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# Deposition of amorphous silicon dioxide from molecular complexes by a photoresist free process

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## Abstract

Silicon coordination compounds of the general formula $Si(O_2CCH_3)_2(RCOCH_2COR)_2$ (R = methyl, *tert*-butyl), were studied as precursors for the photochemical deposition of amorphous thin films of $SiO_2$. Solutions of the inorganic complexes were spin coated on p-type silicon (1 0 0) substrates and photolyzed at room temperature using a 254 nm UV light. The acetylacetonate derivatives underwent a photochemical reaction [quantum yield ($\Phi$) ∼ 0.01], resulting in the formation of amorphous $SiO_2$ thin films. Auger electron spectroscopy indicated that the final film is carbon-free $SiO_2$ while FTIR spectroscopy indicated the film has characteristics of silica glass rather than silica gel. Thin films prepared with the precursor complexes were photolyzed through a lithography mask, followed by rinsing with a chloroform/petroleum ether mixture, to yielding 2 μm feature patterned lines of $SiO_2$ without need for a photoresist/etching process.

*Keywords:* Amorphous films; Photochemistry; Lithography; Silicon dioxide

## 1. Introduction

$SiO_2$ is one of the most important materials in electronic devices [1]. For example, it is used as a gate dielectric in metal oxide semiconductors (MOS) transistors, as insulator between interconnect levels, and as protective/passive coatings [2,3]. The importance of $SiO_2$ stems from its dielectric constant and the excellent electronic properties of the Si/$SiO_2$ interface [4]. There are several methods for growing $SiO_2$ films including thermal oxidation of silicon [5], low pressure chemical vapor deposition (LPCVD) [6–8], and plasma enhance chemical vapor deposition (PECVD). Other methods to prepare thin films of $SiO_2$ include sputtering and chemical vapor deposition (CVD). As in most deposition and etching processes used in microelectronics device fabrication, kinetically controlled reactions such as reactant adsorptions, surface oxidation (or reduction) and byproduct removal are driven by energy delivered to the surface via substrate heating or by other means including plasma and photon or ion bombardment. These methods have the disadvantage that the substrate may reach temperatures high enough to induced surface diffusion and may cause damage to the desired device [9]. The development of deposition methods that cause minimal device damage are of interest and have attracted great attention [10].

$SiO_2$ layers can also be formed at low temperature by use of deposition methods like anodic oxidation, metal enhance oxidation, UV–ozone oxidation, sol–gel, spin-on-glass, etc. A favorite process to deposit $SiO_2$ is the sol–gel process, which involves the transition of a system from a liquid “sol” (mostly colloidal) into a solid “gel” phase. The most used precursors for $SiO_2$ deposition are tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) [11]. One of the most attractive features of the sol–gel method is that thin films can be prepared without need for expensive equipment and at low processing temperatures [12]. In spite of much effort, sol–gel derived films have micron sized pores and organic impurities in their structures, and thus actually require heat treatments at temperatures above 400 °C to obtain a dense homogeneous structure [13–15]. Another low temperature technique for deposition of $SiO_2$ is spin-on-glass (SOG). SOG thin films are promising, because the process is simple and causes no damage [16]. Currently, $SiO_2$ deposited by SOG is widely use as an interlayer between metal intercon-

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nections in large scale integrated (LSI), and it is effective for planarization on rough surfaces. Some applications of this technique are also envisioned in the area of optical waveguides [17]. Moreover, these inorganic SOG films (silicate-based polymers) have superior adhesion compared with CVD films and a great capacity for planarizing surfaces with severe topography [18]. Although SOG films systematically need thermal annealing, the choice of silica as a material eliminates problems caused by oxygen deficiency around the silicon atom, as is generally found in CVD and sputtering films [19].

As indicated, silicon oxides are indispensable materials for MOSFET gates and passivation of LSIs. A selective deposition of an oxide on a surface is a desirable asset for any deposition method. Local oxidation on hydrogen passivated silicon surfaces has been introduced using STM, AFM, or electron beam lithography [20]. Of course, these methods are not suitable for large area patterning due to the long writing times and cost of operation. Optical lithography is an alternative way to deposit $SiO_2$ selectively. However, photochemical CVD is the only previously reported approach to directly deposit $SiO_2$ patterns [21]. It is important to emphasized that deposition of metal oxide pattern without the used of photoresist/etching process is highly desirable so our interest in a method to directly pattern materials using molecular precursors [22]. Our approach involves the use of a photosensitive inorganic complex that can be deposited on silicon substrates by spin coating. The resultant amorphous thin film can be selectively irradiated by UV light through a lithography mask. The film reacts in a similar fashion to a negative-tone resist. The exposed areas will convert into a metal or metal oxide, which is insoluble in the developing solvent. Upon rinsing, the unexposed areas will be removed leaving a patterned metal or metal oxide on the surface.

In this paper, we report our study of silicon compounds containing acetate and 1,3-diketo ligands of the type $Si(O_2CCH_3)_2(RCOCHCOR)_2$ (R = methyl, *tert*-butyl), on silicon (1 0 0) surfaces and their photochemical reactivity. In this study, we explore the development of these as precursors for the photochemical deposition of thin films of $SiO_2$. We also are able to establish procedures for the successful use of these materials for the patterning of micron feature size patterns without using photoresist/etching processes.

## 2. Experimental

All synthetic procedures were performed under anhydrous nitrogen atmosphere using standard Schlenk techniques. Tetraacetoxysilane, 2,4 pentandione, 2,2,6,6 tetramethyl-3,5-heptadione, chloroform and petroleum ether were purchase from Aldrich. 2,4 Pentandione, 2,2,6,6 tetramethyl-3,5-heptadione were dry and distillated prior to use. FTIR spectra were obtained using a Bomem-Michelson 120 FTIR spectrometer. Electronic absorption spectra were obtained in the range from 190 to 800 nm using a Hewlett Packard HP8452A photodiode array spectrophotometer. Auger electron spectra were obtained using a PHI double pass cylindrical mirror analyzer (CMA) at 1 eV resolution. Films thickness was determine using a Leitz Laborlux 12MES optical microscope with a Michelson interference attachment. The irradiation source was a 254 nm low pressure Hg lamp from Orion, Co. Cut off filters and a water filter were used to remove unwanted wavelengths and thermal effects, respectively.

### 2.1. Synthesis of silicon complexes

Following the synthetic approach of Pike and Loungo [23], the compounds *bis*(2,4-pentadiono)diacetatosilicon(IV) ($Si(acac)_2(O_2CCH_3)_2$) and *bis*(2,2,6,6-tetramethyl-3,5-heptadiono)diacetatosilicon(IV) ($Si(t\text{-butylacac})_2(O_2CCH_3)_2$) were synthesized. In the synthetic approach, silicon(IV) tetraacetate was refluxed with the corresponding diketone in chloroform for 3 h under nitrogen. After the evolution of acetic acid was complete, a white yellow precipitate was isolated by cooling the solution. The products were purified by successive precipitation from chloroform/petroleum ether.

### 2.2. Film preparation

Silicon (1 0 0) wafers were cut into 2 cm × 2 cm chips and cleaned in $H_2O_2/H_2SO_4$ mixtures to remove organic contaminants. The thin films were deposited on the chip by spin coating a chloroform solution of the silicon acetate diketonate complex at 3000 rpm for 30 s.

## 3. Results

Silicon diacetato *bis*(β-diketonate) complexes were initially described by Plitke, et al. (Fig. 1). In the $Si(acac)_2(O_2CCH_3)_2$ complex, both monodentate acetato ligands and bidentate acetylacetonate ligands are found. Thin films of both $Si(acac)_2(O_2CCH_3)_2$ and $Si(tert\text{-acac})_2(O_2CCH_3)_2$ were prepared by spin coating from a chloroform solution and characterized by UV–vis and FTIR spectroscopies.

The FTIR absorption spectrum of a thin film of $Si(acac)_2(O_2CCH_3)_2$ shows strong absorption bands at 1694, 1570, 1545 and 1289 $cm^{-1}$. These bands are associated with the carbonyl group in the carboxylate and acetylacetonate groups. The bands at 1694 and 1289 $cm^{-1}$ are associated with the symmetric and antisymmetric modes of the carboxylate group. The energy difference between the symmetric and antisymmetric bands, a parameter often used to characterize the bonding mode, is consistent with a monodentate carboxylate group ($\Delta\bar{\upsilon} = 405\,cm^{-1}$). This agrees with the published experimental structure [4]. Coordination of the acetylacetonate ligand is confirmed

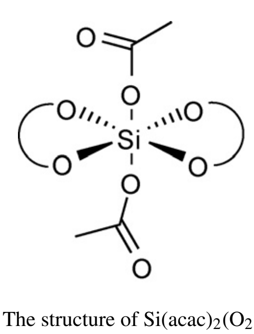

Fig. 1. The structure of $Si(acac)_2(O_2C_2H_3)_2$.

Table 1
Representative FTIR and UV Spectroscopic data for silicon complexes as thin films on silicon

| Complex | Absorption ($\varepsilon$, mol$^{-1}$ cm$^2$) | | Assignment |
|---|---|---|---|
| | FTIR (cm$^{-1}$) | UV (nm) | |
| $Si(acac)_2(O_2C_2H_3)_2$ | | 248 ($1.2 \times 10^6$) | Carboxylate CT |
| | | 290 ($3.0 \times 10^6$) | acac CT |
| | 1694 ($6.5 \times 10^5$) | | $\nu_a(CO_2)$ |
| | 1570 ($7.4 \times 10^5$) | | $\nu_{C=C}$(diketone) |
| | 1545 ($9.0 \times 10^5$) | | $\nu_{C=O}$(diketone) |
| | 1289 ($3.4 \times 10^5$) | | $\nu_s(CO_2)$ |
| Si(*t*-butylacac)$_2$($O_2C_2H_3$)$_2$ | | 248 ($6.0 \times 10^5$) | Carboxylate CT |
| | | 306 ($1.9 \times 10^6$) | *t*-Butylacac CT |
| | 1701 ($7.3 \times 10^5$) | | $\nu_a(CO_2)$ |
| | 1549 ($1.8 \times 10^6$) | | $\nu_{C=C}$(diketone) |
| | 1516 ($1.4 \times 10^6$) | | $\nu_{C=O}$(diketone) |
| | 1277 ($1.2 \times 10^6$) | | $\nu(CO_2)$ |

by the shift of the carbonyl group from 1600 cm$^{-1}$ in the free ligand to the observed absorption in the complex at 1545 and 1570 cm$^{-1}$. Deformation vibrations from the alkyl groups in the region from 1500 to 1350 cm$^{-1}$ are also evident. The FTIR of the film correlates with the literature values reported for the complex in a KBr disk [24]. All the results are consistent with the complex in the film having a structure similar to the previously reported structure in other media.

The same procedure was followed to obtain the FTIR of a film of Si(*t*-butylacac)$_2$($O_2CCH_3$)$_2$ on silicon. The vibrations from the carbonyl group on the acetate and *tert*-butylacetylacetonate ligands dominate the spectrum. The symmetric and antisymmetric vibration bands due to the carboxylate group are found at 1701 and 1277 cm$^{-1}$, respectively. The energy difference between the antisymmetric and symmetric vibrations of the carboxylate group ($\Delta\bar{\upsilon} = 424$ cm$^{-1}$) also agreed with a monodentated carboxylate [25]. The strong absorptions in the region 1600–1500 cm$^{-1}$ are characteristic of a chelating acetylacetonate group, confirming the bidentate bonding of the *tert*-butylacetylacetonate group. The deformation vibrations due to the $CH_3/CH_2$ groups appeared at 1410 and 1364 cm$^{-1}$, in agreement with the expected range from 1450 to 1250 cm$^{-1}$ [26]. The absorption bands for the complexes studied are summarized in Table 1.

The solid-state electronic spectra of $Si(acac)_2(O_2CCH_3)_2$ and Si(*t*-butylacac)$_2$($O_2CCH_3$)$_2$ as thin films were also determined. The same spin coating technique described was used to form optical quality thin films of $Si(acac)_2(O_2CCH_3)_2$ on $CaF_2$ optical flats. The spectrum is well resolved and shows two absorption bands in the charge transfer region. These transitions are localized at 248 and 290 nm. Holm and Cotton have reported that acetylacetonate complexes are characterized by strong absorptions in the 270–300 nm region [27]. Therefore, the latter absorption at 290 nm can be assigned as LMCT due to the acetylacetonate group. The former absorption is the LMCT transition associated with the carboxylate group.

The same procedure was followed to obtain the solid-state UV–vis spectrum of Si(*t*-butylacac)$_2$($O_2CCH_3$)$_2$. Again, two absorptions are observed at 248 and 306 nm. The absorption at 248 nm corresponds to the carboxylate to silicon charge transfer transition. The transition at 306 nm is assigned as the terbutylacetylacetonate to silicon charge transfer transition. The UV–vis spectra are also summarized in Table 1.

### 3.1. Photochemistry of thin films of the complexes

A thin film of Si(*t*-butylacac)$_2$($O_2CCH_3$)$_2$, was prepared as above and the FTIR spectrum obtained. The film was photolyzed at 254 nm wavelengths and the FTIR spectrum recorded again. This process was repeated and the result is summarized in Fig. 2. As previously indicated, a water filter was used to remove thermal effects of UV irradiation.

During the photolysis of Si(*t*-butylacac)$_2$($O_2CCH_3$)$_2$, the intensity of the absorption bands associated with the carboxylate (1701 and 1277 cm$^{-1}$) and *tert*-butylacetylacetonate ligands (1549 and 1516 cm$^{-1}$) decreased upon photolysis. The FTIR bands of the alkyl groups were also observed to decay. It is notable that bands associated with both the diketonate and the

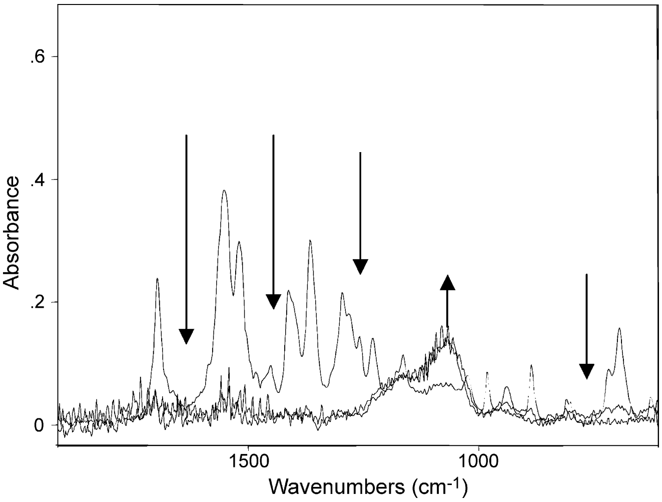

Fig. 2. The FTIR spectra associated with the photolysis of a thin film of Si(*t*-butylacac)$_2$($O_2CCH_3$)$_2$ for 1, 5, 20 and 35 min. Some spectra have been omitted for clarity.

Table 2
Composition of $SiO_2$ thin films produced by the photolysis of β-diketonates precursor films as determined by Auger electron spectroscopy

| Precursor complex | Sputtering time (s) | Atomic percent as deposited | | | Atomic percent after annealing at 100 °C | | |
|---|---|---|---|---|---|---|---|
| | | Si | O | C | Si | O | C |
| $Si(acac)_2(O_2C_2H_3)_2$ | 0 | 22 | 50 | 28 | 33 | 67 | $0^a$ |
| | 30 | 23 | 54 | 23 | 34 | 66 | $0^a$ |
| $Si(t\text{-butylacac})_2(O_2C_2H_3)_2$ | 0 | 19 | 46 | 35 | 32 | 68 | $0^a$ |
| | 30 | 20 | 48 | 32 | 30 | 70 | $0^a$ |

[a] Below detection limits.

carboxylate ligand decayed at similar rates during the photolysis. As a result we obtained no evidence for thermally stable intermediates during the photochemical reaction.

The growth of a broad absorption band in the region from 1241 to 1000 $cm^{-1}$, with a peak centered at 1039 $cm^{-1}$ was observed. This band is associated with the deformation vibration of the Si–O–Si bonds in the silica network [28].

The thin film formed in this reaction was analyzed by Auger electron spectroscopy. Films formed by the photolysis of $Si(t\text{-butylacac})_2(O_2CCH_3)_2$ were composed of silicon (19%), oxygen (48%) and carbon (35%). Sputtering with Ar ions only slightly changed the film composition. The sample was then annealed at 200 °C for 15 min and the analysis repeated. Analysis of the film after heat treatment indicated that it was composed of only silicon (30%), oxygen (70%) with no signal attributable to carbon. The results are summarized in Table 2.

A similar experiment was conducted with a thin film of $Si(acac)_2(O_2CCH_3)_2$ on a silicon surface. Photolysis of this film resulted in a loss of all absorption bands associated with the complex. The loss of all bands occurred in approximately the same ratio and no evidence for thermally stable intermediates was obtained. A broad absorption band indicated the presence of Si–O–Si bonds in the product film. Auger electron spectroscopy indicated that the film as initially formed contained 20–30% carbon. A brief heat treatment resulted in the loss of all detectable carbon from the film.

Resist-free lithography was demonstrated with thin films of the silicon(IV) complexes. In a typical experiment, a chloroform solution of $Si(acac)_2(O_2CCH_3)_2$ was spin coated on a silicon chip. A thin film was formed and a photolithography mask was clamped directly on the film. The film was then exposed to the UV light through the lithography mask. After exposure, the mask was removed and the silicon chip was developed with chloroform, dissolving the unexposed areas; and leaving a pattern of 2 μm resolution on the silicon surface (Fig. 3).

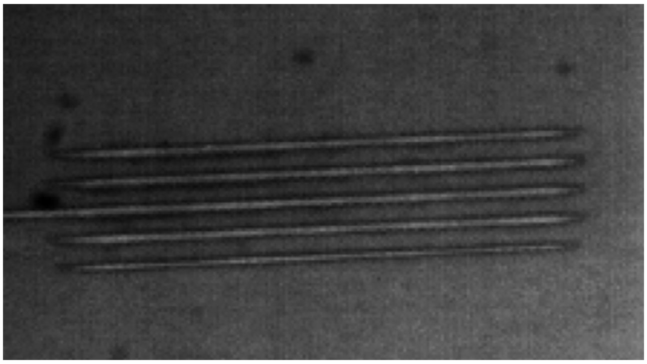
Fig. 3. Optical micrograph of patterned silicon dioxide structures formed by the photochemical deposition from a thin film of $Si(acac)_2(O_2C_2H_3)_2$. Lines are 50 μm × 2 μm.

### 3.2. Quantum yields

Quantum yields were measure as an indication of the efficiency of the photochemical reaction. Previous studies have provided equations, which describe the time evolution of the amount of photoreaction as function of photolysis time [29]. When considering the thermal instability of the silicon complexes, the quantum yield can be calculated using Eq. (1) (see Appendix A for derivation).

$$A_t = A_0\, e^{[-(2.303\varepsilon I_0 \Phi+\kappa)t]} \qquad (1)$$

In this equation, $\varepsilon$ is the extinction coefficient of the molecular complex at the irradiation wavelength of 254 nm, $I_0$ the light intensity (Einstein s), $\Phi$ the quantum yield of the reaction and $\kappa$ is the thermal decomposition rate constant.

A thin film of $Si(t\text{-butylacac})_2(O_2CCH_3)_2$ was prepared and its thermal decomposition monitored by FTIR. In order to account for any effect of thermal heating of the sample during photolysis, the sample was exposed with the same source but with the lamp directed at the back side of the silicon (i.e. the non coated face). Because of the high thermal conductivity and thickness (∼300 μm) of the silicon chip used, the temperature gradient between the front and back of the substrate is assumed to be minor. FTIR spectra were recorded at several time intervals to monitor the loss in intensity. From that data, a thermal decomposition constant $\kappa$ of $8.94 \times 10^{-6}\ s^{-1}$ was calculated.

The photolysis of a thin film of $Si(t\text{-butylacac})_2(O_2CCH_3)_2$ has been described. From the data collected in that experiment a plot of the decay of the absorbance at 1701 $cm^{-1}$ versus time was constructed and is shown in Fig. 4. The analysis of the exponential graph indicates that the decay of the complex was consistent with a first order exponential, indicative of a one-photon process. Using the thermal decomposition constant calculated previously in equation 1 a fit to the data provided a quantum yield of $0.014 \pm 0013$ for the disappearance of $Si(t\text{-butylacac})_2(O_2CCH_3)_2$.

Table 3
Thermal decomposition rates and quantum yields for the reaction of the silicon(IV) complexes

| Complexes | $I_0$ (Einstein s) | $\varepsilon_{UV}$[a] ($cm^2\ mol^{-1}$) | $k$ ($s^{-1}\ K^{-1}$) | $\Phi$ |
|---|---|---|---|---|
| $Si(acac)_2(O_2C_2H_3)_2$ | $1.6540 \times 10^{-8}$ | $1.00 \times 10^{6}$ | $3.00 \times 10^{-5}$ | $(6.6 \pm 1.9) \times 10^{-3}$ |
| $Si(t\text{-butylacac})_2(O_2C_2H_3)_2$ | $1.3461 \times 10^{-8}$ | $3.28 \times 10^{5}$ | $8.94 \times 10^{-6}$ | $(1.4 \pm 0.1) \times 10^{-2}$ |

[a] Extinction coefficient at 254 nm.

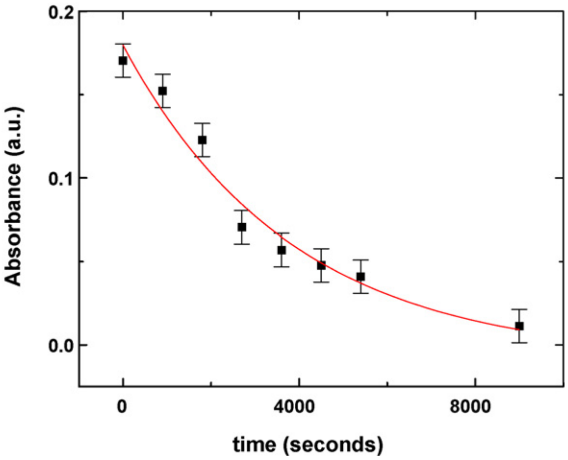

Fig. 4. Exponential decay for the photolysis of $Si(t\text{-butylacac})_2(O_2C_2H_3)_2$ in air at 1701 $cm^{-1}$.

A similar process was undertaken with a thin film of $Si(acac)_2(O_2CCH_3)_2$. The rate of the thermal decay of this complex was measured under the photolysis conditions and the constant for thermal decay was found to be $3.00 \times 10^{-5}\ s^{-1}\ K^{-1}$. This data was used in conjunction with the results of the photochemical reaction to calculate the quantum yield for disappearance of $Si(acac)_2(O_2CCH_3)_2$ as $0.0069 \pm 0.0018$. These results indicate that although $Si(t\text{-butylacac})_2(O_2CCH_3)_2$ is more thermally stable than $Si(acac)_2(O_2CCH_3)_2$, it is also more photosensitive. All calculated values are presented in Table 3.

## 4. Discussion

Amorphous thin films of $SiO_2$ were prepared on silicon substrates by photochemical decomposition of silicon diacetato *bis*(β-diketonate) complexes. During exposure to 254 nm UV light, the vibration bands due to the carboxylate and acetylacetonate ligands were observed to decrease in their intensity. No evidence of intermediate formation was found and only the growth of a wide vibration band centered at ~1100 $cm^{-1}$ was detected. The bands are in the characteristic region (1100–950 $cm^{-1}$) for the vibration bands of $SiO_2$, indicating the formation of new Si–O bonds during photolysis.

The original Si–O vibrations due to the starting material were seen to decrease in intensity upon photolysis (peaks at 1044 and 1026 $cm^{-1}$ in Fig. 2). A peak centered at 1087 $cm^{-1}$ is seen to grow in, without simultaneous growth of any other absorption bands. Precautions were taken in the careful analysis of the OH region (3300–3500 $cm^{-1}$) of the FTIR spectra. No indication of bands associated with hydroxide formation was found. Kim and Jang have showed that the lack of OH vibrations is indicative of the formation of a silicon oxide matrix that resembles silica glass rather than silica gel type of material [30]. Vibrations in the range from 1000 to 900 $cm^{-1}$ were also observed in the spectra although in low intensity. The Si–OH vibrations are expected in this region of the spectra [3]. These results indicated that the photolyzed film was amorphous silica, with very low levels of OH groups.

Auger spectroscopy showed a high content of carbonaceous products retained in the films produced from the photolysis of $Si(acac)_2(O_2CCH_3)_2$, in contrast to the films produced from the $Si(t\text{-butylacac})_2(O_2CCH_3)_2$. This difference can be attributed to the lower stability of the acetylacetonate complex, resulting in a faster formation of an amorphous matrix which can trap hydrocarbon products before they can escape from the film. The small difference between the surface composition before and after sputtering is consistent with the deposited material being a silicon dioxide matrix with absorbed hydrocarbons. This would also explain the low temperature needed to remove the carbon contamination from the film. After soft annealing, even at short times (~10 min), complete removal of carbon is achieved. This is in contrast to sol–gel systems in which higher temperatures are necessary to remove bound or inorganic forms of carbon [13]. Also in contrast with sol–gel type, we were able to successfully pattern lines with 2 μm feature size without need of photoresist. We do not believe that this feature size is a limitation of this process but rather indicative of the simple optics and mask used for this demonstration.

## 5. Conclusion

In this paper, we have presented the photochemical deposition of $SiO_2$ thin films from molecular precursors such as $Si(acac)_2(O_2CCH_3)_2$ and $Si(t\text{-butylacac})_2(O_2CCH_3)_2$. It was shown that compounds of this type can be used to photochemically deposit optical quality amorphous thin films of $SiO_2$. These films contain low concentrations of O–H groups, making the films more silica glass type rather than silica gel type. Deposited films show carbon contamination; however, carbon-free $SiO_2$ films can easily be formed by brief annealing at low temperatures. The patterning of $SiO_2$ was demonstrated to be compatible with current lithographic techniques. While the lithographic experiments shown here use a long photolysis time to achieve complete conversion to $SiO_2$, developing of patterns does not require completeness. The photolysis time can be shortened by developing the film with a mixture of solvents, like chloroform and petroleum ether mixture. We note that a change in solubility of the photolyzed regions of the film make the selective dissolution of the unphotolyzed regions possible before complete conversion to $SiO_2$. After rinsing, complete conversion to $SiO_2$ can be achieved by a fast thermal annealing or UV flood exposure of the remaining patterned thin film. This process is attractive; as it would limit the amount of time the film would spend in high capital cost optical systems such as steppers. We see great potential of these precursors as source of low dielectric materials.

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## Appendix A

For a reaction with both thermal and photochemical contributions to a conversion of starting material, $S$, to product $P$ we can represent the thermal reaction, characterized by rate constant $k$ by Eq. (A.1) and the photochemical reaction of quantum yield, $\Phi$, by Eq. (A.2).

$$S \xrightarrow{h\nu} P \tag{A.1}$$

$$S \xrightarrow{k} P \tag{A.2}$$

The differential equation describing the change in the amount of $S$ is given by Eq. (A.3). It should be noted that the change in quanta of light in this equation refer only to the light absorbed by the starting material. At any point in time the absorbance of light by the starting material is given by Eq. (A.4) where $x$ is the mole fraction of starting material and $A_t$, $A_0$ and $A_\mathrm{f}$ are the absorbance of the film as at time $t$, zero and infinity. For small absorption values then we can make the approximation that $1 - 10^{-A_t}$ is given by $2.303A_t$ and this results in Eq. (A.5).

$$-\frac{\partial S}{\partial t} = \frac{\partial h\nu}{\partial t}\Phi + kS \tag{A.3}$$

$$\frac{\partial h\nu}{\partial t} = \left[\frac{xA_0}{xA_0 + (1-x)A_\mathrm{f}}\right][1 - 10^{-A_t}]I_0 \tag{A.4}$$

$$\frac{\partial h\nu}{\partial t} = \left[\frac{xA_0}{xA_0 + (1-x)A_\mathrm{f}}\right]2.303A_tI_0 \tag{A.5}$$

$$\frac{\partial h\nu}{\partial t} = 2.303xA_0I_0 \tag{A.6}$$

Since the mole fraction $S$, $x$, is given by $(A_0 - A_t)/(A_0 - A_\mathrm{f})$ then we can solve for $A$ which is then substituted in the denominator of Eq. (A.5) resulting in (A.6). The initial absorbance times the mole fraction starting material is simply the absorbance associated with the starting material and is given by the product of extinction coefficient of the starting material, $\varepsilon^S$, and the amount of the starting material, $S$. Making this substitution into (A.6) and then substituting the result into (A.3) results in Eq. (A.7). This equation is then rearranged (A.8) and solved to yield (A.9). This equation can be written as (A.10) and the substitution of the ratio of amount of starting material, $S$, at a point in time with the original amount with the ration of the absorbance at a point in time with the original absorbance is valid if the products do not absorb in the region where the absorbance is monitored. This substitution results in (A.11) which yields Eq. (1).

$$-\frac{\partial S}{\partial t} = 2.303I_0\varepsilon^S S\Phi + kS \tag{A.7}$$

$$-\frac{\partial S}{S} = (2.303I_0\varepsilon^S\Phi + k)\partial t \tag{A.8}$$

$$\ln S_0 - \ln S_t = (2.303I_0\varepsilon^S\Phi + k)t \tag{A.9}$$

$$\frac{S_t}{S_0} = \mathrm{e}^{-(2.303I_0\varepsilon^S\Phi + k)t} \tag{A.10}$$

$$\frac{A_t}{A_0} = \mathrm{e}^{-(2.303I_0\varepsilon^S\Phi + k)t} \tag{A.11}$$

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