\text{C}$  then to  $22^{\circ}\text{C}$  and finally opening the cryostat to air.

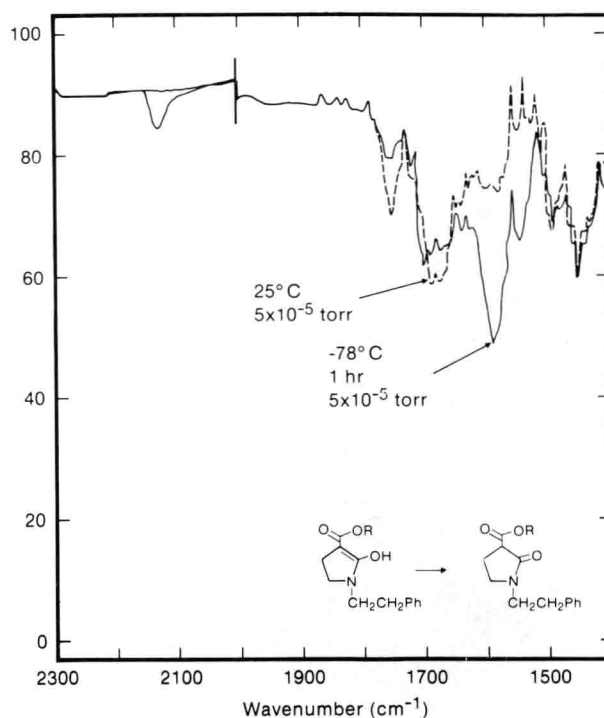


**Figure 13.** Stability study of ketene derived from diazopiperdinedione in novolak resin. Note rapid disappearance of ketene band at  $-78^{\circ}\text{C}$ . This should be compared to Figure 11.





**Figure 14.** Time dependent changes in the infrared spectrum of the ketene derived from photolysis of diazopiperdinedione. Note absence of an ester band. The spectrum after 1 hour at  $-78^{\circ}\text{C}$  is consistent with formation of the unusual enol which tautomerizes at higher temperature.



**Figure 15.** Infrared spectra showing the tautomerization of the initially formed enol to the ester amide.

In the continuing search for photochemical precursors to ketenes whose thermal stability in novolac resins mimics those produced from classical diazonaphthoquinone photosensitizers, we have studied the photodecomposition of a number of acyclic phosphorous and sulfur substituted diazoketones. These materials are synthetically available, thermally stable, absorb strongly in the deep U.V. and survive the baking process. Irradiation of these analogs in a novolac host at  $77^{\circ}\text{K}$  produced the expected ketene as evidenced by the appearance of a strong band at  $2120\text{ cm}^{-1}$  (Figures XVI and XVII). These ketenes are quite stable and survive for sometime even at temperatures of  $0^{\circ}\text{C}$  or above. (Figure XVIII). Similar thermal stability was observed for ketenes produced from the sulfonyl derivatives. The observed thermal stability of the ketenes produced photochemically from these derivatives is encouraging and suggests that materials such as these whose optical and physical properties may be varied by altering the substituents on the basic chromophore may be useful as dissolution inhibitors for deep U.V. resists.

#### Low Temperature Irradiation

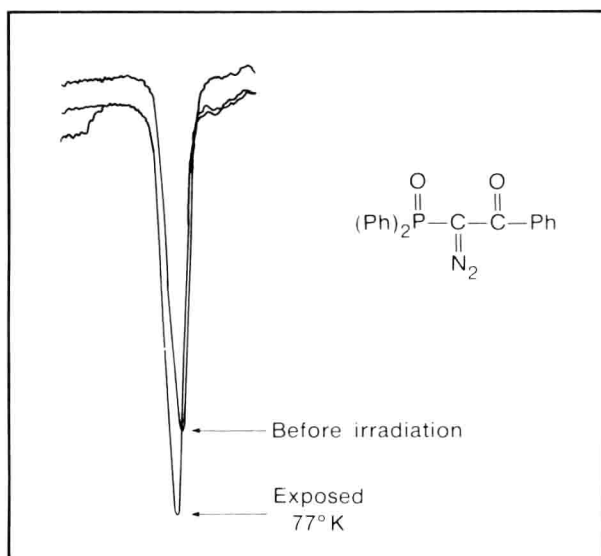
Stock solutions containing  $\sim 50\%$  by weight of a standard metacresol novolac resin containing the appropriate quantities of each diazo derivative were prepared so that the dry film concentration was  $\sim 0.8$  molal (mmol of sensitizer/gram of resin). Films were prepared by spinning these solutions onto a CsI wafer (4000 RPM) and baking at  $90^{\circ}\text{C}$  for 15 minutes. Films prepared in this manner were irradiated for 1-2 hours at  $77^{\circ}\text{K}$  using a variac EIMAC mercury-xenon lamp employing a 254 nm solution chemical isolation filter.<sup>7</sup> The progress of the photolyses was monitored by IR for those examples where the position of the ketene band of the product and the diazo band of the starting material were sufficiently different. For other samples, the irradiation was continued until all of the diazo material was destroyed as evidenced by the lack of IR absorption between  $2000\text{-}$  and  $2200\text{ cm}^{-1}$  upon warmup and opening of the cryostat to air.

#### Preparation of Dissolution Inhibitors

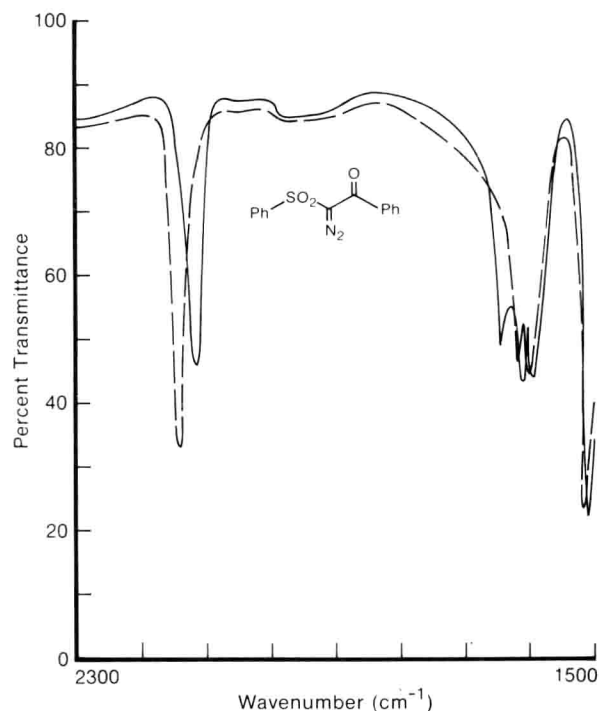
The sensitizers of interest for this study have been prepared by diazotization of the corresponding 1,3-dicarbonyl compound. The preparation of diazo Meldrum's acid was carried out by the reaction of Meldrum's acid with tosyl azide in the presence of triethylamine.<sup>8</sup> Similarly the diazopyrazolidinedione derivatives were prepared by the diazotization of 4,5-dialkyl-1,3-pyrazolidinedione.<sup>9</sup>

Diazopiperidinedione sensitizers were prepared in several steps (Figure VI). The method is analogous to the published procedure for the preparation of the five membered ring (tetramic acid) series.<sup>10</sup> A primary amine was added to methyl acrylate and the resulting Michael adduct was condensed with ethyl hydrogen malonate in the presence of dicyclohexylcarbodiimide to give the corresponding diester. The diester was then cyclized in the presence of sodium methoxide to give an intermediate which on heating with aqueous acid produced the keto-lactam. Finally diazotization with tosyl azide in the presence of triethylamine gave the desired material. These materials were characterized by satisfactory combustion analysis and by nmr, U.V. and IR spectroscopy.



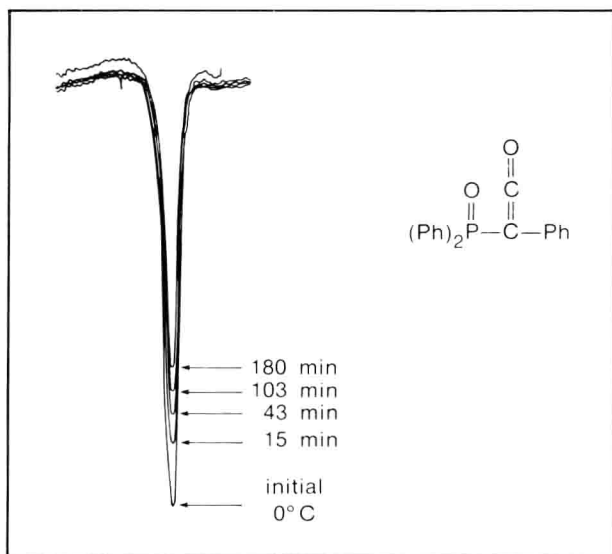


**Figure 16.** Infrared spectra of a diazophosphinyketone before and after exposure showing the clean conversion to the corresponding phosphinyketene.



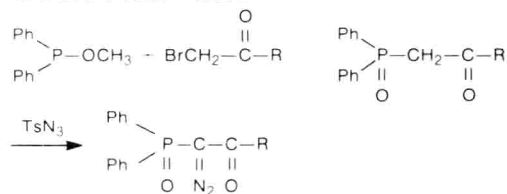
**Figure 17.** Infrared spectra of a diazosulfonylketone before and after exposure at  $-78^\circ\text{C}$  showing the clean conversion to the corresponding sulfonylketene.

The diarylphosphinylacyldiazomethane derivatives are prepared by the diazotization of diarylphosphinoacylmethanes (Figure XIX). The latter compounds are available from the Arbuzov reaction of diarylethoxyphosphine with  $\alpha$ -halocarbonyl compounds.<sup>11</sup> Alternatively, the diazo compounds are available from the reaction of  $\alpha$ -bromocarbonyl compounds with the silver salt of diarylphosphinyldiazomethane (Figure XIX).

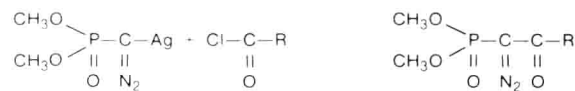


**Figure 18.** Infrared spectra of the phosphinyketene in novolac resin. The stability of this ketene should be compared with those in Figures 11 and 13.

#### A. Michaelis-Arbuzov Reaction



#### B. Electrophilic Diazoalkane Substitution



**Figure 19.** Synthetic routes to diazophosphinyketones.

### Acknowledgement

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