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Toward the Design of a Sequential Two Photon Photoacid Generator for Double Exposure Photolithography

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Simulations of a novel two exposure process to extend a form of photolithography known as double exposure (DE) have revealed the need for nonlinear responsive materials.[1] We describe the design and experimental realization of sequential two photon photoacid generation for the nonlinear production of acid for photolithography at 193 nm and shorter wavelengths.

Since 1965, the prediction has been made that the number of transistors on a chip will double about every two years; the semiconductor industry has kept pace with that prediction for several decades. The industry however is reaching the limits of optical lithography at 193 nm. In addition, efforts to develop lithography at 157 nm and extreme ultraviolet (EUV, 13.4 nm) are proving difficult, and their implementation does not seem likely in the near term.[2,3] Given this state of events, for economic reasons, there is an increased need for alternate methods of decreasing feature size employing the currently available tools that operate at 193 nm until alternative methods for reducing feature size are invented. Double exposure (DE) appears to be capable to meet requirements of current imaging technology as a potential method for reducing feature size.[1,4] DE is based on the use of staggered exposures, with each exposure having twice the desired pitch to form the eventual pattern. Importantly, DE does not require the removal of the wafer from the imaging tool between passes (Scheme 1), a feature that is of great economical advantage over other methods.

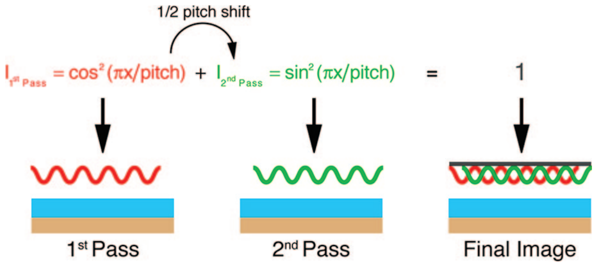
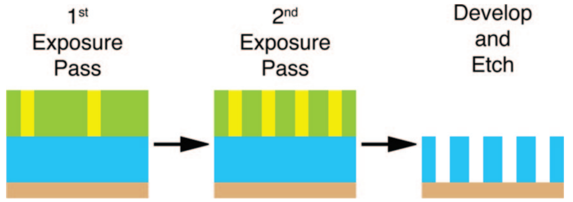


Figure 1. Summation of two exposures on a conventional resist material is a constant.

Scheme 1. Schematic of Double Exposure Photolithography



Although, in principle, double exposure may be achieved using conventional lithographic tools, new resist materials must be designed and invented before practical applications are possible.[1] From simulations, the linear behavior of conventional resist materials disqualifies their use in DE applications because a "memory" effect is introduced between exposures that prevents proper replication of the image (Figure 1). For example, the summation of two normalized aerial intensities for a pattern of equal lines and spaces following a cosine and sine function results in a constant (Figure 1). The two individual patterns are not resolved when double exposed using conventional resist materials with linear response but are predicted from simulations to be resolved if nonlinear DE is employed.

In addition, the simulations[1] show that there are other requirements for a successful DE. The required resist material must exhibit photoreversibility and nonlinearity in photoresponse in order to overcome dose reciprocity. Several materials with nonlinear responses that could be used in DE applications have been proposed. For example, a two photon photoacid generator involves the nonlinear absorption of two photons to induce a photochemical event, such as acid generation in the photoresist. Conventional two photon systems simultaneously absorb two photons and are highly conjugated systems with strong electron donors and acceptors.[5] However, the simulations showed that the simultaneous absorption of two photon materials was unreasonable for DE because of issues related to low quantum yields, laser pulse doses available to current lithographic tools, and inevitable absorption at wavelengths much longer than 193 nm. However, the simulations indicated that successful materials should be reversible and should *sequentially* absorb two photons.

The design of a sequential two photon photoacid generation system is shown in Scheme 2. This system is composed of a photochemically inactive photoacid generator and a latent/inactive sensitizer. The photochemical photoacid generator is designed to be transparent to the lithographic light

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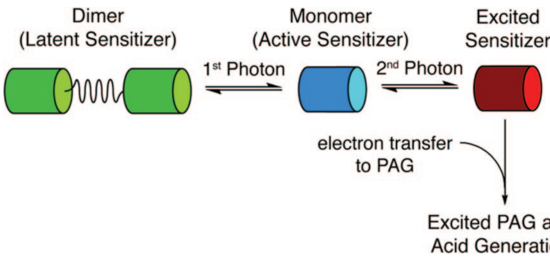
Scheme 2. Design of Sequential Two Photon PAG System



in the deep UV and therefore does not generate acid when the system is directly excited with the selected wavelength. The first photon absorbed transforms the “latent photosensitizer” into a potentially “active photosensitizer”. In our design, when a second photon is absorbed by the “active photosensitizer” the resulting photoexcited species transfers an electron to the photoacid generator, causing a reaction to produce acid; that is, the photoacid generator is triggered indirectly through photosensitized electon transfer via a two photon process. We note in passing that in addition to the two photon nature of the photoacid generation, a successful system will require reversibility to be successful.

Thus, in designing a latent sensitizer that corresponds to Scheme 2, we examined photoreactions that could be used to reversibly transform the latent photosensitizer into an active photosensitizer. After a search for potential candidates, we narrowed our search of photochromic reactions to the pericyclic photoreactions of conjugated π-systems which are known to be reversible.[6] We reasoned that we could utilize the dimeric form of a sensitizer as the latent form (Scheme 2) and that photoexcitation of the dimer would produce an active photosentizer. Our nonlinear process would be comprised of an initial irradiation with the first photon to form the monomeric active form and then a subsequent irradiation with the second photon to excite the active sensitizer. The electronically excited active sensitizer could then transfer an electron to the photochemically inactive photoacid generator (PAG) or reversibly deactivate to the ground state. For example, aromatic hydrocarbons such as anthracenes are known to undergo reversible [4 + 4] photodimerization.

First we address the issue of the design of the required transparency of the photoacid generator. Saturated analogues of photoacid generators are transparent to the lithographic wavelengths in the deep UV and are therefore photochemically inactive since they can easily be designed not to directly absorb selected wavelengths.[7] However, acid can be produced by photosensitized electron transfer to these transparent PAGs. Chart 1 displays two imide triflates: bicycloheptane imide triflate **1** and oxabicycloheptane imide triflate **2**. Both imide triflates possess good transparency in the deep UV (absorbance < 0.05 for a 10^{-3} M solution in acetonitrile at 210 nm). The photochemical inactivity of **1** and **2** as photoacid generators was demonstrated by irradiation of **1** and **2** at 254/185 nm with low pressure mercury lamps for several hours. Acid production was monitored by the absorption change of a fluorescein acid sensor, **4a** (Figure 2b).[8] No acid generation or change in absorption spectra was observed.

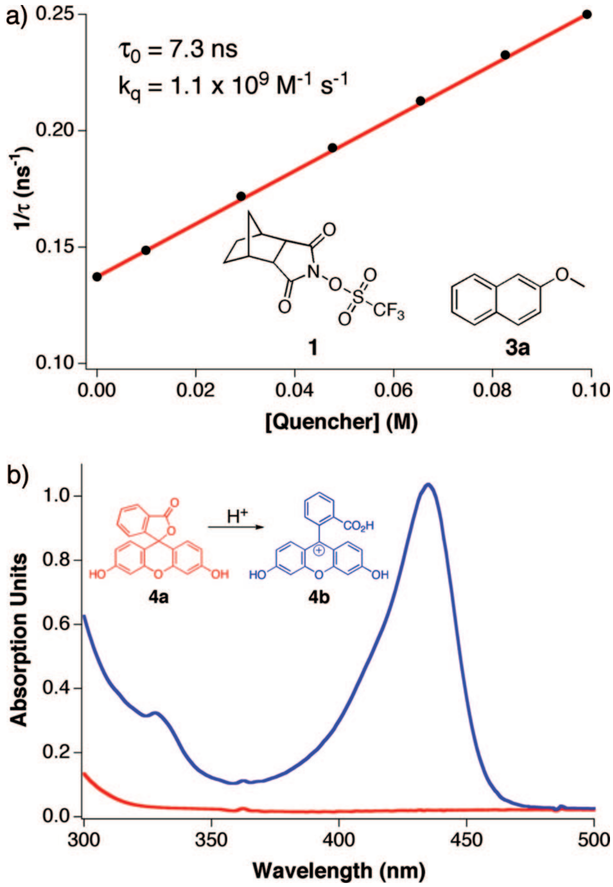
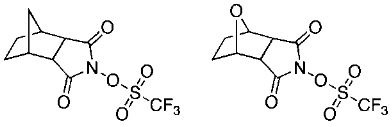


Figure 2. (a) Determination of the quenching rate constant of 2-methoxynapthalene singlet excited states by PAG **1**. Fluorescence lifetime of **3a** vs concentration of **1** (λ_{ex} = 326 nm). (b) Acid generation from PAG **1** in the absence (red line) and presence (blue line) of **3a** in acetonitrile when irradiated at 300 nm. Acid detected by absorbance spectroscopy with fluorescein (**4**).

Chart 1. Photochemically Inactive PAGs



1 **2**

Central to the sequential two photon PAG system is the design of the latent photosensitizer. Our design incorporated the following desirable characteristics: (1) that in its latent form the photosensitizer must be inactive to acid production, (2) that the conversion of the photosensitizer to the activated state is reversible, and (3) that once in the activated state it is capable of sensitizing acid generation. We envisioned a photosensitized electron transfer reaction from the activated photosensitizer to the PAGs **1** and **2** to trigger acid generation. The feasibility of photoinduced electron transfer can be predicted from the Rehm−Weller relationship[9] which relates the rate constant for electron transfer to the redox potentials of the sensitizer and PAG and the electronic excitation energy of the photosensitizer. Estimations of the

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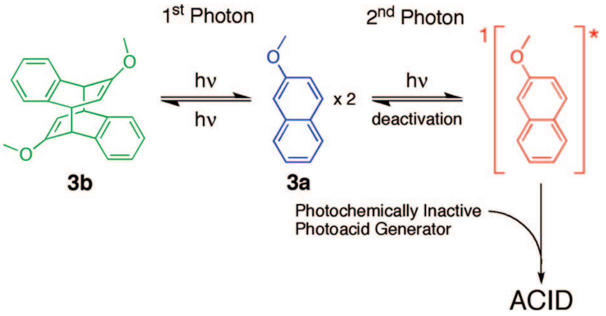
redox potential of our designed imide triflate PAGs from their calculated HOMO−LUMO band gap showed that sensitizers of high energy would be necessary to generate acid. Thus, candidates possessing long wavelength absorption (and corresponding low excited-state energy) are less attractive than candidates possessing accessible short wavelength absorption.

Imide triflates are known to decompose through their excited singlet states. This behavior is also expected for the photochemically inactive PAGs **1** and **2**.[10] Common singlet sensitizers including various anthracenes, perylene, pyrene, and phenothiazine were found to be experimentally ineffective at sensitizing acid generation, consistent with calculations that showed that they did not have the reducing power to generate acid production by electron transfer to **1** or **2**. Triplet sensitizers acetophenone and anthraquinone were also found to be ineffective at photosensitizing acid generation. These considerations led to the conclusion that photosensitized imide triflate decomposition to produce a photoacid must occur through a relatively high energy singlet photsensitizer.

From a literature survey, an attractive candidate for a high energy singlet photosentizer appeared to be 2-methoxynaphthalene (**3a**) which is known to dimerize (potentially reversibly) to produce **3b**.[11] **3a** has a large reduction potential (−1.42 V) and a relatively large singlet excitation energy (~ 90 kcal/mol). Indeed, **3a** was found to sensitize acid generation from the photochemically inactive PAGs **1** and **2** (Figure 2). Under air saturated conditions the fluorescence lifetime of **3a** was found to be 7.3 ns and fluorescence quenching by **1** in acetontrile resulted in a large quenching rate constant ($k_q = 1.1 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, Figure 2a), consistent with the singlet state of **3a** being quenched by **1**. Acid production was observed to occur when **1** and **2** were irradiated at 300 nm in the presence of **3a** (Figure 2b). However, no acid was generated by triplet sensitization of **3a** using acetophenone conducted in the prescence of PAG. We conclude that all of the experimental and computation results are consistent with a singlet mechanism for photosensitizing acid generation from **1** and **2**. In addition, acid generation was inhibited when the electron scavenger NaI was present, confirming an electron transfer mechanism.

Scheme 3. Sequential Two Photon Acid Generation with Latent Sensitizer



2-Methoxynaphthalene is known to undergo [4 + 4] cyclodimerization upon direct photochemical excitation with the *trans* isomer (**3b**) as the major product (Scheme 3). The dimer is produced by irradiating **3a** at 300 nm and it thermally reverts to the monomer at high temperatures ($t_{1/2}$ = 8.25 h at 122 °C). The photochemical reverse [4 + 4] retrocycloaddition reaction has not been reported. However, we found that when irradiated with either 300 or 254 nm light the dimer reverted to the monomer, demonstrating the desired reversibility of the photodimerization. Irradiation of our sequential two photon PAG system of 2-methoxynaphthalene *trans* dimer (**3b**) and photochemically inactive photoacids **1** and **2** both resulted in acid, detected by the fluorescein acid sensor (**4**) mentioned above. This demonstrates the nonlinear absorption of two photons to generate acid.

In conclusion, we have designed a system that demonstrates the feasibility of producing new materials for DE photolithography. On the basis of simulations of materials that could operate with 193 nm photolighographic tools it was concluded that materials suitable for successful DE applications must possess a number of characteristics: a nonlinear photoresponse to produce acid, reversibility, and special features at 193 nm. Toward the eventual design of these materials, we have experimentally demonstrated the existence of a system that possesses the characteristics indicated by the simulations.

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Supporting Information Available: Instrumentation, general methods and synthetic procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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