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Two-Photon Acid Generation in Thin Polymer Films. Photoinduced Electron Transfer As a Promising Tool for Subwavelength Lithography

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When Gordon Moore first predicted more than 40 years ago that the number of transistors per computer chip would double every 2 years,[1] an edict now referred to as "Moore's Law", the typical dimension of lithographic features were many times larger than the wavelengths employed to record the images. In stark contrast, current state-of-the-art lithographic processes can pattern features with widths of <40 nm using 193 nm irradiation,[2] significantly below the $\sim\lambda/3$ resolution limit expected by basic physics; a combination of optical, positioning, and engineering techniques have made this possible. However, with 193 nm still the preferred lithographic wavelength, further resolution improvement will require photochemical "tricks". One possible approach to improving resolution is the development of multiphoton, particularly two-photon, technologies. If two-photon acid production is coupled with double exposure lithographic processes,[3] the resolution required for the 16 nm lithographic node would be achievable.

Two-photon processes are reasonably well understood; in fact, our group reviewed the topic more than two decades ago.[4] From a photolithographic point of view, there are two subtlety different mechanisms for two-photon processes that could allow for the desired increases in resolution: (1) the excited state of a molecule is reached by absorption of two photons that combined have enough energy to reach this state, whereas the light used is such that no one-photon absorption occurs at that wavelength;[5] and (2) a one-photon process excites a molecule in a conventional way to yield a reaction intermediate (which could include an excited state) that can absorb a second photon, leading to chemical or spectropscopic consequences sometimes different from those achieved by just one photon.[4] This case is best described as the "photochemistry of reaction intermediates". Mechanism 1 is ubiquitous in the current lithographic literature, specifically in holographic and 3D lithographic patterning.[5,6] However, this mechanism will not be relevant to lithography with 193 nm as it requires very high peak powers, frequently only achievable with picosecond or femtosecond lasers. As the energies delivered per pulse of lithographic laser sources are typically ≤ 1 mJ/cm^2 for pulse durations around 100 ns, the power density would be far too low for mechanism 1. In addition, many of the materials used in lithography readily absorb 193 nm photons. Therefore, we think mechanism 2 is the most promising pathway for two-photon acid production that will be directly relevant to current photolithographic tools. Although two-photon acid generating schemes have been proposed before,[7] the nonreciprocity was not inherent in the chemical system; they would require a second wavelength of light to drive the intermediate back to reactants. This additional engineering difficulty is overcome by using unstable intermediates, as we present herein.

The excited states of simple molecules are always better electron acceptors and donors than the corresponding ground states.[8] The latter property is of interest in the context of our work. Lithographic images are usually created by the photoactivation of a "photoacid generator", or PAG, that produces acids that are subsequently employed to either enhance (positive tone) or reduce (negative tone) the solubility of a polymer composition referred to as a resist or photoresist.[9] Certain PAGs, particularly those derived from onium salts, can be readily activated by electron transfer.[9,10] Earlier studies from

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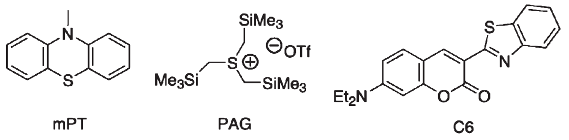
Chart 1



our group and others have shown that phenothiazine can lead to acid generation following one-photon electron transfer.[11,12] In this system, the proton is released from the phenothiazine radical cation following excited state electron transfer (see Scheme S1 in the Supporting Information).

In the case of *N*-methylphenothiazine (mPT), the process in Scheme S1 cannot occur, because the N-center is substituted by CH_3, making a 1-photon acid generation process more reluctant to occur. On the other hand, mPT is known to undergo photoionization under two-photon excitation conditions.[13] We wondered whether a system could be designed in which the photoejected electrons could be used to trigger acid release from a PAG, in what is usually described as a trivial electron transfer.[8] Alternatively, the process may be assisted by the PAG as a true participant in the electron transfer process (orbital interaction), rather than just a recipient of the electron.

Our experiments for the current study were carried out in polymethylmethacrylate films (PMMA), typically about 900 nm thick, deposited on a fused silica disk in order to facilitate the spectroscopic experiments described below. The formation of acid was monitored using coumarin-6 (C6) as a dopant in the film, as described in an earlier publication.[14] We noted that the absorbance of the protonated form of C6 increased for about 20 min following exposure due to acid diffusion through the film and equilibration. Therefore all measurements were performed at least 30 min after exposure. A number of control experiments to support the applicability of this methodology to the experiments reported here are described in the Supporting Information. The structures of mPT, C6, and the particular PAG we used are illustrated in Chart 1.

There are several approaches to establishing if a chemical or spectroscopic change has its origin in a two-photon process. For example, one can monitor if the change follows a quadratic dependence with the laser power/dose for increased energies with other parameters remaining constant. In our case, we apply a methodology that is particularly well-suited for lithographic experiments. That is, each sample film is irradiated to the same total energy delivered, but the energy per pulse and the number of pulses are varied. Repetition rates were typically 1 Hz although a few experiments carried out at higher frequencies (≤90 Hz), indicated that this had no effect under our experimental conditions (see the Supporting Information). The spectral results showing changes to the C6 probe for a series of experiments, delivering a total dose of ~175 mJ/cm^2, are shown in Figure 1. We were careful to only go to relatively low conversion to avoid any saturation or significant bleaching effects.

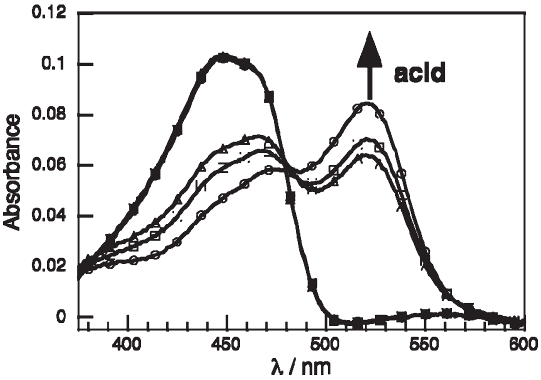


Figure 1. UV−vis absorption spectra of a PMMA containing a 4:1 molar ratio of mPT to PAG (PAG is 4% by weight of polymer) and 1% C6 used as acid reporter. Spectra are recorded before and 35 min after exposure with ~175 mJ/cm^2 of 193 nm total laser irradiation energy delivered by pulses of 29.5 (●, ○), 9.7 (■, □), or 2.2 (▲, △) mJ/cm^2; filled points correspond to the spectra before irradiation and open points to the spectra after irradiation. The appearance of the protonated C6 absorption band at ~520 nm is observed in each sample, indicating acid formation. An increased yield of acid is observed with increasing pulse energy.

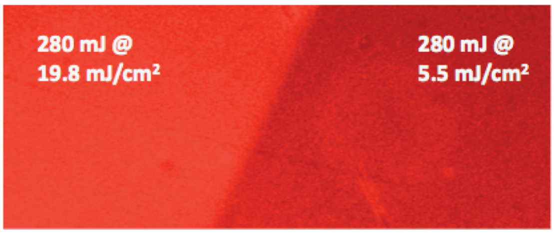


Figure 2. Fluorescence microscope image (λ_{ex} = 546 nm, λ_e > 590 nm) of film prepared as in Figure 1. The left side of the film was exposed to 280 mJ of 193 nm irradiation at 19.8 mJ/cm^2 per pulse and the right was exposed to the same total dose at 5.5 mJ/cm^2 per pulse. The brighter red, the result of protonated **C6**, on the left side of the image as compared to the right indicates that significantly more acid is generated with the higher pulse energy, in spite of the fact that the same total energy was delivered.

The changes at ~520 nm in Figure 1 reflect the formation of acid, as reported by the protonation of C6. It is clear that different yields of acid are obtained for different forms of energy delivery, with better yields when the individual 193 nm pulses are of higher energy (Figure 2). An alternate way of displaying the data is presented in Figure 3, where the protonated C6 signals are plotted against the energy per pulse, for the same total energy of ~175 mJ/cm^2.

If only "linear" photochemistry was involved in acid production, the plot of Figure 3 would give a horizontal line; clearly this is not the case. The positive slope of the plot suggests the involvement of a multiphoton, most likely two-photon, process. The fact that the *y*-intercept is not zero indicates that some acid is also formed in a one-photon process. This is not surprising since the PAG used

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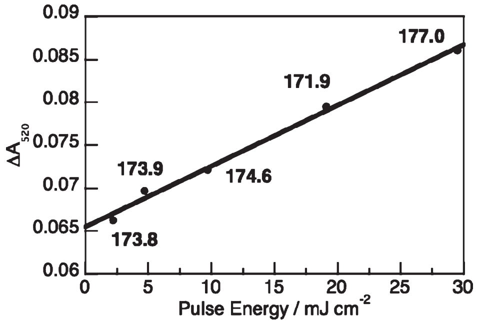
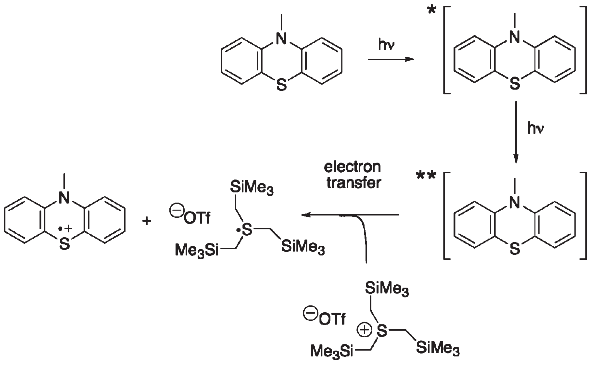


Figure 3. Plot showing the yield of protonated C6 in PMMA films prepared as in Figure 1 with an almost equal dose (~175 mJ/cm^2) delivered to each film but with varying energy per pulse. The increasing acid yield with increasing pulse energy is indicative of a multiphoton sensitization mechanism. The values associated with each point indicate the exact dose, in mJ/cm^2, delivered to that film.

Scheme 1



has some absorbance at 193 nm (ε = 860 M^{-1} cm^{-1}) and is known to yield some acid by direct photolysis (see the Supporting Information). We have tested mPT with some other trialkylsulfonium PAGs and did not observe any nonlinearity in acid formation. We tentatively attribute this to the relative energies of donor and acceptor orbitals; in the other trialkylsulfonium systems, we believe that the energy of the first excited state of mPT (before a second photon is absorbed) is high enough to transfer an electron to the PAG. We are in the process of carrying out electrochemical and computational studies to verify this. It must also be noted that at more lithographically relevant pulse energies (< 1 mJ cm^{-2} pulse^{-1}), the current system does not exhibit the desired nonlinear behavior.

The first steps of the proposed mechanism for acid generation in the present system are illustrated in Scheme 1. We favor the electron transfer mechanism of Scheme 1 based on the reported mechanism for acid generation from sulfonium salts via electron-transfer sensitization from polyaromatic systems.[9] Product studies have been inconclusive thus far in determining the fate of the initially formed electron-transfer products in the mPT-PAG system, although we anticipate that acid is generated in a radical mechansim similar to that proposed for previous electron-transfer sensitization processes.

Scheme 1 does not specify the nature of the first or second excited state of mPT. At this time, we favor a singlet state process although further work will be required to firmly establish the nature of the excited states. Our reasons for believing that the mechanism proceeds via the singlet state are: (a) Monophotonic electron transfer from the parent phenothiazine to PAGs in films occurs from the singlet state in spite of the presence of a long-lived triplet[11] and (b) although preliminary laser flash photolysis in PMMA suggest the presence of a very long-lived triplet in the case of mPT, the yield of acid seems independent of the laser repetition rate (see the Supporting Information). If the triplet was involved, one would expect that at higher repetition rates the triplet state would be re-excited by subsequent laser pulses; we presume that both photons of Scheme 1 are delivered within the same 10 ns pulse.

The second excited state of Scheme 1, formed after absorption of the second photon, is not necessarily a spectroscopically observable intermediate. It is possible that absorption of the second 193 nm photon directly ionizes the first excited state of mPT. We have attempted to glean insight into this mechanism by performing concentration studies. As we vary the PAG loading of films containing a constant loading of mPT and C6, we saw a predominantly linear dependence on acid production with PAG concentration (see the Supporting Information), indicating that in the current system the 1-photon photolysis of the PAG (vide supra) is a significant interference. As the distance is increased between donor (mPT) and acceptor (PAG) in the rigid polymer matrix, the significance of either trivial or orbital overlap mechanisms of electron transfer would decrease dramatically, allowing the linear, direct absorption of the PAG to dominate. At high PAG loadings, where mPT would be in closest proximity, the direct absorption by PAG becomes competitive with mPT and "hides" the contribution from the two-photon sensitization. Preliminary NMR experiments have been unsuccessful in identifying the final products of the reaction in Scheme 1.

The work reported here provides the first clear proof of concept that two-photon photoacid generation in polymer films is indeed feasible and in an energy range within an order of magnitude of that employed for chip manufacture. Further development of two-photon sensitization mechanisms (see Scheme 1) certainly requires the use of more transparent (at 193 nm) PAGs. Further improvements may be achieved by tethering the donor and acceptor structures, so as to enhance the yield of electron transfer. Such studies are now in their early stages in our laboratory, as are more detailed mechanistic studies on the reaction presented herein, including product studies, and the evaluation of resist performance by the usual dissolution-contrast parameters.

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Supporting Information Available: Control experiments, frequency dependence, thin film preparation, and synthetic procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.