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Final Technical Report for "Application of IRIS to Semiconductor Plasma Processing" (CRADA #1031)

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Final Technical Report for
"Application of IRIS to Semiconductor Plasma Processing"
(CRADA #1031)

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Abstract

This report describes technical work done at Sandia National Laboratories (SNL) under CRADA #1031, a Technology Transfer Initiative (TTI) collaborative project with Texas Instruments, Inc. (TI). The overall objective of the work was to improve specific semiconductor processing technologies by the use of numerical modeling and in situ sensors. On a technical level, this collaboration was very successful. The project had three parts, unequal in size. The first part involved the use of the IRIS (Imaging of Radicals Interacting with Surfaces) technique to measure the reactivities of radical species at surfaces. The second, and smallest, part of the work involved the evaluation and transfer of sensor technologies for monitoring source stability in MOCVD (metal-organic CVD) of compound semiconductors. The third part of the work involved experimental and theoretical investigations into the chemical reactions occurring during the CVD of SiO_2 from TEOS (tetraethoxysilane).

I. Introduction

This report describes technical work done at Sandia National Laboratories (SNL) under CRADA #1031, a Technology Transfer Initiative (TTI) collaborative project with Texas Instruments, Inc. (TI). The overall objective of the work was to improve specific semiconductor processing technologies by the use of numerical modeling and/or in situ sensors. Improving the understanding of a process in this way can lead to improved equipment designs and faster process optimization.

Collaborative R&D projects of this kind can provide numerous benefits to all of their participants. In this particular case, the collaboration provided TI with access to SNL's experience in modeling semiconductor processing technologies and unique experimental capabilities, while providing SNL with more insight into industrial applications and problems plus access to process information and data. The topics studied were chosen to be of mutual interest to SNL and TI, but actually have much wider applicability. In the long term, this project should benefit DOE/DP by improving the availability of low-cost, high-reliability microelectronic devices and by strengthening the US semiconductor industry.

The interaction between TI and SNL predated the TTI program. In the summer of 1989, Drs. Mary Ellen Weber and Dan White approached SNL about possible collaborations on the development of chemical reaction mechanisms for numerical models for chemical vapor deposition (CVD) and plasma processing technologies. This led to several visits and technical exchanges between the sites. Researchers from SNL visited TI to transfer modeling software and install it on TI computers. Dr. Weber made extended visits to SNL to work on experiments studying the surface reactivities of SiO using SNL's IRIS (Imaging of Radicals Interacting with Surfaces) technique. SNL researchers gave TI researchers access to thermochemical data on Si-N-H species from quantum chemistry calculations a year and a half before the results appeared in print (there was no other source for these data). When the TTI program was started by DOE, a proposal was

written to continue and expand the SNL/TI interaction, and it was approved for funding in 1989. Unfortunately, the project funding did not actually start at SNL until the fall of 1992 because of delays in the CRADA approval process.

The technical tasks evolved to meet the changing needs of TI as the project start was delayed. In particular, the MMST (Microelectronics Manufacturing Science and Technology) program at TI presented an excellent window of opportunity for the work done under this TTI project to influence a new generation of semiconductor-processing equipment. Unfortunately, this window was missed because of the delays, so the benefits of this R&D will be realized on a longer timescale.

The technical work done under this project will be described in more detail in the following sections. The work was divided into three parts, unequal in size. The first part involved the use of the IRIS technique to measure the reactivities of radical species at surfaces. This kind of information is particularly important for modeling and controlling plasma processes. It is the fact radicals are produced by the plasma that allows the reduction in process temperature which is the major advantage offered by plasma techniques. The second part of the work involved the evaluation and transfer of sensor technologies for monitoring source stability in the MOCVD (metal-organic CVD) of compound semiconductors. Source stability is a significant technological problem associated with the use of liquid or solid precursors in CVD, but this was the smallest part of this particular TTI project. The third part of the work involved experimental and theoretical investigations into the chemical reactions occurring during the deposition of silicon oxide from TEOS (tetraethoxysilane). TEOS is an important precursor for low-temperature oxide deposition industry-wide; advancing the understanding of TEOS chemistry will improve plasma TEOS, TEOS/ozone and doped TEOS processes as well as traditional LPCVD (low pressure CVD) TEOS processes.

II. IRIS Measurements of Radical Reactivities at Surfaces

In many semiconductor-processing technologies, the chemistry that occurs when gas-phase species collide with a surface determines important process outputs such as deposition/etch rates, film composition and morphology. In some cases, including virtually all plasma processes, the initial reactants are relatively unreactive with the surface and the process relies on the generation of radical species that are more reactive with the surface. Although radicals are generally accepted as being highly reactive, there are almost no data in the literature on radical/surface reactivities. Thus, all numerical process models to date contain estimates. The IRIS technique was developed at SNL to provide experimental determinations of the reactivity of radicals with surfaces. It combines molecular beam and laser spectroscopy methods to provide this unique capability. No other technique exists that provides direct measurements of this kind. Before this TTI project, we used the IRIS technique to show that the SiH radical had near-unit reaction probability with the surface of an amorphous hydrogenated silicon film, while in contrast, SiO unexpectedly exhibited a near-zero reaction probability with the surface of a silicon oxide film.

A. Description of Experiment

The details of the IRIS technique have been described elsewhere,^{1,2} so we include only a brief description here. Figs. 1 and 2 show schematics of the experimental apparatus used. An effusive molecular beam produced from a plasma impinges on a sample at a fixed angle relative to the surface normal. This beam contained virtually all the neutral and ionized species present in the plasma. A beam from a tunable laser, directed parallel to the surface, was set to an absorption frequency of a particular molecular species and thus selected one chemical component of the beam for study. The laser simultaneously excited both the molecules in the incident beam and molecules scattered from the surface. The spatial dependence of the fluorescence excited by the laser beam was measured by imaging light from the interaction region on an optical multichannel analyzer (OMA).

The diode array was oriented with its long axis parallel to the laser beam. Measurements were made with the surface positioned a known distance from the laser beam and also with the surface removed. The difference between the spatial distribution of fluorescence with the surface in and out of the molecular beam thus gave a measure of the radicals that hit the surface but did not react. The distance between the laser beam and the surface was varied to map out the angular distribution of any desorbing molecules, which gave information on the nature of the radical/surface interaction.

Obtaining a numerical value for the radical reactivity from the fluorescence measurements required a quantitative model of the experiment. The calculation was divided into three parts: 1) simulation of the spatial distribution of the number density of the selected radical at the intersection of the molecular beam and the laser beam, 2) calculation of the spatial distribution of flux of the radicals at the substrate surface, and 3) simulation of the spatial distribution of desorbed radical number density along the line defined by the laser beam. These calculations have been described in detail elsewhere.^{1,2}

B. NH

Ammonia-containing plasmas are widely used in semiconductor processing for the deposition of silicon nitride and oxynitride films at relatively low temperatures. These thin films are used as interlayer dielectrics as well as passivating layers in both silicon and compound-semiconductor devices. Optical emission from the NH radical is generally one of the more prominent features observed in emission spectra of plasmas used for depositing these materials. This clearly showed that NH was present in the discharges, so it was reasonable to propose that NH surface reactions were responsible for the incorporation of nitrogen atoms into the growing films.

The IRIS technique was used to measure the reactivity of NH with the surface of a silicon nitride film. These experiments have been described in detail elsewhere,³ so we include only a limited discussion here. Fig. 3 shows spatially resolved laser-induced fluorescence signals corresponding to NH in the molecular beam plus NH desorbing from the surface for several laser-surface distances. The data clearly showed that substantial amounts of NH desorb from the surface. The change in shape as the laser-surface distance was increased indicated that the incident NH molecules were adsorbing on the surface and equilibrating with it, rather than scattering specularly. The dashed curves in the figure result from numerical simulation of the experiment assuming that NH radicals desorb from the surface with a cosine angular distribution and 100% probability. The

experimental data thus indicate that NH has a surface reaction probability of essentially zero with an upper limit of 0.1 for substrate temperatures of 25 to 400°C. The IRIS technique was originally designed to measure reaction probabilities near one and has lower precision at low reaction probabilities.

Figure 3. IRIS measurement of NH surface reactivity. Spatially resolved laser-induced fluorescence is shown for NH in the molecular beam as well as NH emanating from the substrate.

Our observation that NH had a low reactivity with the surface of a silicon nitride film showed that NH does not contribute significantly to film deposition, despite the presence of NH in the plasma. Models of nitride or oxynitride deposition systems should thus concentrate on NH_2 or SiNH_x molecules formed by gas-phase reactions as important film-forming species.

C. OH

Silicon dioxide is the dominant insulating material used in microelectronic devices. Although gate dielectrics generally require oxides grown at relatively high temperatures, other insulating layers are often deposited using lower temperature methods, including a variety of plasma processes. To improve the understanding of these oxygen-containing

plasma processes, we earlier applied the IRIS technique to the SiO molecule and observed a low reaction probability. Continuing our studies of these plasmas, we extended the IRIS studies to OH radicals as part of this CRADA.

The experiments on OH have also been described in detail elsewhere,⁴ so we again include only a brief discussion here. The experiments showed that substantial amounts of OH in a molecular beam adsorbed on a surface, equilibrated, and then desorbed with a cosine spatial distribution. The OH data appeared qualitatively similar to the NH data shown in Fig. 3, but with a significant difference. In contrast to the NH and SiO results, Fig. 4 shows that OH had the fairly high reactivity of 0.57 with an oxidized silicon nitride surface at room temperature, with the reactivity decreasing to ~ 0 as the surface temperature was increased above $\sim 230^\circ\text{C}$. This inverse temperature dependence could be modeled either as a competition between desorption of physisorbed OH and its loss by reaction on the substrate, or as desorption of the surface species that reacts with the incident OH. In either case, no net reaction occurred with the underlying substrate at steady state. Rather, the surface appeared to serve as a substrate on which OH recombined with other species from the plasma.

Figure 4. Temperature dependence of OH surface reactivity measured using the IRIS technique.

OH radicals may also be important in plasma etching processes, where oxygen-containing plasmas are used to etch photoresist and insulator layers. In gas-phase chemistry, OH often reacts in a manner similar to halogen atoms, so it was reasonable to propose a significant role in etching reactions. To investigate this class of plasma processes, IRIS experiments were done for OH interacting with a PMMA (polymethyl methacrylate) film at room temperature using a variety of plasma compositions. For OH from either a H_2O or $\text{H}_2\text{O}/\text{CF}_4$ plasma, a reactivity of 0.6 was observed with the PMMA surface, although adding CF_4 to the H_2O plasma decreased the amount of OH in the plasma. Adding oxygen, making a $\text{H}_2\text{O}/\text{CF}_4/\text{O}_2$ plasma, decreased the OH reactivity to 0.2 while decreasing the amount of OH further. In contrast, PMMA etch rates were highest with the $\text{H}_2\text{O}/\text{CF}_4/\text{O}_2$ plasma, low with the $\text{H}_2\text{O}/\text{CF}_4$ plasma, and essentially zero with the H_2O plasma. This suggested that OH was not an important species in etching PMMA. This was confirmed by experiments with CF_4/O_2 and pure O_2 plasmas that showed net production of OH at the surface. Thus, it is likely that OH is a product, rather than a reactant, in photoresist etching, and that it is not playing a halogen-like role in these etching plasmas.

III. Optical Sensors for Compound Semiconductor Deposition

The use of metalorganic precursors for CVD is becoming increasingly common as researchers try to reduce deposition temperatures or to deposit new materials. MOCVD (metal-organic CVD) has proven particularly important for the fabrication of compound semiconductors for high-speed devices. Many of these metalorganic precursors, however, are liquids or solids at room temperature and have accordingly low vapor pressures. Thus, bubblers and/or heated sources are required to deliver these materials to the process chamber. Unfortunately, instabilities in such sources are a significant technological problem in both R&D and production environments.

Optical techniques offer the potential for real-time, non-intrusive monitors of source stability in MOCVD. Previously, SNL demonstrated that UV absorption can be used as a

good optical sensor for species such as TMGa (trimethylgallium) and TMIn (trimethylindium).⁵ Researchers at TI Central Research Labs were interested in setting up a similar system, so as a small part of this TTI project, SNL researchers shared their experiences with their TI counterparts.

TI has now installed a UV absorption monitor based on a UV spectrometer on one of their MOCVD systems. They regularly use it to monitor tBAs (tertiary butyl arsenic), TMGa and TMIn source performance. As shown in Fig. 5, TI has found that monitoring allows process corrections, such as bubbler changeouts, to be made in a timely manner. They have also used it to observe flow transients, which are important for growth of complex structures such as graded layers or superlattices.

Figure 5. MOCVD source stability monitored by UV absorption.

Ultrasonic sensors are also good candidates as monitoring systems for MOCVD source stability, and a commercial system is produced by the Epison company. As part of this project, the performances of the UV absorption and ultrasonic methods were compared for a range of experimental conditions. We found that both methods work as monitors of source stability, but that the UV absorption method gives superior performance for source

total pressures of less than 300 Torr, where the acoustic sensor signal is low. These low pressures are important for solid sources such as TMIn.

IV. Deposition of silicon oxide from TEOS

The deposition of silicon oxide from alkoxysilane precursors, particularly TEOS, has gained importance in the fabrication of microelectronic devices because these processes provide good step coverage along with lower hazards than silane-based processes. TEOS LPCVD processes are used widely in production although processes for in situ doping have severe problems with non-uniformity. Plasma TEOS and TEOS/O₃ processes allow deposition at lower temperatures, but involve some trade-offs in film composition and uniformity. Understanding the chemistry occurring in TEOS CVD could thus potentially improve a number of semiconductor-processing technologies. For this part of the TTI project, we applied a variety of experimental and theoretical techniques to the TEOS system. The details of this work will be given elsewhere,⁶ but the results clearly showed that gas-phase reactions form a more reactive intermediate in this system, which undoubtedly determines deposition uniformities.

A. Molecular Beam Measurements of TEOS reactivity

The reactions of stable molecules, such as CVD starting compounds, with surfaces can be studied much more easily than reactions of radicals. One of our techniques involves forming a molecular beam of the species of interest, having it impinge on a heated substrate in a high-vacuum chamber, and determining the reactive sticking coefficient (RSC) from the measured deposition rate. Determining reaction probabilities from molecular beam experiments rather than from deposition rates in a reactor offers a number of advantages. 1) The gas-surface reactions occur under single collision conditions. This allows RSCs to be determined in a straightforward manner from measured deposition rates and molecular beam fluxes. 2) Reactant depletion, which often

complicates the interpretation of reactor deposition rate data, is not an issue. 3) The effects of gas-phase reactions can be cleanly separated from gas-surface reactions.

We previously used this molecular beam technique to measure RSCs for silane and disilane, so the method and the experimental apparatus have been described in general elsewhere.⁷ Briefly, the molecular beam was formed by flowing TEOS through a 6 mm diameter copper tube into a stainless-steel vacuum chamber where it impinged on a silicon sample (native-oxide coated). The sample was resistively heated and the temperature monitored with a two-color optical pyrometer. The effective pressure of TEOS at the substrate was 1.7×10^{-3} Torr while the base pressure of the vacuum chamber was 10^{-7} Torr. Deposition rates were determined by masking, etching and profilometry.

The molecular beam experiments showed that the deposition of silicon oxide from TEOS itself is not very efficient. Measured RSCs ranged from 2.6×10^{-4} for a 1000°C substrate to 3.6×10^{-5} at 870°C . These data exhibited a linear relationship on an Arrhenius-type plot, and extrapolating to reactor temperatures ($\sim 700^{\circ}\text{C}$) yielded an RSC of $\sim 10^{-6}$. These RSCs, when combined with TEOS fluxes present in LPCVD reactors, are much too low to explain observed LPCVD deposition rates. These results thus strongly suggested that gas-phase reactions in LPCVD reactors form another chemical species that has a substantially higher RSC than TEOS.

To test this hypothesis, the molecular beam apparatus was altered so the gas was heated before impacting the surface. This was done by flowing the TEOS through a heated section of tubing before expanding it into the vacuum chamber to form the molecular beam. Heating the tube to 830°C increased the deposition rates on the samples in the vacuum chamber dramatically ($\times 10$ -40). This confirmed that the thermal decomposition of TEOS leads to the formation of a more reactive species. The experimental results suggested that this intermediate species had an RSC on the order of 10^{-2} .

B. IR Measurements of TEOS Decomposition Products

The thermal decomposition of TEOS can lead to a number of gas-phase products along with the deposited SiO_2 . Although ethylene, ethanol, water and acetaldehyde have all been reported as products, little quantitative information is available on the amounts of these products. Such information provides important clues about chemical reactions occurring in the system and is needed for development of good chemical reaction mechanisms. We therefore carried out TEOS pyrolysis experiments in order to analyze the product distribution with infrared spectroscopy.

TEOS was pyrolyzed in a cold-wall static cell that contained a small silicon sample that could be resistively heated. The cell was filled with 0.1–0.8 Torr of TEOS before the sample was heated to $\sim 750^\circ\text{C}$. FTIR (Fourier transform infrared) spectra were taken periodically during the 10 to 60 minute pyrolysis times to monitor progress of the reaction. At the end of the pyrolysis, a cold trap was used to collect the condensable gases, leaving the non-condensable gases in the FTIR cell. By comparison with reference spectra taken in the same apparatus, the amounts of TEOS, ethylene, ethanol and acetaldehyde were determined. In all experiments, a volume of non-condensable gas remained. This gas showed no features in the IR, and we believe it to be H_2 . The amount of SiO_2 deposited on the substrate was also determined.

These experiments showed that, on average, one TEOS molecule pyrolyzed to give 0.2 SiO_2 , 3 C_2H_4 , 0.7 $\text{C}_2\text{H}_5\text{OH}$, 0.3 CH_3CHO , 0.3 H_2 , plus water. Water cannot be accurately measured with IR, but was estimated using mass balance arguments. Several aspects of these results merit further mention. 1) Only one out every five TEOS molecules led to SiO_2 on the substrate, which suggested that reactive species formed from TEOS were diffusing to the cold walls of the cell and reacting. 2) C_2H_4 was the dominant product, which suggested that it may be directly formed by the gas-phase and/or surface decomposition of TEOS. 3) Acetaldehyde and H_2 were minor products that may be

formed by secondary reactions. Ethanol pyrolysis experiments in the same apparatus showed the formation of ethylene, acetaldehyde, and hydrogen at significant rates.

C. Thermochemistry of TEOS and Related Compounds

The best reaction mechanism for use in modeling a CVD process (or any other chemically reacting flow system such as combustion) is one based on known kinetic and thermochemical data. In most cases, however, the desired kinetic measurements have not been done, so kinetic parameters must be estimated from thermochemical data. Unfortunately, in many cases, including the alkoxysilanes, the necessary thermochemical data are not known either. To meet this need, SNL has developed quantum chemistry methods using high-level *ab initio* electronic structure calculations combined with empirical bond-additivity corrections that provide thermochemical and kinetic data. In the past, we have applied these methods to compounds composed of first-row elements plus a number of silicon compounds (with H,⁸ Cl,⁹ F,¹⁰ N,¹¹ and/or C^{12,13}). As part of this project, we have now extended these methods to a number of methoxy and ethoxy silicon compounds.

These calculations have been described in detail elsewhere¹⁴ so only a brief discussion of the theoretical methods is included here. The electronic structure calculations were done using the Gaussian series of codes.¹⁵ Equilibrium geometries and vibrational frequencies were obtained using Hartree-Fock theory and the 6-31G* basis set. To determine atomization energies, and hence heats of formation, single-point Moller-Plesset perturbation theory calculations were done at the equilibrium geometries using the 6-31G** basis set. In most cases, fourth-order perturbation theory was used, but for some of the larger molecules, such as TEOS, second-order perturbation theory was used due to computational limitations. Bond additivity corrections were used to account for systematic errors in the *ab initio* calculations which result primarily from basis-set truncation. These corrections depend mainly on bond type and length, and require a reference compound (with a known heat of formation) for each bond type. This

calculational procedure can provide enthalpies that are generally good to a few kcal/mole, as well as entropies and free energies as a function of temperature, for stable molecules, radical species and transition states.

Table 1. Calculated ΔH°_f for Si-O-H-C Compounds (kcal/mole)			
Compound	ΔH°_f (298)	Compound	ΔH°_f (298)
Si(OC ₂ H ₅) ₄	-317.5	Si(OCH) ₄	-284.4
Si(OC ₂ H ₅) ₃ OH	-319.3	Si(OCH ₃) ₃ OH	-293.2
Si(OC ₂ H ₅) ₂ (OH) ₂	-319.8	Si(OCH ₃) ₂ (OH) ₂	-301.0
C ₂ H ₅ OSi(OH) ₃	-320.5	CH ₃ OSi(OH) ₃	-312.0
Si(OH) ₄	-320.8	Si(OCH ₃) ₃	-161.3
HSi(OC ₂ H ₅) ₃	-233.1	Si(OCH ₃) ₂ OH	-168.9
C ₂ H ₅ OSiH ₃	-66.1	Si(OCH ₃)(OH) ₂	-177.1
O=Si(OC ₂ H ₅) ₂	-192.5	Si(OH) ₃	-185.8
Si(OC ₂ H ₅) ₃	-186.1	Si(OCH ₃) ₂	-99.3
Si(OC ₂ H ₅) ₂ OH	-186.0	CH ₃ OSiOH	-107.1
Si(OC ₂ H ₅)(OH) ₂	-185.9	Si(OH) ₂	-115.4
Si(OC ₂ H ₅) ₂	-115.8	SiOCH ₃	8.4
Si(OC ₂ H ₅)OH	-115.6	SiOH	1.4
SiOC ₂ H ₅	0.2	O=Si(OCH ₃) ₂	-175.8
O=Si(OC ₂ H ₅)OH	-192.4	O=Si(OCH ₃)OH	-184.7
OSi(OC ₂ H ₅) ₃	-245.4	O=Si(OH) ₂	-192.3
OSi(OC ₂ H ₅) ₂ OH	-245.9	OSi(OCH ₃) ₃	-217.7
OSi(OC ₂ H ₅)(OH) ₂	-246.6	OSi(OCH ₃)(OH) ₂	-238.1
HSi(OC ₂ H ₅) ₂ OH	-233.6	OSiOCH ₃	-39.1
HSi(OC ₂ H ₅)(OH) ₂	-234.1	OSi(=O)OCH ₃	-108.9
(CH ₃) ₃ SiOSi(CH ₃) ₃	-187.5	CH ₂ OSi(OH) ₃	-266.0
OSi(OCH ₃) ₂ OH	-226.3	(CH ₃) ₃ SiOH	-119.6
HSi(OCH ₃) ₃	-208.2	(CH ₃) ₃ SiO	-49.5

Table 1 lists the self-consistent set of heats of formation that were calculated for molecules in the Si-O-H-C system. For the few cases where comparisons with experimental values in the literature are possible, there was good agreement between theory and experiment. Although not shown here, heats of formation were also estimated for another 15 species.

These heats of formation gave valuable insight into the energetics of possible decomposition reactions for TEOS (as well as many related compounds). The reaction enthalpies listed in Table 2 for a variety of TEOS decomposition reactions illustrate several trends. 1) Simple bond scission reactions had the highest endothermicities by far and should not be important in the thermal decomposition of TEOS. 2) Reactions forming silanones covered a range of endothermicities ≥ 65 kcal/mole, but the reactions go through multicenter transition states so the activation energies should be substantially higher than the endothermicities. 3) TEOS decomposition to $\text{HSi}(\text{OC}_2\text{H}_5)_3$ and acetaldehyde had a 45 kcal/mole endothermicity, which would make it energetically accessible except that the activation energy should again greatly exceed the endothermicity. 4) TEOS decomposition via the beta-hydride elimination of ethylene had a very low endothermicity of 10.5 kcal/mole, which made it a very likely thermal decomposition pathway, even in the presence of a substantial activation barrier.

Table 2: Calculated Enthalpies for TEOS Decomposition Reactions		
Reaction		$\Delta H^\circ_{\text{rxn}}$
$\text{Si}(\text{OC}_2\text{H}_5)_4$	$\rightarrow \text{Si}(\text{OC}_2\text{H}_5)_3 + \text{OC}_2\text{H}_5$	130.9
	$\rightarrow \text{OSi}(\text{OC}_2\text{H}_5)_3 + \text{C}_2\text{H}_5$	100.9
	$\rightarrow \text{O}=\text{Si}(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{OH}$	80.2
	$\rightarrow \text{O}=\text{Si}(\text{OC}_2\text{H}_5)_2 + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_6$	65.6
	$\rightarrow \text{O}=\text{Si}(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	64.7
	$\rightarrow \text{HSi}(\text{OC}_2\text{H}_5)_3 + \text{CH}_3\text{CHO}$	45.8
	$\rightarrow \text{Si}(\text{OC}_2\text{H}_5)_3\text{OH} + \text{C}_2\text{H}_4$	10.5

To gain more insight into the TEOS ethylene elimination reaction, transition states were calculated for ethylene elimination from $\text{C}_2\text{H}_5\text{OSi}(\text{OH})_3$ and $\text{C}_2\text{H}_5\text{OSiH}_3$. The transition states were found to be 70.7 and 68.3 kcal/mole above $\text{C}_2\text{H}_5\text{OSi}(\text{OH})_3$ and $\text{C}_2\text{H}_5\text{OSiH}_3$, respectively. This confirmed the presence of a large kinetic barrier, although we believe that our calculated values may be somewhat high. These results strongly suggested that TEOS decomposition occurs via ethylene elimination and that the experimental observations by Lin and coworkers¹⁶ should be identified with the formation of $\text{HOSi}(\text{OC}_2\text{H}_5)_3$ rather than the silanone. The thermochemistry and kinetics for subsequent ethylene elimination reactions should be similar to the first. Thus it is likely that sequential decomposition occurs during TEOS pyrolysis, eventually producing some $\text{Si}(\text{OH})_4$, given a sufficiently long reaction time.

The quantum chemistry calculations thus identified a likely reaction for the gas-phase decomposition of TEOS, the beta-hydride elimination of ethylene. This produces the $\text{HOSi}(\text{OC}_2\text{H}_5)_3$ species, which we expect to be significantly more reactive with the surface than TEOS because of the presence of the hydroxyl group. We note that tetramethoxysilane (TMOS) has no analogous low-endothermicity reaction and must decompose via different, more endothermic pathways. This is consistent with lower decomposition temperatures for TEOS than for TMOS, and thus the preference for TEOS in CVD processing.

D. Analysis of Reactor Residue

An experimental observation at TI was that the TEOS CVD reactors regularly built up a solid white residue on the cold walls downstream of the deposition zone. This material was produced when byproducts of the deposition reactions reacted at the cold wall. The presence of this residue is consistent with our observation, described in section IV.B., that only a small fraction of the TEOS decomposition resulted in SiO_2 on the heated substrate.

A sample of this residue was brought to SNL and analyzed for elemental and chemical composition.

C^{13} NMR (nuclear magnetic resonance) analysis of the residue resulted in the spectrum shown in Fig. 6. The two sharp peaks correspond to C in ethoxy groups and the spectrum showed no evidence for C in any other chemical environments. This indicated that TEOS decomposition does not involve C-C bond scission. Si^{29} NMR analysis yielded the spectrum shown in Fig. 7. Silicon oxide and alkoxide materials in condensed phases have been well characterized during studies of sol-gel processes, so with appropriate deconvolution, this spectrum could be cleanly analyzed. The Si^{29} NMR analysis showed that 29.9% of the Si atoms in the residue were bonded to 4 (OSi) groups, 35.9% were bonded to 3 (OSi) groups and 1 (OR) group ($R = C_2H_5$ or H), 29.3% were bonded to 2 (OSi) and 2 (OR) groups, while 4.9% were bonded to 1 (OSi) and 3 (OR) groups. This corresponds to an average of almost exactly one (OR) group per silicon atom in the solid.

Figure 7. Si^{29} NMR analysis of TEOS reactor residue shows Si in varying chemical environments (differing numbers of bonds to OSi and OR groups).

Elemental analysis, using ICP-AES for Si and combustion analysis for C, H, and N, indicated that the residue was $32.6 \pm 0.57\%$ Si, $15.91 \pm 0.77\%$ C, and $3.69 \pm 0.25\%$ H by weight with less than 0.1% N. By difference, oxygen thus represented 52.2% of the weight of the sample. Converting to atomic abundances and assigning all C to ethoxy groups led to a composition of $\text{Si}(\text{OC}_2\text{H}_5)_{0.575 \pm 0.25}(\text{OH})_{0.285 \pm 0.3}(\text{O})_{2.01 \pm 0.38}$. Combined with the results of the NMR experiments, this suggested that the residue had a chemical composition of roughly $\text{Si}_3(\text{OC}_2\text{H}_5)_2(\text{OH})\text{O}_6$.

E. Mechanistic Implications

The work presented above provided a great deal of new insight into the chemistry occurring during TEOS CVD processes. The molecular beam experiments showed that TEOS itself is sufficiently unreactive that it cannot account for observed deposition rates in CVD reactors. The molecular beam experiments also provided direct evidence that heating TEOS led to the formation of a different chemical species that is more reactive

with the surface. The quantum chemistry calculations identified the beta-hydride elimination of ethylene as the most likely reaction for the gas-phase decomposition of TEOS, and suggested that a silanol species, such as $\text{HOSi}(\text{OC}_2\text{H}_5)_3$, was a good candidate for the reactive intermediate. This was consistent with the fact that the IR measurements identified C_2H_4 as the major gas-phase byproduct. The production of a silanol intermediate species was also consistent with the formation of residues on cold reactor walls that contain significant numbers of ethoxy groups.

This new picture of TEOS reactions is also consistent with the results of TI's reactor experiments and modeling work done under the MMST program. TI researchers empirically found that models using a gas-phase reaction to form an intermediate gave much better correlations with experimental deposition rate data than did models with direct deposition from TEOS.

The information on TEOS chemistry gained under this program forms the basis for a new reaction mechanism to be incorporated in numerical models of TEOS CVD now being developed as part of the SEMATECH RTP program. At TI, although the MMST modeling effort has ended, the results from these studies should prove useful in continuing modeling work being done for process control. In particular, the fact that much of the SiO_2 results from a gas phase intermediate could have substantial consequences in addressing issues of deposition uniformity and step coverage.

V. Summary

On the technical level, this collaborative research project between Sandia National Laboratories and Texas Instruments was very successful. A substantial amount of scientific data was obtained that will improve the understanding of the chemistry occurring during plasma deposition of silicon nitride and oxide, as well as the deposition of silicon oxide from TEOS. Most of the work is published separately in the open literature where other researchers studying semiconductor processing technologies can

benefit from the work. Certain of the results are already being used in separate projects funded by other sources, such as SEMATECH.

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