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半導體表面的有機金屬低維化反應

Miniaturized Structures at Reduced Dimensions of Organometallic Chelates on Semiconductor Surfaces

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Abstract

Fabrication of metallic structures at reduced dimensions poses a great challenge to scientists as the microelectronic and optoelectronic industries are moving to the world of the single-digit nanometer. In order to provide a more detail understanding of the detrimental cause of surface reactions on the gate oxide of silicon MOS structures, studies on the model system of the adsorption and chemical reactions of ethanol on silicon dioxide samples have been performed. To the best of our knowledge, this is the first report on the details of hydrocarbon reactions on metal-free, high-purity silicon dioxide films prepared by thermal oxidation. Key questions related to the production of the breakdown-prone hydrogen-containing species and to the identities of chemical bonds disrupted and formed during ethanol reactions on the silicon dioxide surface are addressed. Discussions about the implications of the results obtained in this study are presented in the context of the role of surface reactions and their products on the stress-induced leakage current.

Key Words: copper CVD, cupric β -diketonate, acetoacetate, Cu film contamination

Introduction

A solid chemical basis of the metal-surface contact technology is essential, upon which not only the microscopic structure-reactivity correlation can be drawn but also the manipulation strategy of the contact chemistry may be extracted. This may explain why the diverse and perplexing range of chemistries exhibited in chemical vapor deposition used for electronic materials growth and processing has attracted much attention in the microelectronic industry. At the center of the effort, however, lies a

poor understanding of the interaction between a semiconductor substrate and hydrocarbon. The composition and the purity of the metal film deposited by chemical vapor deposition depend in part on the properties of the hydrocarbon chelated to the metal atom in the precursor molecules. It is essential that the precursor used is able to incorporate the desired chemical elements into the substrate and leave out the undesirable contaminants. The interaction and the reactivity of the precursor complex, including its ligands, on the substrate determine the fate of these elements and contaminants.

As copper is more and more popularly used to replace aluminum as the metal of choice in an attempt to reduce the problems related to the conductivity and the electromigration resistance of the contact material, new classes of complexes have emerged as potential CVD precursors of copper. Among the various classes of copper precursors developed, the ones containing β -diketonate hydrocarbons [1-4] appear to be quite promising. Studies reported in the literature [5,6] about the reactivity of bis(tert-butylacetoacetate)copper(II) on the solid surface have shown that thermal deposition of this copper precursors led to incorporation of less carbon and oxygen impurities into the copper film during film formation than those containing other ligands.

In this paper, the chemical reaction of β -diketonate on a single-crystal silicon surface was examined using tert-butyl acetoacetate as a model compound. The goal of this study is twofold: to provide a more complete description of the reaction of alkyl acetoacetate on the silicon surface and to determine the chemical reactivity on Si(100) of the alkoxy group attached to carbonyl in the absence of

metal atoms. Results of this study show that, in contrast to the surface reaction reported in the literature about the chemistry of small ester molecules adsorbed on solid surfaces [7-9], tert-butyl acetoacetate does not adsorb molecularly on the surface at small exposures even at very low substrate temperature. The molecular decomposition may occur through bonding via the ester oxygen to the surface. Isobutene is produced by further dehydrogenation through various β -hydride elimination pathways of surface tert-butyl fragments or tert-butoxy species.

Experimental

This study is carried out using a stainless steel ultrahigh vacuum surface analysis system. The vacuum of the system was achieved by an ion pump, with the base pressure maintaining at $<2 \times 10^{-10}$ torr. The secondary ion mass spectrometry (SIMS) spectra were obtained using a quadrupole mass spectrometer (from VG Microtech) and with the ion gun operated at a base pressure of 3×10^{-9} . A bias voltage of 22 V was applied to the sample to increase measured yield of secondary ions. The typical data collection time was <10 min/spectrum. The temperature-programmed desorption (TPD) spectra were obtained using a quadrupole mass spectrometer (from Inficon) which contains an electron impact ionizer for detecting neutrals. The sample was placed ~ 0.1 in. away from a stainless skimmer which was fitted on the Inficon mass spectrometer. Measurements of the intensities of desorbing species were controlled by interfacing the spectrometer control unit to a personal computer. A heating rate of $3 \text{ }^\circ\text{C/s}$ was used in all TPD experiments.

The Si(100) sample used for this study is antimony-doped ($\rho = 0.0001 - 0.02 \text{ } \Omega\text{-cm}$). Following a wet-chemical cleaning process, the silicon sample was annealed in ultrahigh vacuum to $\sim 900 \text{ }^\circ\text{C}$ followed by a slow cooling to room temperature. The Si(100)-2x1 surface was then generated by repeated cycles of Ar ion sputtering and annealing. Examination of the sample by AES, LEED and SIMS confirmed its cleanness and perfection. The tert-butyl acetoacetate was acquired from Acros and further purified by several freeze-pump-thaw degassing cycles prior to dosing. A variable leak valve with a directed capillary array was used to admit tert-butyl acetoacetate onto the Si(100) surface. The delivery tube terminates 0.5

cm away from the sample surface. All doses reported in this study are in langmuirs ($1 \text{ L} = 1 \times 10^{-6}$ torr-s) of exposure at the sample surface. The reading of the gauge is uncorrected for the corresponding sensitivity.

Results and Discussion

Figure 1 displays the SIMS spectra taken by exposing a clean Si(100) surface to several different doses of tert-butyl acetoacetate at $-170 \text{ }^\circ\text{C}$. These spectra were taken using a primary beam of Ar ions of 2 keV energy to bombard the sample surface. The clean Si(100) surface exhibits a SIMS spectrum with peaks at m/e 28, 56, 84 and 112. These peaks result from the sputter desorption of Si^+ and its clusters from the surface.

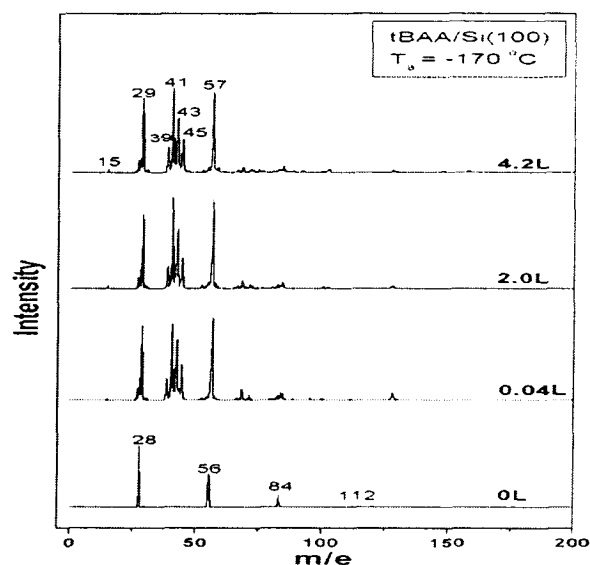


Figure 1. Secondary ion mass spectrum of a Si(100) surface exposed to the indicated doses of tert-butyl acetoacetate. The spectra have been normalized to a constant total peak area between m/e 28 and m/e 31.

Also shown in Figure 1 are SIMS spectra taken after the Si(100) surface was exposed to various amounts of tert-butyl acetoacetate at $-170 \text{ }^\circ\text{C}$. A number of major peaks at m/e 28, 29, 41, 43, 45, and 57 can be identified in each spectrum. None of these spectra exhibits a peak at m/e 158 for molecular sputter desorption of tert-butyl acetoacetate. Since the secondary ions ejecting from the sample may originate from the positions, located a few tens angstroms away from the point of impact, where the ion-induced fragmentation of adsorbates does not take place[10], the absence of the

molecular peak in Figure 1 thus reveals that, in the dose range studied, tert-butyl acetoacetate may decompose completely on the Si(100) surface upon adsorption even at low substrate temperature.

Assuming that the appearance of the m/e 59 signal in Figure 1 is an indication of the presence of tert-butyl acetoacetate molecules, a TPD study was then carried out by tuning the mass analyzer to m/e 59 to monitor if tert-butyl acetoacetate desorbed molecularly, when the substrate temperature was raised, from the Si(100) surface exposed to a small amount of tert-butyl acetoacetate. Figure 2 shows the m/e 59 TPD spectra measured after the Si(100)

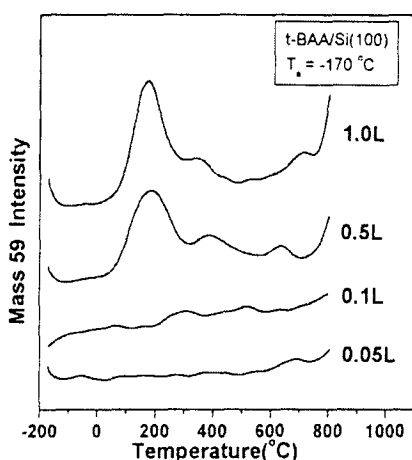


Figure 2. TPD profiles for the m/e 59 species desorbing from Si(100) after various exposures of tert-butyl acetoacetate at -170 °C.

surface was exposed at -170 °C to tert-butyl acetoacetate of 0.05, 0.1, 0.5, and 1.0 L, respectively. As shown in the figure, no desorption signal can be identified in the spectrum when the exposure is less than 0.1 L. The TPD spectrum measured thus shows an absence of molecular signals for tert-butyl acetoacetate desorbing from the sample surface. Coupling with the SIMS results shown in Figure 1, it appears that all tert-butyl acetoacetate molecules of low doses decompose readily upon adsorption on the Si(100) surface at -170 °C.

The observation of the decomposition of all tert-butyl acetoacetate molecules of low exposure on the low-temperature clean Si(100) surface is in contrast to the adsorption chemistry exhibited by many ester molecules [8,9]. The enhanced catalytic reactivity of tert-butyl acetoacetate on Si(100) at -170 °C may be accounted for by tert-butyl acetoacetate bonding to the sample surface either via the ester group [11] or via its diketone moiety. The

tert-butyl fragments are formed when tert-butyl acetoacetate bonds to the surface via the ester oxygen, which induces a bond scission at the tBu-O bond. It results in the appearance of the intense m/e 57 peak in the SIMS spectrum (Figure 1). In addition, the bond cleavage at the tBuO-CO bond results in the formation of the tBuO-Si bond on the surface, which in turn gives rise to the signal detected at m/e 45 (SiOH) in the SIMS spectrum after hydrogenation.

Comparing the TPD profiles measured at different m/e values with the electron-impact-induced fragmentation pattern of isobutene reveals that, following the bond cleavage through binding of tert-butyl acetoacetate via the ester group, isobutene is the major species produced on the sample surface. Shown in Figure 3 are TPD spectra taken with the

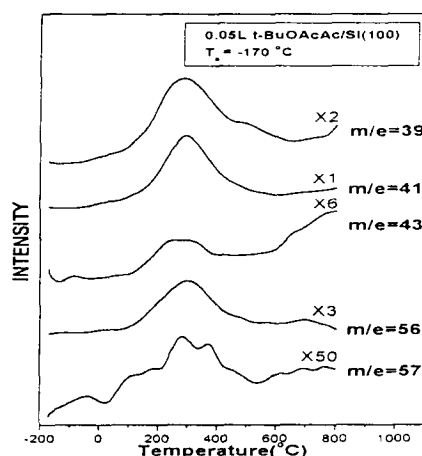


Figure 3. TPD profiles for a 0.05 L dose of tert-butyl acetoacetate on Si(100) at -170 °C.

mass analyzer tuned to the indicated m/e values after the sample surface is exposed to 0.05 L tert-butyl acetoacetate at -170 °C. At this exposure, m/e 56 is observed to desorb in the substrate temperature range between 150 and 400 °C. In addition, the TPD profiles obtained at m/e 39 and 41 are in close resemblance to the one obtained at m/e 56, indicating that the m/e 39 and 41 species are the fragments in the TPD ionizer of the one with m/e of 56. The ratios of the integrated areas of the TPD peaks is also close to the reported ratios [12] of the signals in the electron-impact mass spectrum of isobutene. The large difference in the m/e 41 and m/e 43 TPD profiles shown in Figure 3 excludes the possibility, as predicted based on the electron-impact fragmentation pattern [12] for isobutane, that isobutane is the major product of the surface reaction following the surface-induced bond scission in the

ester group of tert-butyl acetoacetate.

It has been reported that, through a β -hydride elimination reaction, the alkyl [13-16] and alkoxy [17] fragments produced on the Si(100) surface from various alkylmetallic complexes may yield alkenes. The production of alkene from these fragments has been verified in FTIR annealing studies [17] based on a characteristic increase in the intensity of the surface hydride symmetric stretch vibration with the formation of alkene. For the surface-catalyzed decomposition of tert-butyl acetoacetate, isobutene may be produced from the surface tert-butyl fragment through two β -hydride elimination pathways. The first pathway involves the abstraction, by an adjacent silicon dangling bond, of β -hydrogen to form surface hydride. The second takes place when the eliminated hydrogen is deposited onto the Si atom in which the tert-butyl fragment binds. Similar reaction pathways are expected for alkoxy reaction on the surface [17]. Since gaseous isobutene is formed, these mechanisms, when take place, should lead to a clean removal of the alkyl fragments from the CVD precursor containing tert-butyl acetoacetate as the ligand.

Results from TPD studies also suggest that the surface-catalyzed bond scission may occur at the C-C bond in the diketo moiety of tert-butyl acetoacetate. For the surface reaction to proceed through tert-butyl acetoacetate bonding mainly via the carboxylic keto oxygen, acetaldehyde radical may be produced on the surface, which contributes to the observed m/e 43 peak in the SIMS spectrum (Figure 1). Another product is a surface bond carboxylate, which can further react on the surface to yield isobutene. For the surface reaction to proceed mainly via the aceto oxygen, formic acid radical may be produced on the surface, which contributes to the observed m/e 45 peak in the SIMS spectrum (Figure 1), along with the generation of isobutene and isopropenoxy species. The surface reaction proceeding via the aceto oxygen is more favored, due to the steric hindrance of the tert-butyl group, than via the carboxylic keto oxygen. The surface population of isopropenoxy species and formic acid should thus be higher than that of acetaldehyde radical. Since hydrogen has high surface mobility, [18] the isopropenoxy group formed on the surface can subsequently undergo an enol-keto conversion by acquiring surface hydrogen to yield acetone.

Indeed, our TPD studies reveal that a noticeable amount of acetone can be formed on the surface after tert-butyl acetoacetate is decomposed on Si(100). Figure 4 displays the TPD spectra taken from the Si(100) surface exposed to 1.0 L tert-butyl acetoacetate at -170 °C. As shown in the figure, the spectra measured at m/e where the main peaks in the electron-impact mass spectrum of acetone are detected have similar profiles. It confirms that the C-C bond in the diketo moiety of tert-butyl acetoacetate is cleaved mainly by surface bonding via the aceto oxygen.

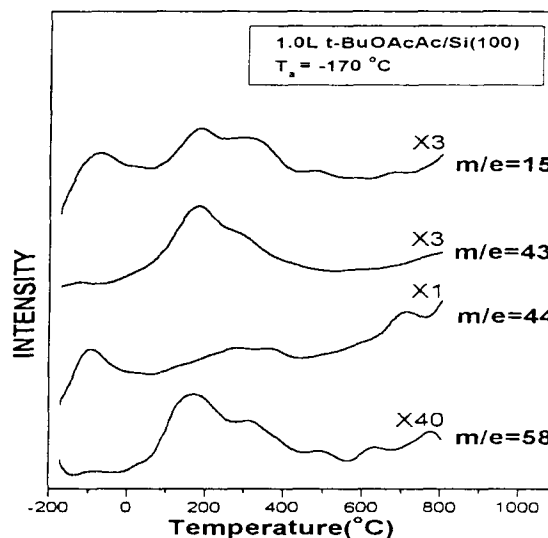


Figure 4. TPD profiles for a 1.0 L dose of tert-butyl acetoacetate on Si(100) at -170 °C

In contrast to the reaction taking place in the solution for β -keto acids and their corresponding carboxylate anions, the m/e 44 TPD profile displayed in Figure 4 shows little desorption of carbon dioxide occurring in the temperature range between 0 and 350 °C where acetone desorbs after the decomposition of tert-butyl acetoacetate. However, at substrate temperature of more than 600 °C, a desorption maximum can be observed. It shifts to higher substrate temperature as the exposure of tert-butyl acetoacetate to Si(100) is increased. The observed m/e 44 desorption at high substrate temperature is not due to the adsorption of ambient carbon dioxide, since the reaction rate of ambient carbon dioxide on Si(100) is negligible [19]. A study of water adsorption on Si(100) [20] has shown that, after dissociative adsorption of water, the hydroxyl decomposed upon heating to produce a substoichiometric silicon oxide, probably in a

bridge-bonded oxygen arrangement [21]. The gasification of the resulting substoichiometric silicon oxide then occurred above 600 °C. In this study, surface hydroxyl groups can be generated from the surface tert-butoxy group produced after a bond cleavage at C-O bond of the ester group. Furthermore, the decomposition of other oxygen-containing species on the surface, such as those produced through the reaction pathways proposed above, may also contribute to the observed peak in the m/e 44 TPD spectrum. Studies on the temperature dependence of ester reactions on Si(100) using TPD^[22] and high-resolution EELS [22] have shown that, by heating to more than 400 °C, carboxylate species will decompose. The oxygen atoms thus formed react with the silicon surface to produce silicon oxide. Subsequent increases of substrate temperature cause silicon oxide to sublime, although the oxide becomes stable to higher substrate temperature [23] when there is greater oxygen coordination for each Si atom. Our observation of a shift of the desorption maximum in the m/e 44 TPD profile to higher temperatures thus supports the catalytic transformation processes discussed above for tert-butyl acetoacetate decomposition on the Si(100) surface.

As discussed above, no molecular peak at m/e 158 can be detected at low exposures of less than 3.0 L. Instead, the measured SIMS spectra are dominated with signals of low masses. The tBAA molecules are rather fragile and appear to decompose on the silicon surface upon adsorption to form species of small masses. This is somewhat surprising considering that, unlike the electron-impact ionization process in gas phase mass spectrometry, the secondary ion ejection process often preserves the adsorbate intact [24]. Further SIMS studies were thus carried out at high exposures of tBAA to examine if tBAA may adsorb molecularly on Si(100). Figure 5 shows the SIMS spectra taken from the Si(100) surface exposed to more than 4.2L of tBAA at -170 C. For all tBAA exposures of less than 3.0 L to Si(100) at -170C, the m/e 129 signal dominates the high-mass region of above m/e 100 and appears as the highest mass in the SIMS spectrum. At an exposure of 4.2 L, m/e 158 became the highest mass in the SIMS spectrum and the high-mass region begins to be dominated by the m/e 103 signal, instead of the m/e 129 signal. Trace amounts of the m/e 232 species became discernible at

a tBAA exposure of 8.3 L, at which other higher mass signals can also be detected. At a tBAA exposure of 16.5 L, the m/e 103 signal became the dominate feature of the entire SIMS spectrum. The signal intensity of the m/e 57 signal remains about the same at tBAA exposures between 0.08 L and 5.0 L and between 8.3 L and 16.5 L. Further increasing the tBAA exposure results in a rapid growth of the m/e 57 signal, which dominates the entire SIMS spectrum at a tBAA exposure of more than 25L.

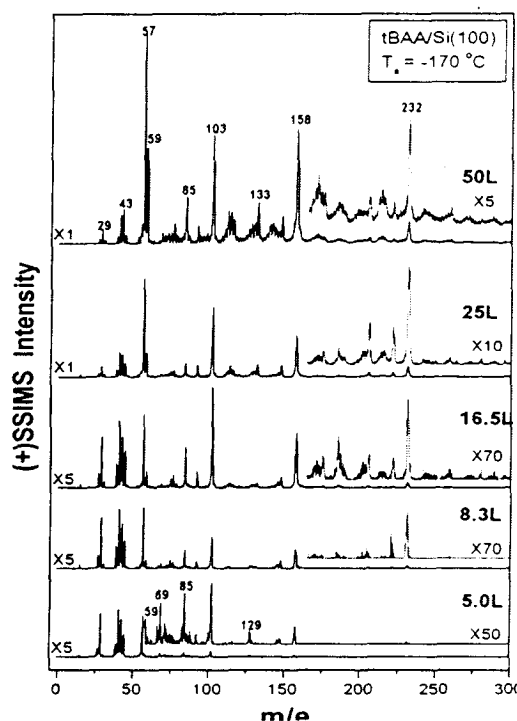


Figure 5. Secondary ion mass spectrum of a Si(100) surface exposed to the indicated doses of tert-butyl acetoacetate. The spectra have been normalized to a constant total peak area of m/e 28

Examining the SIMS intensity at (m/e + 1) and (m/e + 2) of the main peak showed that surface species containing Si may contribute to the SIMS intensity observed at m/e 29, 45, and 57. As shown in the figure, there are small SIMS intensities appearing on the high-mass side of the m/e 29, 45, and 57 signal. An isotope exchange study was carried out to help identifying the surface species and their bonding on the surface. It showed that after first exposing the Si(100) surface to deuterium, the subsequent decomposition of tBAA upon adsorption on such a deuterium-covered surface would result in appearance of SIMS signals extending several m/e's above the main peak for m/e 29, 45, and 57. Both

SiH and C₂H₅ may thus contribute to the observed m/e 29 signal intensity in Figure 5. The m/e 45 signal can be attributed to the presence of SiOH and C₂H₅O on the surface. Because of the large intensity observed at m/e 46 from the deuterated surface, one cannot rule out the possibility that HCOO may also be present on the surface. The m/e 57 signal, on other hand, can be attributed to SiC₂H₅, C₄H₉ (possibly in the form of tert-butyl group, tBu), and CH₃COCH₂. The signals appearing at m/e 27, 39, 41, and 43 are temporarily assigned as mainly due to the presence of C₂H₃, C₃H₃, C₃H₅, and CH₃CO (acetyl group). The m/e 69 signal, which is a major peak at low exposure and its intensity decreases as the exposure is more than 4.2 L, is attributed to SiC₃H₅ and C₄H₅O.

The high-mass signals appearing in the SIMS spectrum are assigned as follows. The m/e 129 signal is the highest mass observed in the low exposure regime of less than 4.2L. Its dominance in the high-mass regime becomes less important and the signal becomes negligible as the exposure is increased. This signal is also associated with the desorption of acetoacetic acid at -82C. Thus, the m/e 129 signal is attributed to the acetoacetate fragment (CH₃COCH₂COO, abbreviated as AcAcO hereinafter) formed on the surface. At low exposure, acetoacetate may bond strongly on the surface, which results in the observed m/e 129 signal for AcAcOSi. As the Si surface is more and more covered by the adsorbate at high coverages, it is expected that the contribution of the Si-containing species to the SIMS signal should decrease as the tBAA exposure is increased. The rise of the SIMS intensity at m/e 103 at 4.2 L, as the relative intensity of the m/e 129 signal decreases at increasing tBAA exposures, may thus be attributed to the increase of the acetoacetate population on the adsorbate-covered surface. It may appear as AcAcOH₂⁺ (m/e = 103) in the SIMS detector. The rise of m/e 103 intensity is also accompanied with the emergence of the molecular signal of tBAA at m/e 158. At the tBAA exposure of 4.2 L, the surface electronic structure may be altered by the adsorbing fragments to such an extent that not all incoming tBAA molecules are decomposed upon adsorption. A tBAA exposure of 4.0 L will thus be arbitrarily assigned for the discussion purpose as reaching a stage of the surface reaction between tBAA and Si(100) when the first overlayer of adsorbates (or the hydrocarbon layer) is

formed..

As the tBAA exposure is increased to above 17 L, there is a substantial increase in the amount of high-mass species present on the surface, as revealed in the SIMS spectrum. Comparing the FAB spectrum with the SIMS spectrum taken with a tBAA exposure of 25L on Si(100) showed that the SIMS signals appearing at m/e 260, 232, 206, 186, 158, 103, 85, 57, 43, 41, 39, and 29 may be related to the fragmentation of tBAA alone, not to the fragments bonding with Si or species produced from surface reactions other than decomposition, although species containing Si may in some cases happen to have a mass equal to one of the list above. The m/e 260 signal is assigned as due to the presence of tBAA-AcAcOH or tBAA-HCOOtBu on the surface. The m/e 232 signal may arise from the presence of tBAA-tBuOH. The m/e 206 signal may be associated with (AcAcOH₂)₂. The m/e 186 signal may be related to the presence of AcAcOAcAc or to a less possibility, tBAA-C₂H₄. The m/e 85 signal may be assigned as due to the presence of AcAc on the surface, and the m/e 57 to CH₃COCH₂ and tBu. Some of the assignments here can be verified using the results obtained from SIMS and TPD studies at increasing substrate temperatures. The m/e 59 surface species is associated with the desorption of acetone and can thus be assigned as due to the presence of (CH₃)₂COH on the tBAA-exposed surface. The substantial increase of the m/e 59 signal at large exposures revealed that tBAA may also be present on the surface in the enol form.

In conclusion, secondary ion mass spectrometry and temperature-programmed desorption studies on the reactivity of tert-butyl acetoacetate on Si(100) showed that, upon adsorption, all tert-butyl acetoacetate molecules of low doses dissociated readily upon adsorption on the surface at substrate temperatures as low as -170 °C. Analyzing the desorption profiles at various masses showed that isobutene and surface hydroxyl and hydride species were produced as tert-butyl acetoacetate decomposed via a bond scission occurring at either the tBu-O or the tBuO-CO bond on the surface. With this process, the tert-butyl fragment may be removed cleanly from the surface, leaving no carbon impurity on the substrate. The surface oxygen generated from the decomposition of tert-butyl acetoacetate, however, survived at high substrate temperature. The copper film produced

using the cupric complex of tert-butyl acetoacetate as its CVD precursor is thus expected to contain oxygen impurity.

*** A portion of the results reported above has been included in a paper to be published in J. Chem. Phys.**

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