Demonstration of a Directly Photopatternable Spin-On-Glass Based on Hydrogen Silsesquioxane and Photobase Generators

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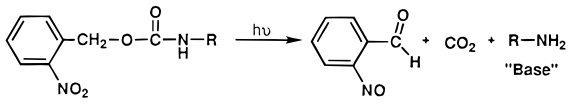
ABSTRACT: A commercially available spin-on-glass material, hydrogen silsesquioxane, has been rendered photopatternable to micrometer dimensions by the introduction of a photobase generator at concentrations of <5 wt %. The cure process proceeds via hydrolysis of the silyl hydride linkage by residual water in the film, as activated by a photogenerated base catalyst. Subsequent reaction of the generated silanol with neighboring silyl hydride groups yields a thermally stable siloxane cross-link. The photochemical cross-linking of hydrogen silsesquioxane shows high sensitivity (<40 mJ/cm^2) and is not inhibited by molecular oxygen. The resultant oxide films can be further cured at elevated temperature either under an inert atmosphere to minimize the dielectric constant or heated in an air atmosphere to complete the conversion to silica glass. The oxidative nature of both the photo and thermal cure processes and the release of only traces of hydrogen as byproduct results in minimal weight loss in the film during processing.

Introduction

Photocurable compositions based on the concept of chemical amplification are becoming increasingly important in both electronics and coating industries. The advantage of chemically amplified photochemical processes over standard processes is their high sensitivity to light, which is due to the photogeneration of an active catalyst that can catalyze a multitude of chemical reactions.[1,2] This catalysis results in several chemical events (chemical conversions or cross-links) for every photochemical transformation. Most of the chemically amplified cure systems developed to date rely on the photochemical generation of a strong acid to catalyze the desired chemical transformations. Recently, new systems that utilize photochemical base generating compounds (PBGs) to effect these chemical transformations have appeared,[3−13] but research into these systems has been minor compared with that extended to the photoacid systems. Although photobase technology has not reached the same level of maturity as the photoacid-generating systems, progress is being made as evidenced by a number of new PBGs recently described in the literature. The most common of these are the 2-nitrobenzyl carbamates that liberate an amine upon photolysis.[5,11] These PBGs are readily soluble in a range of organic materials and possess relatively high quantum yields. Ultraviolet irradiation of these materials results in intramolecular hydrogen abstraction by the excited nitro group that is then followed by a redistribution process that culminates in the release of a free amine, carbon dioxide, and 2-nitrosobenzaldehyde (Scheme 1). Having been released, the free amine can proceed to catalyze chemical transformations.

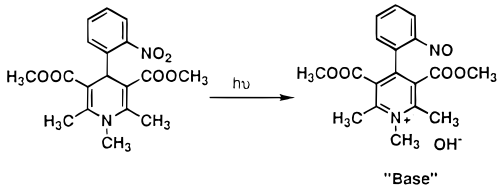
Analogous to the 2-nitrobenzyl carbamates, *N*-methylnifedipine when exposed to UV light also undergoes a hydrogen abstraction and rearrangement process to yield an alkylammonium hydroxide base[4] (Scheme 2). It might be expected that this base would be a stronger base than the amines derived from the 2-nitrobenzylcarbamates, however, data relating to this and the quantum yield for conversion do not appear to be available.

Scheme 1. Photodecomposition of 2-Nitrobenzyl Carbamates

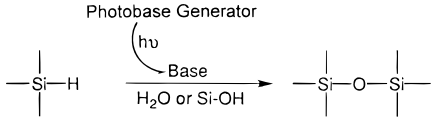


Photobases Prepared: R = Ph-CH_2-; Ph-; CH_3-$(CH_2)_7$-

Scheme 2. Photorearrangement of *N*-Methylnifedipine



Scheme 3. Photobase-Catalyzed Silyl Hydride Hydrolysis and Crosslinking



Within the realm of silicone chemistry it is known that the silyl hydride functionality will undergo hydrolysis to silanol when exposed to moisture in the presence of a base catalyst.[14−16] In some instances the transformation is very rapid, with concomitant generation of hydrogen and the formation of Si−O−Si linkages from base-catalyzed reactions between available silyl hydrides and the generated silanol functionalities. The new photocure technology introduced in this report takes advantage of the high sensitivity of the silyl hydride link to base-catalyzed hydrolysis and reaction, and controls it by the introduction of a latent base that is in the form of a PBG. Irradiation of the PBG results in base generation with subsequent cross-linking of the hydrolyzed silyl hydride linkages, as illustrated in Scheme 3.

Hydrogen silsesquioxane $(HSiO_{3/2})_n$, is an inorganic polymer that when prepared under specific conditions

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forms a stable solution in a wide range of moderately polar and nonpolar organic solvents. Solutions of hydrogen silsesquioxane are quite amenable to spin-coating processes that allow for the preparation of planar uniform thin films on a variety of substrates such as glass, plastics, polished metals, and silicon. These processing advantages, combined with the excellent thermal stability and low dielectric constant after cure of the resins, have contributed to the commercialization of this material as a spin-on-glass material for microelectronics fabrication.[17] The abundance of silyl hydride units within the resin structure and the lack of detectable silanol species make it an ideal candidate for demonstrating this new photobase\Si−H resin cure system. In this report, a preliminary evaluation of the performance of this novel cure system and its utility in providing a new easily photopatternable spin-on-glass material based on hydrogen silsesquioxane (FOx Flowable Oxide) are discussed.

Experimental Section

Preparation of [[(2-Nitrobenzyl)oxy]carbonyl]octylamine.[5] Into a 200-mL round-bottomed flask equipped with a condenser and drying tube were added 10 g of 2-nitrobenzyl alcohol, 100 mL of dry toluene, and 11.4 mL of *n*-octyl isocyanate. Boiling chips were added to the mixture and the solution was heated to reflux for 2 h. The solution was cooled to room temperature, and the organic phase was washed several times with deionized water. After drying over anhydrous sodium sulfate, the solution was filtered and the solvent was removed by rotary evaporation. The solid product was recrystallized twice from hot hexane and dried under reduced pressure to yield 12.5 g of slightly yellow needles, mp 70−71 °C. IR: 3331 cm^{-1} (s, N−H str.), 1692 (s, C═O str.), 1520 (s, asym N−O str.). ^{1}H NMR: δ 0.9 (t, 3H, $-CH_3$), 1.0−1.7 (multiple peaks, 12H, $-CH_2$-), 3.4 (m, 2H, N$-CH_2$-), 4.9 (broad, 1H, N−H), 5.5 (m, 2H, Ar$-CH_2-$O), 7.4−8.2 (multiple peaks, 4H, aromatic C−H).

Preparation of [[(2-Nitrobenzyl)oxy]carbonyl]benzylamine.[5] Into a 25-mL round-bottomed flask equipped with a condenser, drying tube, and magnetic stirrer were added 5 g of benzyl isocyanate, 5.75 g of 2-nitrobenzyl alcohol, and 10 mL of dry toluene. The reaction was stirred at reflux for 3 h and cooled to room temperature. An additional 50 mL of toluene was added to the solution, which was then washed several times with deionized water and dried over anhydrous sodium sulfate. After filtration, the solvent was removed by rotary evaporation, and the solid product recrystallized three times from a hexane/toluene solvent system. The product was isolated as slightly yellow crystals, 7.3 g, mp 110−111 °C. IR: 3308 cm^{-1} (s, N−H str.), 1696 (s, C═O str.), 1520 (s, asym. N−O).

Preparation of *N*-Methylnifedipine.[18] In a three-necked round-bottomed flask equipped with a magnetic stirrer and condenser, 12 g of nifedipine (Sigma Chemical) was dissolved in 50 mL of dry tetrahydrofuran under a nitrogen atmosphere. With constant stirring, 1.66 g of sodium hydride dispersed in oil (60% NaH) was added to the flask. The solution assumed a red color, with the sodium salt of nifedipine precipitating from solution as orange crystals. To the solution was then added 10 mL of methyl iodide, and the reaction was heated to 38 °C. Slow dissolution of the precipitate was observed and after 1 h no precipitate remained. To the solution was then added 200 mL of warm ethyl acetate (warm to avoid precipitation of the product), and the organic phase was washed three times with deionized water. The isolated organic phase was dried over anhydrous sodium sulfate and filtered, and the solvent was removed by rotary evaporation. The product was dissolved in 200 mL of hot methyl isobutyl ketone and recrystallized by slowly adding hexane to the solution. Following a second recrystallization, 8.9 g of product was isolated as yellow crystals, mp 184−187 °C. IR: 1690 cm^{-1} (s, C═O), 1524 (s, asym. N−O str.). ^{1}H NMR: δ 2.5 (6H, s, $-CH_3$), 3.3 (3H, s, N$-CH_3$), 3.6 (6H, s, $-OCH_3$), 5.7 (1H, s, C−H), 7.2−7.6 (4H, m, aromatic C−H).

Thin Film Preparation. The PBGs dissolved in a polystyrene matrix were prepared as follows: Polystyrene (Mw ∼ 45 000) was dissolved in toluene at a concentration of 25 wt %. To this solution was added the PBG at a concentration of 10 wt % relative to polystyrene. The solution was spin coated onto the surface of a clean silicon wafer at a speed of 1500 rpm with a Mikasa 1H-DX II spin-coater. The film was then dried in an oven at a temperature of 100 °C for 1 min. All of the processing steps just described were carried out in a yellow room to avoid premature photodecomposition of the PBG.

The PBGs dissolved in a hydrogen silsesquioxane matrix were prepared as follows: Hydrogen silsesquioxane (Mn ∼ 6 300), was dissolved in electronics grade methyl isobutyl ketone (MIBK) at a concentration of 25 wt % solids. To this solution was then added the PBG at a concentration of 0.5 to 7 wt % relative to the weight of hydrogen silsesquioxane. The solution was then coated onto clean silicon wafers at a speed of 1500 rpm. The films were dried in an oven or on a hotplate at a temperature of 80 °C for ∼30−60 s to remove residual solvent.

Photopatterning and Sensitivity Determinations. To measure the sensitivity profiles, the hydrogen silsesquioxane/PBG films were irradiated using an Ushio Inc. Deep UV Projector Model VIS-500C (4.8 mW/cm^2 at 254 nm). After a postexposure bake on a hot-plate, the negative patterns were developed by dissolving the non-cross-linked portions of the film by placing the wafer on a spin-coater, covering the surface with a layer of methyl isobutyl ketone, *n*-octane, or toluene, waiting for 15 s, and spinning to remove the solvent layer and dry the film. The remaining film thickness after drying was measured with a Tencor alpa-step 200 thickness profiler. The pattern shown in Figure 9 was obtained by patterning with a Yamashita Denso Homogeneous UV light source (Kin-itsukun) equipped with a 200 W mercury−xenon lamp with a power of 7.5 mW/cm^2 at 254 nm. Broadband irradiation was used in all cases.

General Experimental. Infrared spectra were recorded with a Jasco FTIR spectrometer in the transmission mode for samples coated onto silicon wafers, dispersed in KBr or dissolved in chloroform. TG-DTA was performed with a Rigaku TG8101D thermal analysis system, in air, at a heating rate of 10 °C/min. The ^{1}H NMR analysis was performed with a Brüker ACP300 NMR spectrometer at a frequency of 300 MHz for samples dissolved in chloroform-*d*. The UV−vis spectra for the PBGs dissolved in spectral grade tetrahydrofuran were recorded with a Hitachi U-3210 spectrometer.

Results and Discussion

Preparation of the Photobase Generators. At the time this research was conducted, photobase generators were not commercially available but fortunately they could be derived in simple one-step reactions from readily available chemical precursors. In this work, two different types of PBGs were prepared. The 2-nitrobenzyl carbamate PBGs can be prepared by refluxing a 1:1 mixture of an alkyl isocyanate with 2-nitrobenzyl alcohol in toluene.[5] A variety of carbamates with different amine-leaving groups can be prepared in high yield by this route. For this study, *N*-octyl and *N*-benzyl carbamates were synthesized from octyl isocyanate and benzyl isocyanate, respectively. These two materials are crystalline and can be easily purified by recrystallization. They are also highly soluble in a wide range of polar to moderately polar organic solvents. The thermal stability of the carbamate PBGs in the bulk phase are quite good, with an onset of decomposition of ∼180 °C and rapid weight loss between 200 and 300 °C. At 300 °C, virtually all of the PBG decomposes to gaseous volatiles, suggesting that in a spin-on-glass

formulation the residual PBG may be lost as volatiles during subsequent high-temperature thermal cure steps. A preliminary investigation of the decomposition process by thermogravimetric analysis-mass spectroscopy (TGA-MS) suggests that at temperatures >200 °C, the PBG reverts back to its original starting materials; that is, an alkyl isocyanate and 2-nitrobenzyl alcohol.[19]

A second type of PBG that has received little attention in the literature is the *N*-alkylnifedipine system that generates an alkylammonium hydroxide upon exposure to UV radiation.[4] This system is particularly interesting because a strong base is generated upon photolysis, which may offer faster cure rates and be capable of hydrolyzing more hydrolytically stable Si—H species. The starting precursor, nifedipine, is commercially available and only requires alkylation of the amine functionality to convert it to a PBG.[18] This conversion was readily accomplished by dissolving nifedipine in a dry solvent and adding a strong base, such as sodium hydride, followed by the desired alkyl iodide. The product is crystalline and can be easily purified by recrystallization. The solubility of *N*-methylnifedipine in organic solvents is lower than that for the carbamate PBGs but is still sufficiently soluble at low concentrations to be used as a PBG. Thin films of hydrogen silsesquioxane or polystyrene containing 10 wt % *N*-methylnifedipine have been prepared without evidence for phase separation. With respect to thermal stability, *N*-methylnifedipine is slightly more stable than the 2-nitrobenzylcarbamates with an initial weight loss in air, in the bulk phase, at a temperature just above 200 °C. Decomposition takes place in a two-step process, with 50% loss between 200 and 300 °C, followed by a second loss between 500 and 600 °C. No residual material remained when heated to 650 °C.

Photochemical Conversion of the PBGs to Active Base. Photoconversion of the 2-nitrobenzyl carbamates and *N*-methylnifedipine to active base catalysts occurs as the result of a spontaneous rearrangement of the molecule following hydrogen abstraction by the excited nitro functionality. The initial event involves the photoexcitation of the nitrobenzyl chromophore by UV radiation. The UV—vis spectrum for the [[2-nitrobenzyl)oxy]carbonyl]octylamine PBG dissolved in tetrahydrofuran is shown in Figure 1. The absorption band corresponding to the n—π* transition of the nitro group appears with a maximum at 259 nm ($\epsilon_{259} = 5600$). The UV—vis spectrum for *N*-methylnifedipine in tetrahydrofuran is shown in Figure 2, in which a strong band appears in the region of 300 to 400 nm, with a peak maximum at 332 nm ($\epsilon_{332} = 11\,300$). This band is clearly different in both intensity and energy relative to the 2-nitrobenzyl carbamates despite their origin from what is essentially the same 2-nitrobenzyl chromophore. Because the nitrobenzyl group of *N*-methylnifedipine is not in extended π conjugation with the rest of the molecule, a lowering of the energy level for the excited state cannot be expected. A possible explanation may be that *N*-methylnifedipine in solution forms a complex that lowers the energy of the excited state, however this remains to be explored.

The photochemical reactivity of the 2-nitrobenzyl carbamates and *N*-methylnifedipine PBGs were examined in a polystyrene matrix. The films were prepared by dissolving the PBGs in mixtures of toluene and polystyrene and spin coating the solutions onto silicon wafers to give thin films of polystyrene containing 10 wt % of a given PBG. The photochemical conversion of the PBGs to active base as a function of irradiation dose were monitored by IR spectroscopy. For the PBGs examined in this study, the spectral region from 1400 to 1800 cm^{-1} is particularly informative, with clearly identifiable peaks corresponding to the C═O stretching and N—O asymmetric stretching bands. Figure 3 shows the IR spectra for *N*-methylnifedipine before and after

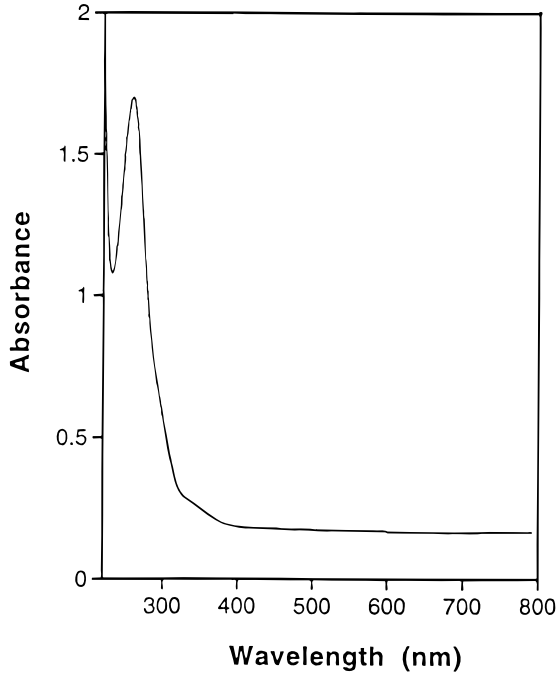

Figure 1. The UV-vis spectrum for [[2-nitrobenzyl)oxy]-carbonyl]octylamine in THF.

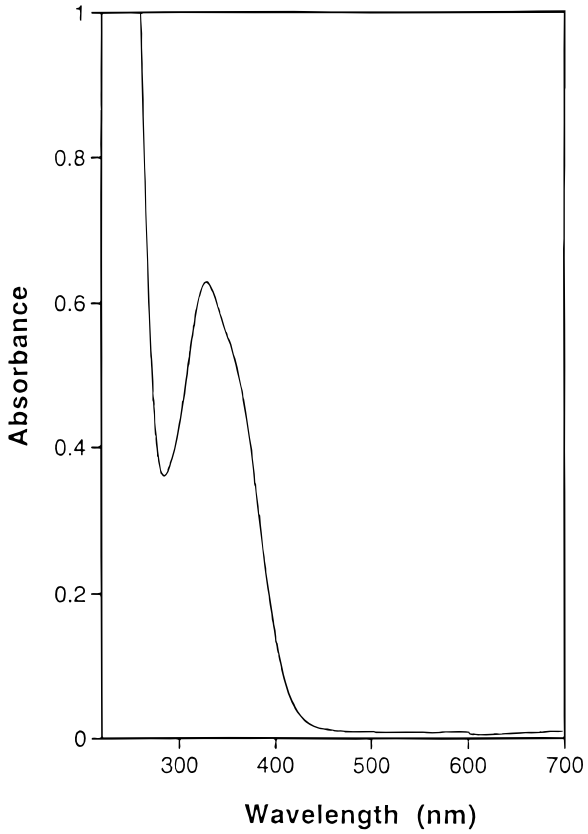

Figure 2. The UV-vis spectrum for *N*-methylnifedipine in THF.

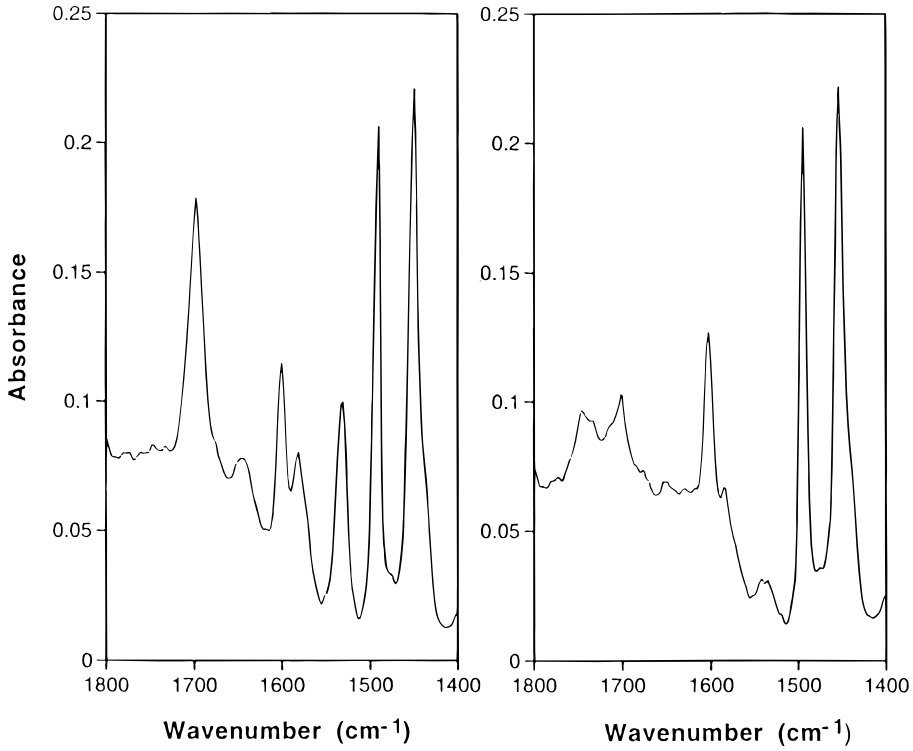

Figure 3. The IR spectra for *N*-methylnifedipine in polystyrene (10 wt %) before (left) and after (right) a 14.7 mJ/cm^2 (at 254 nm) dose of broadband UV radiation.

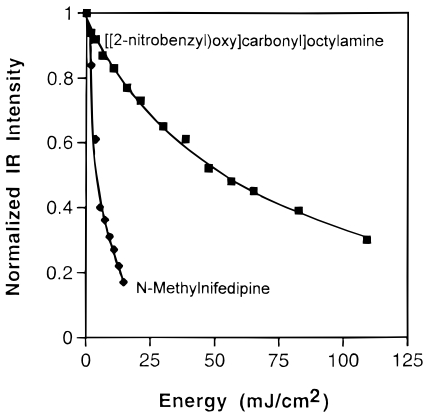

Figure 4. Relative intensity of the IR N−O band as a function of irradiation dose recorded at 254 nm for the *N*-methylnifedipine and [[2-nitrobenzyl)oxy]carbonyl]octylamine PBGs dissolved in polystyrene (10 wt %).

a dose of broadband UV radiation from a high-pressure mercury−xenon lamp (14.7 mJ/cm^2 at 254 nm). Following irradiation, reductions in the intensities of the carbonyl stretch at 1694 cm^{-1}, the C═C overtone at 1578 cm^{-1}, and the asymmetric stretch at 1532 cm^{-1} can be observed. It is interesting to note that upon irradiation of *N*-methylnifedipine, the single carbonyl band disappears and is replaced by two distinct peaks in the same spectral region. This is consistent with a loss of symmetry of the molecule upon conversion to the base, but remains to be examined in detail.

With the polystyrene C═C stretching bands as an internal reference (1493 and 1453 cm^{-1} bands), the degree of conversion of the PBGs to base can be monitored by the relative intensity of the N−O stretching band. Figure 4 shows a plot of the relative intensity of the N−O band as a function of irradiation dose recorded at 254 nm for the *N*-methylnifedipine and [[2-nitrobenzyl)oxy]carbonyl]octylamine PBGs. From this plot it is apparent that under broadband irradiation conditions in a polystyrene matrix the *N*-methylnifedipine PBG undergoes conversion much more rapidly than the carbamate PBG. This result may in part be attributable to the much broader spectral region over which *N*-methylnifedipine is photochemically active and perhaps to the relative differences in quantum yields. To establish that *N*-methylnifedipine is photochemically active in the spectral region above 290 nm, irradiations were performed with a 290-nm high-pass filter placed between the film and the lamp. The IR examination after exposure (37.5 mJ/cm^2 at 254 nm) confirmed that conversion to base had occurred. The same conversion was attempted with a 350−450-nm band-pass filter, again with conversion to the active base compound confirmed by IR. No conversion of the 2-nitrobenzyl carbamate PBGs to base was observed upon irradiation through a 290-nm high-pass filter. The results illustrate that under conditions where irradiation is performed above 290 nm, *N*-methylnifedipine can be used as the PBG.

Photochemical Base Generation and Cure of a Spin-On-Glass Material. *Solution Preparation and Stability.* Hydrogen silsesquioxane with a number average molecular weight of 6300 g/mol and a polydispersity of 2.5, as measured relative to polystyrene standards, was used as the spin-on-glass material. Typically the spin-on-glass is commercially available in an MIBK solution, however, other solvents such as xylene, toluene, simple alkanes, and siloxane fluids can also be used. No modifications of the commercially available molecular weight or molecular weight distribution have been made to optimize the photopatterning process discussed in this report.

Concurrent with the evaluation of the photocure process, solutions of hydrogen silsesquioxane containing the PBG were examined with respect to their relative

Table 1. Gellation Times for Hydrogen Silsesquioxane/PBG Mixtures Dissolved in MIBK at a Concentration of 25 wt % Solids and Placed in White Polypropylene Bottles

photobase generator	environment	gellation time
5 wt % octylamine PBG	white fluorescent light (r.t.)	3 hours
	dark drawer (r.t.)	4 weeks
	yellow room (r.t.)	3 weeks
5 wt % benzylamine PBG	white fluorescent light (r.t.)	6 hours
	dark drawer (r.t.)	4 weeks
	yellow room (r.t.)	3 weeks
2 wt % *N*-methyl-nifedipine	white fluorescent light (r.t.)	1 day
	dark drawer (r.t.)	4 weeks
	yellow room (r.t.)	3 weeks

stability. The PBGs utilized in this study are all amide or amine functional, with the basicity of the nitrogen lone pair greatly reduced through resonance and the electron-withdrawing effects of nearby substituents. However, there was a possibility that a latent weak basicity might undermine the stability of the resin solutions. To test this, solutions of hydrogen silsesquioxane dissolved in standard electronics grade MIBK at a concentration of 25 wt % solids and containing 2−5 wt % PBG relative to resin were prepared. The solutions were placed into 20-mL white polypropylene bottles and then placed under the white fluorescent light of a fumehood or in a dark drawer or in a yellow room, all at room temperature, and the time required for gelation was carefully monitored. Table 1 lists the PBGs, their concentrations, and the times required for gelation. As expected, the solutions exposed to white light gelled within 24 h, however, those stored in a yellow room or a dark drawer were stable for 3 to 4 weeks. Storage of the solutions at lower temperatures and the use of dry solvents are two possible modifications that can be utilized to further increase the shelf-life of the photosensitive compositions. For most of the work discussed in this report, the PBGs were simply dissolved in the hydrogen silsesquioxane/MIBK solutions and the photocure was evaluated within 24 h.

Photocure and Sensitivity Curves for Hydrogen Silsesquioxane/PBG Compositions. The abundance of silyl hydride units within the chemical structure of hydrogen silsesquioxane and the lack of detectable silanol species make it an ideal candidate for evaluating the feasibility of the photobase\Si−H resin cure system. The missing chemical component for the cure of hydrogen silsesquioxane is water, and it was assumed that sufficient trace water from the solvent and atmosphere could be trapped in the film during the coating process. In theory, the conversion of the photobase to base would catalyze the hydrolysis of a fraction of the silyl hydride groups, the product of which would then react with neighboring silyl hydride groups to generate a thermally stable siloxane bridge. The byproduct of the reaction would be a small amount of hydrogen gas that would diffuse from the film. The low molecular weight of this byproduct and the incorporation of oxygen through the introduction of new Si−O−Si linkages means that, in theory, the cure process results in a small weight gain. This reaction is in contrast to other chemically amplified cure systems where the loss of large bulky leaving groups results in a considerable weight loss during the conversion step.[20−22]

To prepare and test these new photopatternable spin-on-glass compositions, a PBG was added to a 25 wt % solution of hydrogen silsesquioxane in MIBK such that

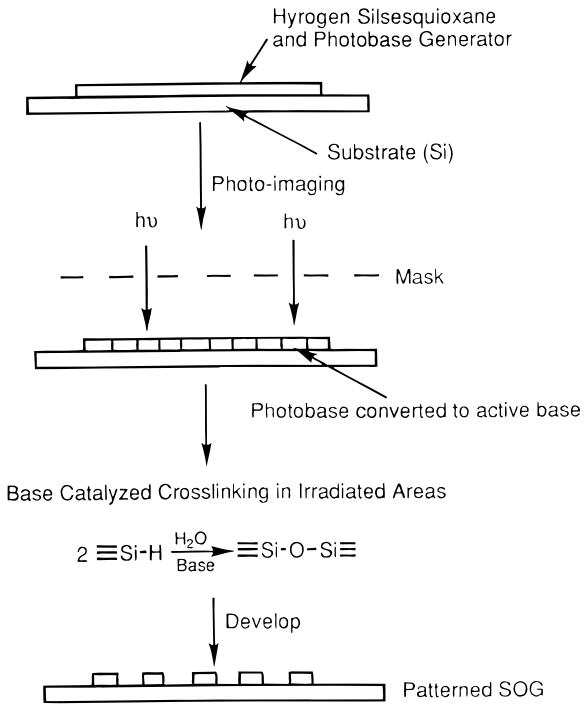

Figure 5. Photopatterning process for hydrogen silsesquioxane/PBG compositions.

a PBG concentration of 0.1 to 7 wt % relative to the weight of the inorganic polymer was obtained. The solutions were filtered through a 0.45-μm filter onto the surface of a silicon wafer and spin coated at a speed of 1500 rpm to give films with a thickness of $\sim$1 μm (the silicon wafers utilized in the coating process were used as received from the manufacturer and were not surface treated). The coatings were prebaked at a temperature up to 100 °C (more typically 80 °C) for 1 min to remove residual solvent. The films were then exposed through a photomask to broadband UV irradiation from a mercury−xenon lamp. This process is illustrated schematically in Figure 5 and was performed in an air atmosphere because the cure chemistry is not sensitive to atmospheric oxygen. The temperature and relative humidity of the room were 22 °C and 50%, respectively (the relative humidity may be an important variable because the cure chemistry relies on trace water being present in the film). Following irradiation, the films were subjected to a short postbaking step to accelerate cure in the dark reaction, followed by image development using a solvent capable of dissolving the nonexposed (non-crosslinked) regions of the film. Typically, MIBK, toluene, or *n*-octane were used as the developing solvents to give clean negative tone images of the photomask etched into the hydrogen silsesquioxane film. Infrared analysis of the films before and after irradiation with UV light showed that very little change in the intensity of the silyl hydride stretching band at 2240 cm^{-1} had occurred. This result indicated that very few silyl hydride groups participate in the cure process, but the conversion was sufficiently high to prevent solubilization of the UV-exposed regions of the film during development.

An important characteristic of photocure systems is their sensitivity to light and as already described, chemically amplified systems have the potential to display very high sensitivity. Optimization of the sensitivity of this photocurable spin-on-glass system

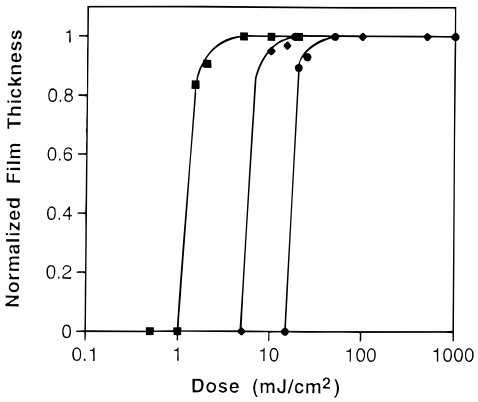

Figure 6. Sensitivity curves for hydrogen silsesquioxane films containing *N*-methylnifedipine at concentrations of 0.5 (circle), 1 (diamond), and 2 (square) wt % developed with *n*-octane after a 150 °C postbake for 1 min.

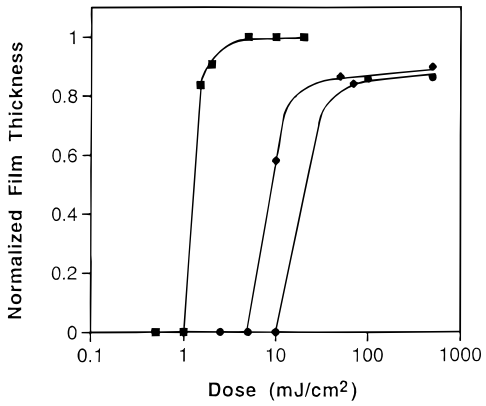

Figure 7. Sensitivity curves for hydrogen silsesquioxane films containing *N*-methylnifedipine at a concentration of 2 wt % developed with *n*-octane after a 150 (square), 100 (diamond), or 80 °C (circle) postbake for 1 min.

requires the evaluation of a series of variables that include the type of PBG, the concentration of the PBG, the level of trace water in the films, the postbaking temperature, the developing solvent, and the resin characteristics, to name a few. In this preliminary survey, work has focused on examining the potential influence of the type of PBG, its concentration in the film, and the postbake temperature on the sensitivity. Sensitivity curves were plotted for ~1-μm-thick films of hydrogen silsesquioxane spin coated onto the nontreated surface of silicon wafers. Hydrogen silsesquioxane films containing [[2-nitrobenzyl)oxy]-carbonyl]-octylamine or *N*-methylnifedipine as the PBGs, at concentrations of 1 to 5 wt % in the film, were easily patterned by exposure to broadband UV irradiation through a mask. However, in the absence of a postexposure bake, the sensitivity was low. The introduction of a postbaking step utilizing temperatures in the range of 80 to 180 °C greatly improved the sensitivity and quality of the imaging process. Figure 6 shows the sensitivity curves for hydrogen silsesquioxane/PBG formulations containing 0.5, 1, and 2 wt % *N*-methylnifedipine. The images were developed with *n*-octane following a postexposure bake of 1 min on a hot-plate heated to 150 °C. The initials slopes of the curves are very sharp ($\gamma > 5$) with sensitivities (D_{50}) of 1.3, 7.6, and 17.8 mJ/cm^2 for films containing 2, 1, and 0.5 wt % PBG respectively.

The effect of postexposure baking temperature on the sensitivity of the hydrogen silsesquioxane/*N*-methylnifedipine system containing 2 wt % PBG in the film is illustrated in Figure 7. A reduction in the 1-min postbake temperature reduces both the contrast and sensitivity as shown for the 150 and 100 °C curves, where the contrast decreases from 4.9 to 2.3 and the sensitivity (D_{50}) from 1.3 to 9.3 mJ/cm^2 at the lower postbake temperature. Sensitivities were also examined for a 1-min postbake temperature of 80 °C, but with different levels of *N*-methylnifedipine dissolved in the films. The sensitivity curves for hydrogen silsesquioxane films containing *N*-methylnifedipine at concentrations of 3, 5, and 7 wt % are shown in Figure 8 (with PBG concentrations of 3 and 5 wt %, the films were developed with *n*-octane, but at 7 wt %, the PBG functioned as a dissolution inhibitor and MIBK was used as the developing solvent). Reasonable contrast ($\gamma > 2.4$) and sensitivity ($D_{50} < 30$ mJ/cm^2) could be obtained under these processing conditions. It is also

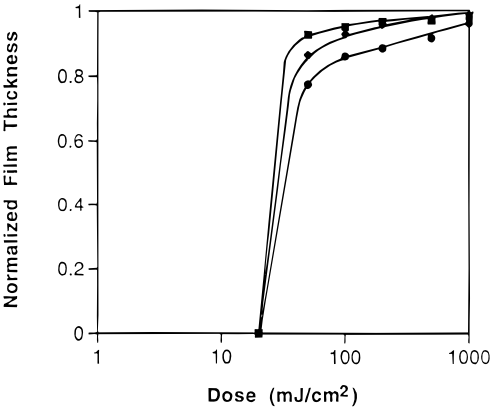

Figure 8. Sensitivity curves for hydrogen silsesquioxane films containing *N*-methylnifedipine at concentrations of 3 (circle), 5 (square), and 7 (diamond) weight percent developed with *n*-octane (MIBK for the latter sample) after an 80 °C postbake for 1 min.

apparent that a significant improvement in the sensitivity is not obtained by using levels of the PBG >5 wt %; however, this result may also be attributable to the limited amount of water in the film under the experimental conditions (it is likely possible to increase the water content of the films by increasing the water content of the coating solvent, however, this remains to be examined).

In addition to *N*-methylnifedipine, the 2-nitrobenzyl carbamate types of PBGs can also be successfully used to pattern hydrogen silsesquioxane films, although at this time the conditions for optimal sensitivity remain to be fully explored.

Resolution of Hydrogen Silsesquioxane/PBG Compositions. In addition to sensitivity and contrast another important characteristic for photopatternable films is resolution, which is defined as the limit to which features are clearly resolvable in the final pattern. Resolution is a function of several variables that include the chemistry of the curable composition, the process conditions, and the quality of the imaging system used to form the pattern. A problem encountered in systems where pattern formation is the result of cross-link generation is that swelling caused by the developing solvent can function to reduce the resolution. Therefore, a careful choice of developing solvents is necessary to minimize swelling in the cured regions yet be capable of completely dissolving the polymer in the uncured

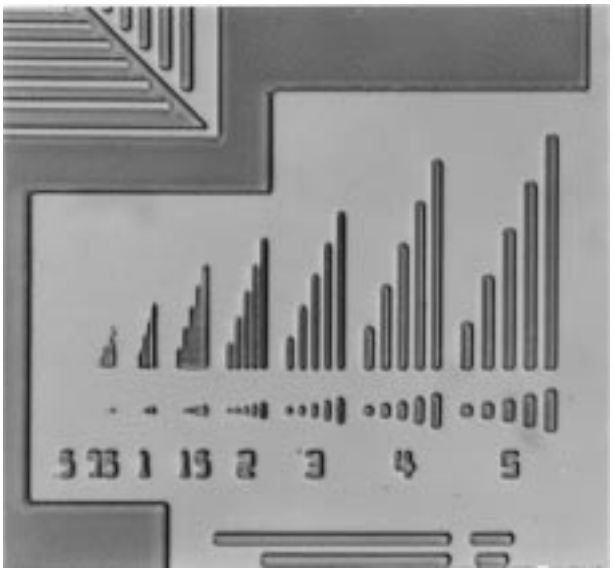

Figure 9. Photomicrograph of a line and space patterned hydrogen silsesquioxane film (thickness = 0.5 μm). The numbers denote the line widths in micrometers.

regions. In this preliminary investigation, MIBK, *n*-octane, and toluene have been used as developing solvents. No significant attempts have been made to survey the performance of other solvents or solvent combinations.

A photomicrograph of the negative image of a line and space pattern etched into a 0.5-μm thick hydrogen silsesquioxane film is shown in Figure 9. The pattern was prepared by prebaking a film containing 2 wt % *N*-methylnifedipine at 80 °C for 40 s, irradiating the film with broadband UV for a total dose of 3 mJ/cm^2 (254 nm) through a photomask with minimum features of 0.75 μm, postbaking at 80 °C for 2 min, and image developing by soaking in MIBK for 15 s followed by spinning at 1500 rpm for 10 s to remove residual solvent from the surface. Given the process and equipment, line and space patterns to a resolution approaching 2 μm were created in the film. Patterns <2 μm were poorly resolved but it is not known if this is the natural limit for this system or a limit defined by equipment or process. Line and space patterns of the same order were also obtained when using the 2-nitrobenzyl carbamates as PBGs.

The results just presented have confirmed hydrogen silsesquioxane/PBG compositions as a facile method for photopatterning a spin-on-glass to micrometer dimensions. The only caution in using this approach is to avoid contamination of the films or the substrates with basic materials, because this will cause premature uncontrolled curing of the film and reduce the resolution of the patterns.

Thermal Stability and Conversion. Following the photopatterning of the hydrogen silsesquioxane films, it may be desirable to completely cure the material to optimize the performance. Hydrogen silsesquioxane when utilized as a carbon-free spin-on-glass material in electronics applications is thermally cured at a temperature of 400 °C under a nitrogen atmosphere. Under these conditions, a low dielectric constant oxide film with excellent surface planarization is obtained.[17] Hydrogen silsesquioxane can also be cured under an oxygen containing atmosphere for partial or complete conversion to a silica glass coating. This procedure offers the potential to provide a range of different film properties through control of the final cure conditions.[17] Figure 10 shows the TGA-differential thermal analysis (DTA) curves for a hydrogen silsesquioxane film containing 1.6 wt % *N*-methylnifedipine as recorded in air. An initial loss of weight appears between room temperature and 100 °C and is due to the loss of volatiles. There is little change in the weight to a temperature of 350 °C, above which the material shows a weight gain. This again is due to the oxidation of the silyl hydride groups to Si−O−Si linkages, which in theory would be expected to result in an increase in the weight of the sample. An important feature of the hydrogen silsesquioxane thermal cure and the photocure processes is that they both function to produce the Si−O−Si cross-links. No other labile cross-linking functionalities that might compromise the thermal stability or mechanical properties of the film have been introduced.

The IR spectrum for a hydrogen silsesquioxane film containing 2 wt % *N*-methylnifedipine, after photopatterning and cure in air at 400 °C, is shown in Figure 11. The spectrum is consistent with that of silica glass with the exception of a small signal at 2240 cm^{-1} that

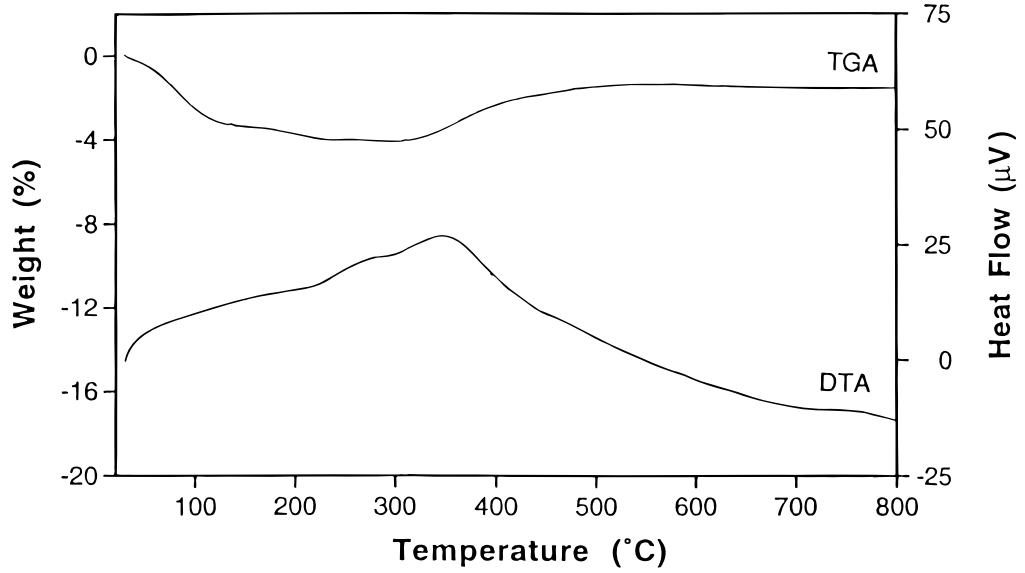

Figure 10. TGA-DTA curves for hydrogen silsesquioxane containing 1.6 wt % *N*-methylnifedipine (rate = 10 °C/min).

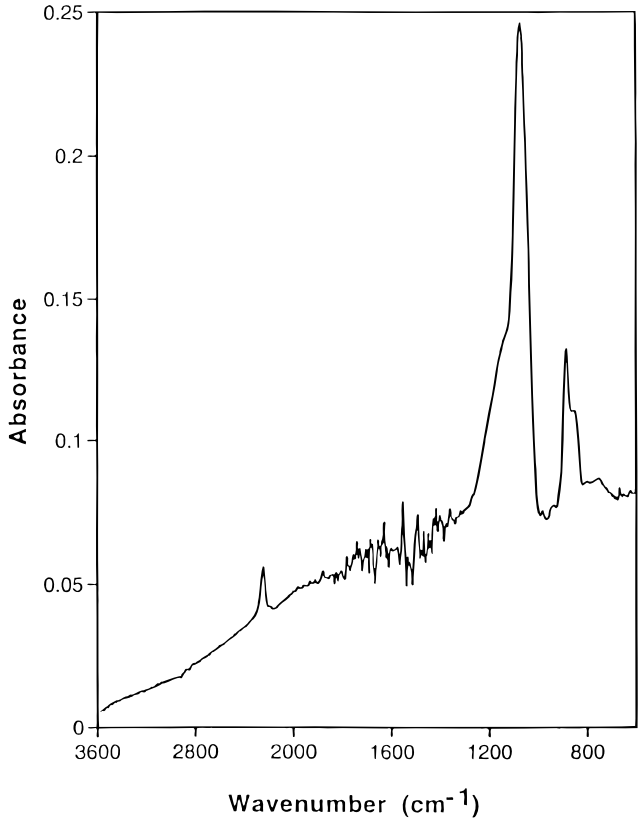

Figure 11. The IR spectrum for a patterned hydrogen silsesquioxane film following conversion to silica glass by heating in air at 400 °C for 1 h.

is indicative of a trace of silyl hydride in the film. There is no indication for carbon-containing species in the film as would be evidenced by C−H stretching bands in the region 2600−2900 cm^{-1}. Microscopic examination of the thermally cured film confirmed that the original pattern was retained on conversion to silica glass.

Conclusions

A novel photocuring process that takes advantage of the rapid hydrolysis of the silyl hydride linkage in the presence of a base catalyst to yield thermally stable siloxane linkages has been demonstrated. Incorporation of a latent base in the form of a PBG allows for the preparation of stable photocurable compositions that can be activated by irradiation with UV light. Stable compositions of a PBG and a commercially available spin-on-glass material, hydrogen silsesquioxane, have been used to prepare photocurable films. Ultraviolet irradiation of these films through a photomask has been utilized to generate a patterned spin-on-glass surface resolvable to micrometer dimensions. The cure process proceeds by hydrolysis of the silyl hydride linkage by residual water present in the film, as activated by the photogenerated base catalyst. Subsequent reaction of the generated silanol with neighboring silyl hydride groups yields a thermally stable siloxane cross-link. The photochemical cross-linking of hydrogen silsesquioxane shows high sensitivity and can be conducted in an air atmosphere. The resultant oxide films can be further cured at elevated temperature either under an inert atmosphere to minimize the dielectric constant or heated in an air atmosphere to complete the conversion to silica glass. The oxidative nature of both the photo and thermal cure processes results in a theoretical weight gain in the film during processing, thus eliminating the film shrinkage observed in other photopatternable spin-on-glass compositions that are based on bulky leaving groups and photoacid chemistries.[20,21]

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References and Notes

(1) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan. T. X. *Chem. Mat.* **1991**, *3*, 394.
(2) Gozdz, A. S. *Polym. Adv. Techn.* **1994**, *5*, 70.
(3) Willson, C. G.; Cameron, J. F.; MacDonald, S. A.; Niesert, C.-P.; Fréchet, J. M. J.; Leung, M. K.; Ackman, A. *Proc. SPIE-Int. Soc. Opt. Eng.* **1993**, *1924*, 354.
(4) Leuschner, R.; Ahne, H.; Marquardt, U.; Nickle, U.; Schmidt, E.; Sebald, M.; Sezi, R. *Microelectron. Eng.* **1993**, *21*, 255.
(5) Cameron, J. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4303.
(6) Fréchet, J. M. J.; Cameron, J. F. *Polym. Mater. Sci. Eng.* **1991**, *64*, 55.
(7) Cameron, J. F.; Fréchet, J. M. J. *J. Org. Chem.* **1990**, *55*, 5922.
(8) Winkle, M. R.; Graziano, K. A. *J. Photopolym. Sci. Technol.* **1990**, *3*, 419.
(9) Weit, S. K.; Kutal, C.; Allen, R. D. *Chem. Mater.* **1992**, *4*, 453.
(10) Davies, J. D.; Daly, W. H.; Wang, Z.; Kutal, C. *Chem. Mater.* **1996**, *8*, 850.
(11) Cameron, J. F.; Willson, C. G.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1996**, *118*, 12925.
(12) Leung, M.-K.; Fréchet, J. M. J.; Cameron, J. F.; Willson, C. G. *Macromolecules* **1995**, *28*, 4693.
(13) McKean, D. R.; Wallraff, G. M.; Volksen, W.; Hacker, N. P.; Sanchez, M. I.; Labadie, J. W. *Polym. Mater. Sci. Eng.* **1992**, *66*, 237.
(14) *Chemistry and Technology of Silicones*; Noll, W., Ed.; Academic Press: New York, 1968; p 90.
(15) Gilman, H.; Dunn, G. E. *J. Am. Chem. Soc.* **1951**, *73*, 3404.
(16) West, R. *J. Am. Chem. Soc.* **1954**, *76*, 6015.
(17) Information regarding Dow Corning FOx Flowable Oxide is available from Dow Corning Corporation.
(18) Iwanami, M.; Shibanuma, T.; Fujimoto, M.; Kawai, R.; Tamazawa, K.; Takenaka, T.; Takahashi, K.; Murakami, M. *Chem. Pharm. Bull.* **1979**, *27*, 1426.
(19) Harkness, B. R.; Tachikawa, M., unpublished results.
(20) Sakata, M.; Kosuge, M.; Jinbo, H.; Ito, T. *Proc. SPIE Int. Soc. Opt. Eng.* **1995**, *2438*, 775.
(21) Ito, T.; Sakata, M.; Endo, A.; Jinbo, H.; Ashida, I. *Jpn. J. Appl. Phys.* **1993**, *32*, 6052.
(22) Ulrich, K. E.; Reichmanis, E.; Heffner, S. A.; Kometani, J. M.; Nalamasu, O. *Chem Mat.* **1994**, *6*, 287.

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