

Surface Chemistry in the Chemical Vapor Deposition of Electronic Materials

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Contents

I. Introduction	1519
II. How Surface Chemistry Controls Unique Features of CVD Film Growth	1520
A. Smooth and Rough Surface Textures	1520
B. Weakly Adsorbed CVD Precursors	1520
C. Conformal Covering of Surface Topography	1521
D. Surface Selective CVD Chemistry	1523
1. Selective CVD Mechanisms	1523
2. Si Substrate Is the Coreactant	1524
3. H ₂ Gas Is the Coreactant	1524
4. Combined Etching and Deposition of Si	1525
III. Free Radical Precursors and Atomic Co-reactants	1525
A. Introduction	1525
B. Atomic Hydrogen and Group IV Semiconductor Surfaces	1525
C. Diamond CVD Using Hydrocarbon Radicals and Atomic H	1526
D. Plasma-Enhanced CVD of Amorphous Hydrogenated Si (a-Si:H)	1526
E. Atomic H and a-Si:H	1527
IV. Modeling of CVD Processes Using Surface Kinetics	1527
A. Introduction	1527
B. Models for Si Epitaxial CVD	1528
C. Aluminum Films from Triisobutylaluminum	1528
D. A Predictive Model for TiSi ₂ Growth	1529
V. Atomic Layer Control over CVD Film Growth	1529
A. II–VI Semiconductors and Metal Oxides	1529
B. GaAs Growth by ALE	1530
C. Extension of ALE to Group IV Semiconductors	1530
VI. Summary	1530
VII. Acknowledgments	1531
VIII. References	1531



Stephen M. Gates received his B.A. in Chemistry from Oberlin College, and his Ph.D. in Inorganic Chemistry from the University of North Carolina at Chapel Hill. He was awarded the Morton Traum award by the Surface Science Division of the American Vacuum Society in 1982 for his Ph.D. thesis work. He was a research assistant professor at the Surface Science Center, Department of Chemistry, University of Pittsburgh, before joining the IBM T. J. Watson Research Center as research staff member in 1985. He has investigated many aspects of Si chemical vapor deposition, from surface chemistry to thin film transistor fabrication. His recent work has focused on growth of amorphous and polycrystalline Si films at reduced growth temperatures.

This review contains two general parts with different objectives. In section II, we review fundamental surface chemistry studies that explain special attributes of CVD film growth. Smooth film surfaces and conformal coating of three-dimensional structures are requirements for many CVD films, so we emphasize the surface chemistry that controls these basic “topography” properties of the product film in sections II.A–C. We then discuss selective growth on the surface of one material, without growth on an adjacent (dissimilar) surface, in section II.D. Thus, section II covers the “state of the art” use of surface reactions in controlling CVD growth, with a focus on the connections between surface chemistry and CVD that exist in the areas of selective growth and topography control. Conformal coating and area selective growth are *unique attributes* of CVD, and are not possible using other thin-film growth methods (evaporation or sputtering).

In later sections of this review, we have selected for emphasis those areas where connections between the fields of surface chemistry and CVD growth are especially strong. These areas are the use of radicals in CVD, processes that are accurately modeled using surface desorption and adsorption rates, and atomic layer control over the CVD growth rate. These are covered in sections III, IV, and V, respectively. We restrict our coverage of the literature to the last 10 years, with a handful of key citations to work before 1985. Our review of radicals in CVD is limited to

I. Introduction

Sophisticated chemical processing allows us to create thin films with selected properties and to pattern these films with shrinking dimensions and increasing precision. Chemical processing pervades the fabrication of microelectronic and optical devices and, thus, supports a large piece of the world's technology-based economy. Perhaps the most sophisticated chemical process in our industry is chemical vapor deposition (CVD), in which gas molecules are decomposed to produce a solid film of specified properties. Here, we explore the ways that surface chemistry can be used as a tool to select and improve the physical, optical, and electrical properties of thin films grown by CVD.

the diamond and amorphous Si systems, because these are technologically the most important examples where CVD based on radical chemistry is actually used. Accurate rate measurements of individual reaction steps in Si and SiGe CVD are available,^{1,2} so the *connections* between surface chemistry and film growth are strong in the Si and SiGe systems, and we emphasize this in the kinetic models section. Our coverage of the field of atomic layer epitaxy (ALE) includes a summary of the field and ALE processes for II–VI semiconductors, metal oxides and gallium arsenide (GaAs). Finally, growth of Si by ALE methods is covered in greater detail.

We do not review here the field of organometallic CVD of II–VI and III–V semiconductors, because these are covered by Stringfellow,³ who reviews all aspects of II–VI and III–V growth from chemistry to device fabrication. A thorough, readable review of CVD processing was written by Jensen,⁴ who emphasized reactor design, precursor transport, and gas-phase and surface chemistry. We do not cover the design, transport, or homogeneous chemistry areas. Other reviews of CVD are found in refs 5–7 which also address these topics. Granneman's paper on thin films in integrated circuits (ICs) goes beyond the content of this article concerning device fabrication, including IC structures, properties of films in ICs, and CVD methods of film growth.⁸ Here, we do not discuss novel precursor chemistry, photon- or electron-induced film growth, or GaAs CVD, but these are covered in the review by J. M. White and co-workers elsewhere in this issue.⁹

The terminology of CVD identifies the reactant gas as the *precursor* to the product film. Conversion of precursor to film can involve both gas phase and surface reactions. An essential concept is that the total pressure (P) in a CVD reactor controls the degree of coupling between the gas and surface chemistries. Heterogeneous and homogeneous pathways are tightly coupled at higher P , on the order of 1 Torr and greater. When the probability of gas–gas collisions is negligible ($P < 10^{-4}$ Torr) *precursor decomposition becomes strictly heterogeneous*, and the film grows only through surface processes, which can provide fine control over the film properties. In principle, mapping and controlling the surface chemistry of a CVD precursor molecule can help us to control the functional characteristics of the product film. This article examines recent progress toward this goal. The coupling of gas and surface processes, and the chemistry that occurs in each phase, is well understood in selected systems. Here, we use many terms and concepts defined in reviews of the growth of Si films from silane precursors.^{1,2}

Among all the available probes, molecular beam reactive scattering (MBRS) has provided the greatest insight into the surface chemistry of CVD growth. Reactive sticking probabilities, surface residence times of adsorbed states, kinetics of surface reaction steps, and product identification are examples of useful data from MBRS studies. Dating from the 1960's, the seminal work of Joyce and co-workers on Si CVD from SiH₄ in UHV conditions set a standard for the field.^{10–12} Recently, molecular beams have been used to decipher the surface chemistry of CVD with great success, and Yu and DeLouise have

reviewed MBRS studies on semiconductors in a thorough paper including both deposition and etching chemistries.¹³ Certain CVD chemistries are treated extensively in this recent review.¹³

II. How Surface Chemistry Controls Unique Features of CVD Film Growth

A. Smooth and Rough Surface Textures

The performance of optical and electronic devices constructed from thin films is often critically dependent on *abrupt interfaces* between two adjacent layers. Effects ranging from electron scattering to light reflection by multilayer mirrors require smooth, abrupt interfaces between films grown by CVD. A smooth top surface on the first film is necessary (but not sufficient) for an abrupt interface. The surface topography of films grown by CVD is of no small consequence. The probability that a CVD precursor molecule reacts directly at the first point of contact with the growth surface is a factor influencing surface roughness (smoothness) and conformal coating of three-dimensional structures. Precursor surface reactivity is our first topic.

The reactive sticking probability, S^R , of a CVD precursor should not approach unity because a high S^R yields a rough film texture. If the precursor is very reactive, it dissociates (chemisorbs) at the point of impact. Two effects may lead to rough surface topography: roughness on the starting surface before growth (perturbations from a flat surface)¹⁴ and random spatial fluctuations in the incoming flux.¹⁵ As the film grows, high and low points preexist or are created by random flux variations, and then the high points intercept more and more of the incoming flux. The flux incident on the low points is depleted ("shadowing"). Random fluctuations in the film surface topography (a rough texture) are the result.¹⁵ This effect is the rule when atoms compose the flux to the surface (evaporative growth) and when the surface T is low so the atoms are immobile after sticking. Deliberate texturing of films using evaporation at an oblique angle is based on the shadowing effect.¹⁶ Stout and Kushner used Monte Carlo simulations to compare the smoothness of films grown from hypothetical atomic precursors after 100 monolayers (ML) growth with $S^R = 0.3$ and 10^{-3} .¹⁵ The figure illustrating the resulting surface topography is quite instructive.¹⁵ Films with random topography characterized by an amplitude of several monolayers were predicted for $S^R = 0.3$, while smooth films with ± 1 ML amplitude were predicted with S^R of order 10^{-3} .¹⁵ The same effect was also predicted in a Monte Carlo simulation of amorphous Si growth by plasma-enhanced (PE) CVD.¹⁷

Two mechanisms are commonly cited for growth of films with smooth surface topography. Surface mobility between the initial sticking event and chemisorption is one mechanism. A low S^R , or order 10^{-2} – 10^{-3} or less, is the alternative mechanism. These same mechanisms are related to the growth of conformal films, as we discuss below.

B. Weakly Adsorbed CVD Precursors

Weak molecule/surface interactions between the intact precursor molecule and the film surface can

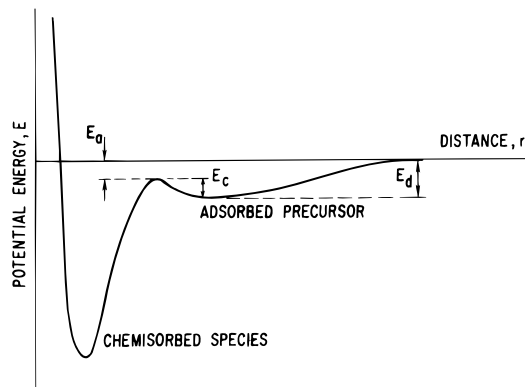


Figure 1. A schematic one-dimensional potential energy diagram, indicating the strength of molecule/surface interaction as a function of distance from a solid surface. The weak interaction of an intact CVD precursor molecule (“adsorbed precursor”) with the dynamic growth surface, the products of dissociative chemisorption, and the energy barriers between different states are emphasized. The energy differences are defined in the text.

influence film roughness and conformality. The strength of van der Waals attraction between a weakly adsorbed precursor and the surface of the growing film is important to many CVD chemistries. The word “precursor” is used in different fields with two different meanings. In the context of CVD growth, a precursor is the reactant gas which is decomposed to make the product film. In the surface science field a weakly adsorbed (physisorbed) molecule is a precursor to chemisorption, and is adsorbed in a “molecular precursor state”. Here, we use the term “adsorbed precursor” for the latter case, meaning an intact CVD precursor molecule trapped via van der Waals attraction in a weakly attractive potential well at the film surface.

Weakly adsorbed molecules are commonly described with a schematic one dimensional potential, shown in Figure 1. The first-order activation energy for desorption from this state is E_d and that for dissociative chemisorption (leading to film growth) is E_c . Direct dissociation, and no surface mobility, is associated with $E_c = 0$, or $E_c \ll E_d$. With no barrier to adsorption into the adsorbed precursor (as drawn in the figure), the kinetic E_d is a good approximation to the isosteric heat of adsorption of the precursor,¹⁸ a measure of the van der Waals interaction strength. This state can be visualized as a two-dimensional gas, and the reader is referred to a seminal paper by King and Wells describing surface mobility in this state.¹⁹ Experimental evidence for these states is seen in angular distributions of scattered molecular beams,²⁰ surface residence times of modulated molecular beams,²¹ temperature dependence of the reactive sticking probability, S^R ,²² nonlinear coverage dependence of S^R ,²³ and low-temperature (T) adsorption studies.¹⁸ The quantity E_a is an apparent activation energy for dissociative chemisorption observed by variation of the surface T .²²

The adsorbed precursor may diffuse on the surface, exercising *surface mobility*, may dissociatively chemisorb (the reaction leading to film growth), or may desorb. The latter is called “reemission” by researchers simulating film growth.¹⁴ Reporting their Monte Carlo model for CVD, Cooke and Harris²⁷ used the

term “settling” for chemisorption and showed useful plots of S^R as a function of $(E_c - E_d)$. The assumption of equal preexponential factors for desorption and chemisorption was used.²⁷ When $(E_c - E_d)$ is negative, as in Figure 1, S^R approaches unity. With a barrier to chemisorption, E_c increases, and $(E_c - E_d)$ can be positive. As $(E_c - E_d)$ becomes more positive, S^R decreases, and S^R of order 10^{-3} corresponds to $(E_c - E_d)/kT \approx 7$, if the preexponentials are equal.²⁷

Various silane molecules are used as precursors in Si CVD growth. The decomposition of Si_2H_6 and SiCl_2H_2 on Si surfaces have been studied in detail.^{1,2,6,21,22} The evidence for an adsorbed precursor in the Si_2H_6 case is extensive, while SiH_4 has E_d either very small, or zero. Using MBRS and a 1 kHz chopping frequency, Kulkarni *et al.* directly observed the surface residence time of intact Si_2H_6 to be of order 50 μs at room temperature, decreasing to 20 μs at 250 °C, respectively.²¹ The data indicated $E_d \approx 4$ kcal/mol, and surface diffusion lengths approaching macroscopic dimensions are implied.²¹ Dichlorosilane, SiCl_2H_2 , and many other molecules exhibit adsorption kinetics on Si surfaces with a weakly adsorbed precursor mediating between gas phase and chemisorbed species.²² In a different system, the growth of SiO_2 from tetraethoxysilane (“TEOS”), an adsorbed precursor is also well characterized.²⁵ In other chemistries for SiO_2 growth, the $\text{SiH}_4 + \text{O}_2$ and the diethylsilane (DES) + O_2 results have been compared. The film conformality observations with SiH_4 versus DES are consistent with no weakly adsorbed precursor for SiH_4 .²⁶ The heavier silane derivatives (Si_2H_6 , SiCl_2H_2 , DES, and many others) all show evidence for a weakly adsorbed precursor.

C. Conformal Covering of Surface Topography

Deposition of a thin film which *uniformly coats all exposed parts of a three-dimensional structure* is known as conformal film growth. The structure is often a trench cut into a substrate (Figure 2), a cylindrical via (Figure 4), or a ridge feature. Without conformal growth, some important steps in current microelectronics fabrication would be impossible. Conformality is a common requirement for dielectric films. It is also useful in filling cylindrical holes with metal contact material (see next section on surface-selective CVD). *CVD is the only conformal growth method*, and surface chemistry controls conformality.

Figure 2 illustrates the coating of a simple three-dimensional structure with films that are conformal (panel B) and nonconformal (panel A). Similar ideas apply to coating of more complex three-dimensional shapes. A very high S^R of order unity destroys conformality, shown in panel A of the figure. The nonuniform film thickness profile in panel A is obtained using line-of-sight delivery of highly reactive precursors (atoms or radicals) with $S^R \approx 1$. This case is known as “physical vapor deposition” (PVD), is typical of film growth by evaporation, and can be produced in plasma-enhanced (PE) CVD under certain conditions. With $S^R \approx 1$, the growth species stick preferentially near the top of the side walls and on the bottom surface, depleting the flux incident on the side walls near the bottom. The thickness profile illustrates the flux gradient in the trench. Making

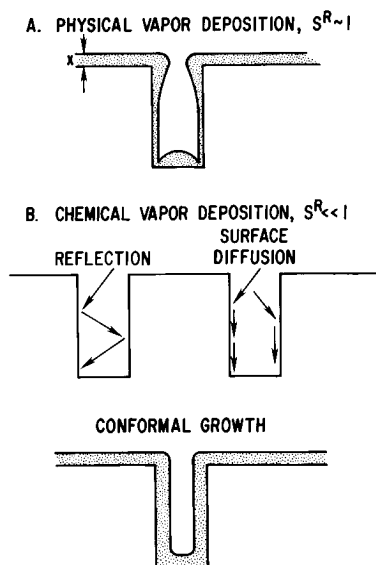


Figure 2. Schematic cross sections showing the thickness profile for a thin film deposited over a three-dimensional trench structure, with the film thickness given by the quantity x . (A) Deposition with a very reactive species, resulting in a nonuniform film thickness (nonconformal covering) over the sidewalls and bottom of the trench. This condition is commonly called "physical vapor deposition". (B) Deposition with a species that has a low probability of reactive sticking at the point of impact, producing the same film thickness on all exposed areas (conformal covering), which is only possible with chemical vapor deposition. Two different mechanisms for conformal covering are shown. Reflection (low reactive sticking probability, S^R) is the most important and controls covering of features with dimensions on the order of microns. Surface diffusion in an adsorbed precursor state is less important, but can affect covering of smaller features.

the assumption of $S^R = 1$, the flux can be measured using the thickness, x , and the time. Cooke and Harris used a Monte Carlo simulation to calculate film profiles similar to those in Figure 2.²⁷ A unity S^R gave a result similar to Figure 2A, while $S^R = 0.05$ gave a profile similar to Figure 2B (conformal).²⁷ The group of Saraswat used an analytical line-of-sight model to calculate similar film profiles. The $S^R = 1$ result was duplicated, and $S^R = 0.01$ gave a conformal profile consistent with Figure 2B.²⁸

The shaded film in panel B of Figure 2 illustrates "perfect step coverage", with equal film thickness on all exposed surfaces.¹² As the figure implies, one of two mechanisms can yield such a conformal film. *Accommodation* into a weakly adsorbed precursor (physisorbed) surface state (see Figure 1), surface diffusion in this state, and finally chemisorption at an open surface site is one means to transport species equally to all exposed surfaces. This mechanism is most important for small feature size ($\approx 1 \mu\text{m}$) and is labeled as "surface diffusion" on the right side of Figure 2B. The small arrows indicate surface diffusion. During diffusion, desorption of the adsorbed precursor competes with chemisorption. Large features cannot be conformally coated by diffusion alone, because desorption occurs before the diffusion length can reach macroscopic dimensions.

The simpler mechanism is also shown in Figure 2B. *Multiple reflections* before reactive sticking (left side

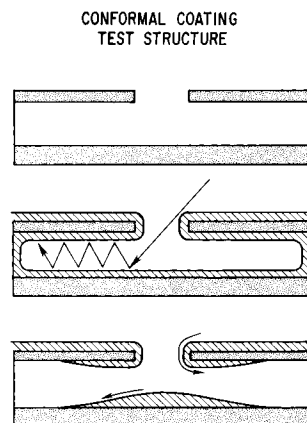


Figure 3. Schematic cross sections of a test structure used to distinguish the reflection and surface diffusion mechanisms of Figure 2B. A cross section of the "overhang" or "cavity" structure appears at the top. The middle picture illustrates growth of a conformal film (cross-hatched) into unexposed sides of the cavity by multiple reflections of precursor molecules with a very low reactive sticking probability, S^R . The bottom picture illustrates film growth near exposed parts of the cavity with surface diffusion of the adsorbed precursor controlling the film thickness.

of Figure 2B) will tend to eliminate the flux gradient in the trench, also resulting in a conformal film. The film thickness profile (Figure 2) cannot distinguish these two mechanisms, but is the basic experimental measurement and is frequently calculated using simulations.

Monte Carlo simulations by two groups have helped us understand conformal growth. For trench features on the micrometer scale and larger, reflection is probably responsible for excellent conformality. Cooke and Harris concluded that the reflection mechanism (low S^R) is crucial to good step coverage, but that surface diffusion can help uniformity and smoothness.²⁷ Note that uniform thickness and smoothness involve a short length scale. Stout and Kushner used "reemission" to label the mechanism we call reflection and concluded that for length scales of micrometers reflection must be active (not surface diffusion).¹⁵ Model calculations with the "reemission" channel turned on or off were compared for trenches of width $0.2\text{--}0.5 \mu\text{m}$. *A mobile adsorbed precursor with long surface residence time could improve conformality, but could NOT produce perfect step coverage.*¹⁵ It was pointed out that the surface diffusion length (rms displacement) of the weakly adsorbed precursor must be of the same magnitude as the feature (trench or step) that is to be conformally coated.²⁷ Large features require reflection, but small features can be influenced by surface mobility.

The "overhang" structure shown in Figure 3 has been used in conformality studies^{26,29} and helps to separate the two mechanisms of Figure 2. The bare structure appears at the top of Figure 3. When a truly conformal coating is deposited, the reflection mechanism must be active, as shown in the middle of the figure.²⁶ If only surface diffusion is active, a film profile similar to the bottom of Figure 3 is produced.²⁹ The surface chemistry literature regarding adsorption kinetics can also help us to generalize. Heavy silane derivatives, such as TEOS or DES,

EXAMPLE VIA STRUCTURES

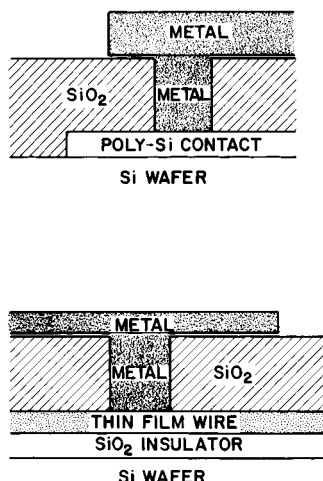


Figure 4. Two structures in which a hole in an insulating SiO₂ layer ("via") is filled with a metal connector "post". The "post" is commonly deposited by metal CVD, and connects two metal layers (bottom), or one metal and one Si layer (top).

produce conformal films and the surface diffusion mechanism is active on small length scales. The SiO₂ growth studies using these large precursors are probably accurate in assuming surface diffusion.^{15,30}

The study of conformal film growth has been coupled with studies of the deposition mechanisms in plasma-enhanced CVD (PE CVD) of amorphous hydrogenated silicon (a-Si:H) for the past 10 years.^{29,31–35} An important paper by Tsai and co-workers from 1986 was based on the effects shown in Figure 2 and illustrated how tuning the plasma conditions produced either PVD or CVD growth.³³ The dimensions of the trench must be smaller than the mean free path (λ) in the gas phase, so that ≈ 1 cm trenches are used for low-pressure growth ($\approx 10^{-3}$ Torr, $\lambda \approx 10$ cm),³⁴ while higher pressures require smaller trenches.³³ Recently, Abelson and co-workers summarized this approach in a very readable form.³⁴ They combined Monte Carlo simulations and film thickness measurements in "macro" trenches to compare a-Si:H growth by PE CVD with growth by reactive magnetron sputtering.³⁴ In their study, the net surface reaction probability of the mixed SiH_x growth species was 0.28 for conformal film growth ("CVD-like" conditions), as in panel B of Figure 2.³⁴ A value close to unity (0.97) was measured for nonconformal growth using sputtered Si atoms and SiH as the growth species,³⁴ as in panel A of Figure 2. We discuss the mechanisms in a-Si:H growth in section III.C.

Many device structures utilize metal layers that require electrical isolation by dielectric films, typically SiO₂, amorphous Si nitride (SiN_x), or a polymer. Example structures are shown in Figure 4. The dielectric films must conform to surface topography, and are typically grown by either thermal CVD or PE CVD. In the SiO₂ system, SiH₄ and an oxygen source such as O₂ or N₂O may be used. A direct comparison of the SiH₄ + O₂ and the diethylsilane (DES) + O₂ systems has been made, and poor film

conformality is observed with SiH₄, while conformal growth is observed with DES.²⁶ This is consistent with no weakly adsorbed precursor for SiH₄. Excellent conformal trench coverage is obtained using TEOS (tetraethoxysilane).^{15,26,30} An adsorbed precursor ("physisorbed") state was studied for TEOS on SiO₂ surfaces by the Crowell group, and the reaction of TEOS with isolated -OH groups on the SiO₂ surface was characterized.²⁵ The heavier silane derivatives (Si₂H₆, SiCl₂H₂, DES, and many others) all show evidence for adsorption through a weakly adsorbed precursor.^{21,22,35} Step-coverage experiments by the AT&T group showed that conditions with a low population (surface coverage) of adsorbed precursor molecules resulted in the best step coverage.³⁰

D. Surface Selective CVD Chemistry

1. Selective CVD Mechanisms

Surface selective (or "area selective") CVD chemistries for metal and Si films exploit differences in surface reactivity to deposit the film on exposed Si surfaces and *not* on adjacent SiO₂. The result is *simultaneous growth and patterning*, and the selectively grown film is perfectly aligned to the preexisting pattern of openings in the SiO₂ layer ("self-aligned"). Selective CVD eliminates a patterning step, and the cost of multilevel device fabrication depends strongly on the number of patterning steps. The ultimate contribution of surface chemistry to the CVD field is the design and refinement of selective processes. The surfaces of Si and of SiO₂ are very different in terms of bonding and reactivity. Si surface chemistry is controlled by the presence or absence of dangling bonds (db), and the "capping" of db by atoms (H, O, or halogens), or larger functional groups. The "uncapped" Si db are highly reactive, even at cryogenic temperatures.^{36,37} SiO₂ surface chemistry is controlled by the presence or absence of surface hydroxyl (-OH) groups, or other reactive sites. Without such groups, the bare SiO₂ surface is inert. These differences are schematically shown in the top of Figure 5.

Carlsson has recently reviewed the field of selective deposition in detail,³⁸ including the selective epitaxial growth (SEG) of GaAs, which we do not cover here. Selective deposition of tungsten (W) and aluminum (Al) may be used to deposit metal contacts through holes in an insulating dielectric layer (SiO₂ or Si₃N₄), making electrical contact to an underlying Si layer, a process known as "via filling". Two example via structures appear in Figure 4. At the top of the figure, a doped polycrystalline Si layer provides low resistance ("Ohmic") contact between metal wiring and the Si substrate. The central column labeled "Metal" is selective W or Al. At the bottom of the figure, the central metal column is called a "stud", and connects two levels of thin film metal wiring. We list the three types of mechanisms that are most effective in selective CVD, before providing more details.

a. Si Substrate Acts as Coreactant. The Si substrate is a reactant in the film growth reaction, while the adjoining SiO₂ or Si₃N₄ surface is inert. Reaction 1 is a general description of the selective

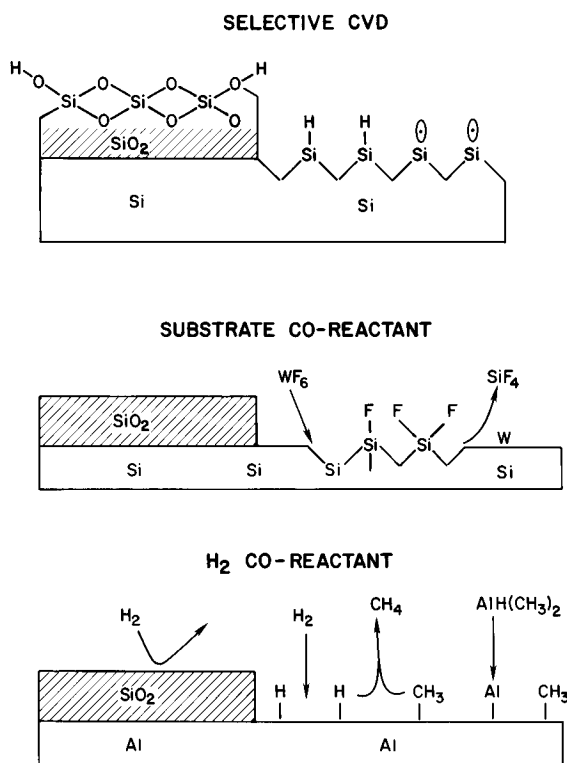
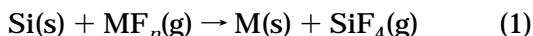


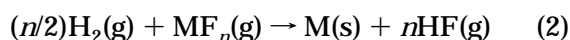
Figure 5. Important concepts used to discuss area selective CVD growth of metal films. The top picture compares SiO_2 and Si surfaces. The strong Si–O bonds which make SiO_2 quite inert and the Si dangling bonds which make clean Si highly reactive are emphasized. The middle picture illustrates use of the Si substrate as a coreactant in the film growth reaction to achieve surface selective CVD growth. Formation of a volatile product with strong bonds to Si (SiF_4) provides a driving force for the deposition of tungsten on exposed Si, and no on SiO_2 . The bottom picture illustrates how a large difference in dissociative sticking probability of the H_2 coreactant leads to selective growth on a metal surface, with negligible growth on SiO_2 .

deposition of the metal M from the metal fluoride MF_n by reaction with the Si surface:

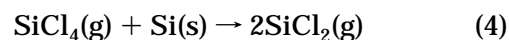
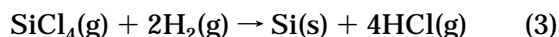


The middle of Figure 5 illustrates this approach, using the selective W CVD process as an example.

b. H_2 Gas Acts as Coreactant. Here, H_2 is a reactant in the film growth reaction. Also, the growth surface is active in dissociating H_2 , and the adjoining SiO_2 or Si_3N_4 surface is not. This is illustrated at the bottom of Figure 5. Reaction 2 for selective deposition of the metal M from the metal fluoride MF_n with H_2 , where H_2 dissociative chemisorption on the M(s) surface is facile:



c. Combined Etching and Deposition on Si. Epitaxial Si is grown on exposed Si, and not on adjacent SiO_2 , by combining two competing pathways: *etching and deposition*. The etching reaction prevents formation of Si nuclei on the SiO_2 surface. Using SiCl_4 and H_2 , an example is given by the deposition reaction 3, and the etching reaction 4:



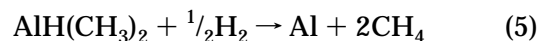
2. Si Substrate Is the Coreactant

When Si participates in the CVD reaction, and SiO_2 does not, a strategy for selective CVD is defined. The WF_6 chemistry shown in the middle of Figure 5 is the classic example, but the chemistry should be general for metal fluoride precursors. The Si–F bond is the strongest single bond (bond energy = 143 kcal/mol³⁹), with about the same strength as the C=C double bond. Thus, reaction 1 is quite exothermic. Considering the stoichiometric reaction of WF_6 with Si (has the form of reaction 1), ΔG° is -615 kJ/mol at 325 °C,⁴⁰ and SiF_4 formation drives the reaction. Hypothetical reactions of WF_6 with SiO_2 are much less exothermic.

Yarmoff and McFeely used photoemission to investigate the details of this reaction on Si(111).⁴¹ The chemistry shown in the middle of Figure 5 results in a surface that is *completely free of F* following WF_6 exposure of the Si(111) surface at 450 °C.⁴¹ Yu and co-workers measured S^R for WF_6 on Si(100) as 0.3, and identified SiF_2 as a second fluorosilyl product, using MBRS.^{13,42} It is assumed that WF_6 is much less reactive with SiO_2 , although this has not been directly measured. At the typical growth T of 300 °C, SiF_4 is the major product, while the SiF_2 pathway dominates at higher T . Very similar results were observed on Si(100) and on W surfaces containing adsorbed Si.^{13,42} The reaction starts on the clean Si surface and then proceeds via segregation of Si through the deposited W layer. For thicker films, the reaction must be continued by the addition of a coreactant to reduce the WF_6 , as in the next mechanism.

3. H_2 Gas Is the Coreactant

An excellent example of the use of H_2 as a coreactant is found in the work of Tsubouchi and Masu.^{43,44} These workers report the selective growth of Al into via holes with an aspect ratio of 3/1 (depth/diameter ratio) using H_2 and the Al precursor dimethylaluminum hydride (DMAH), $\text{AlH}(\text{CH}_3)_2$.^{43,44} Reaction 5 describes the net reaction. The bottom of Figure 5



emphasizes that H_2 “sticks”, or dissociatively chemisorbs, with a much higher probability on Al than on SiO_2 . Both filled and empty wave functions are available at metal and semiconductor surfaces to participate in H_2 dissociation. On insulator surfaces these wave functions are very poorly matched in energy, with respect to the H_2 molecular orbitals. Tsubouchi and Masu also propose that electrons available at the Si, and then Al, surface promote DMAH dissociation⁴⁴ leading to reaction 5. Adjacent SiO_2 surfaces are inert toward the Al precursor because no electrons are available.⁴⁴ Silane is also used as a reducing coreactant for metal halides (analogous to the H_2 coreactant mechanism), resulting in a higher film growth rate (GR) than with H_2 , and fundamental work on reduction of WF_6 by SiH_4

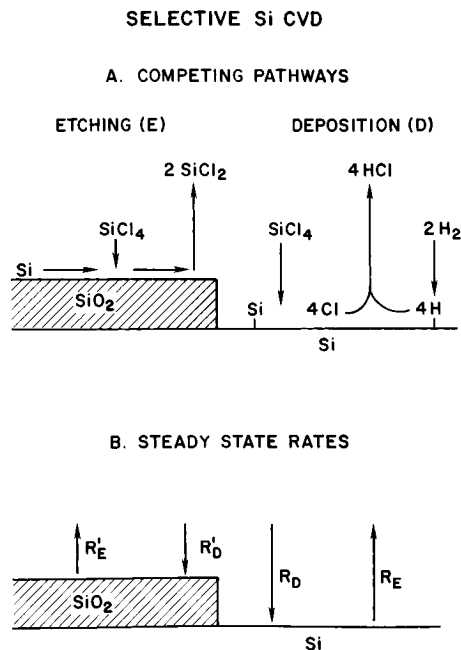


Figure 6. Important concepts in area selective CVD of Si: (A) Using SiCl_4 as an example precursor, the deposition pathway uses reaction with the H_2 coreactant to form HCl and Si film. The etching pathway forms SiCl_2 and removes Si film. Another common precursor is SiCl_2H_2 , also forming HCl and SiCl_2 . (B) Definition of labels to identify the steady-state rates of the etching and deposition pathways on Si (R_E and R_D) and on SiO_2 surfaces (R_E' and R_D').

has been reported.^{13,45} In a later section, IV.D., we discuss a kinetic model for a related CVD process, TiSi_2 deposition from SiH_4 and TiCl_4 .⁴⁶

4. Combined Etching and Deposition of Si

The acronym SEG (selective epitaxial growth) is commonly used in reference to Si and GaAs selective CVD systems. Figure 6 is a highly simplified sketch of the two competing pathways found in the SEG of Si using SiCl_4 and H_2 . This effect was first observed in 1962 by Joyce and Baldrey⁴⁷ and has been examined in detail. Both Cl and H are combined with Si in the reactant gas stream, and the T and P are high^{38,40} compared to most of the CVD processes discussed in this article. Due to the high T (>700 °C) and relatively high P (10 Torr to 1 atm) conditions, both surface reaction steps and homogeneous reactions are fast, equilibrium conditions are approached and the chemistry is controlled by thermodynamics, at least to a good approximation. (See section IV.B. regarding kinetic versus thermodynamic control in this system.) Both Madar⁴⁰ and Carlsson³⁸ have reviewed selective Si CVD using the chlorine + hydrogen + Si system. Madar's calculations illustrate the status of this field, where thermodynamic analysis is noteworthy in understanding and optimizing the SEG process.⁴⁰ The use of Si SEG in fabricating novel devices has been reviewed by Ginsberg and co-workers,⁴⁸ who used the basic $\text{SiCl}_4 + \text{H}_2$ chemistry of reactions 3 and 4, illustrated in Figure 6. The precursor SiCl_2H_2 is also used, and both H_2 and HCl can be added to the reactant gas, with the partial pressures adjusted to optimize selectivity.

Using the subscripts E and D for the etching and deposition reactions, respectively, and the symbol R for the net rate of each pathway, we refer to the bottom of Figure 6. R' indicates the rate on the SiO_2 surface, while R indicates the rate on Si. Adjusting the H_2 partial P allows some control over R_D and R_D' . It is highly likely that R_D has a strong response to H_2 addition, while R_D' does not, due to a greater sticking probability of H_2 on Si, compared to SiO_2 .⁴⁹ Recent papers have reported that H_2 dissociative adsorption on clean Si surfaces is characterized by $S^R \approx 10^{-5} - 10^{-6}$ at temperatures of 300–500 °C,^{50,51} while SiO_2 is inert toward H_2 adsorption.⁴⁹ The optimized conditions include a high H_2 partial pressure so that $R_D > R_D'$, and the two etching rates are probably equal ($R_E = R_E'$). George and co-workers have investigated the decomposition of SiCl_2H_2 and SiCl_4 on Si(111)- 7×7 surfaces in great detail.^{22,35} From this work, we know the pathways shown in Figure 6 (plus H_2 desorption) describe the surface chemistry in the Si + Cl + H system, and desorption kinetic parameters for HCl, SiCl_2 , and H_2 desorption are known.²² A similar strategy of balanced etch and deposition rates has been used by Parsons and co-workers in the Si + H system with plasma processing where the etching is driven by atomic H.⁵² Selective deposition of a mixed amorphous/microcrystalline Si phase on exposed Si, without growth on adjacent SiO_2 , was demonstrated.⁵²

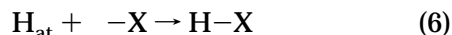
III. Free Radical Precursors and Atomic Coreactants

A. Introduction

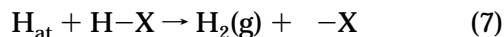
Motivated to deposit films at low temperatures, or fascinated by the chemistry of reactive species, we might propose to make a film using free radical precursors. Could we practically use chemical free energy in place of thermal energy to stimulate growth at reduced T ? Industrial processes that employ radicals as CVD precursors are "plasma-enhanced", or PE CVD, processes. Generation of radicals *in situ* within the CVD reactor using a plasma enables lower growth T , and very high growth rates may be obtained. Now consider a reactive atom used as a coreactant to deliver chemical free energy to the CVD growth surface, but this atom is not incorporated in the product film. The chemistry gets more complex and interesting. Atomic H (H_{at}) is our atom of choice. Highly reactive atoms and low-energy ions are finding increased use in the low-pressure, collision-free environment typical of molecular beam epitaxy and related growth methods.⁵³

B. Atomic Hydrogen and Group IV Semiconductor Surfaces

Adsorption of H_{at} on a covalent semiconductor surface occurs by termination of the surface dangling bonds (DB) according to reaction 6. Here, we consider the group IV semiconductors so $X = \text{C}, \text{Si},$ or Ge , with —X denoting a db on the CVD growth surface, and H—X denoting a surface site terminated with H.



Intuition suggests that the sticking probability of H_{at} is high (approximately unity), but measurements of the rate of reaction 6 as a function of the H_{at} translational energy are lacking.



The abstraction reaction 7 is exothermic for $\text{X} = \text{Si}$ and Ge , and roughly thermoneutral for $\text{X} = \text{C}$. Reaction 8 is obtained by summing reactions 6 and 7, is always exothermic by about 4 eV (the H-H bond energy³⁹), and may be described as "catalyzed" by the surface:



The unique surface chemistry of H_{at} as a coreactant in group IV CVD growth is summarized in these two sentences. Reaction 6 is exothermic and serves to convey the H-X bond energy (roughly 4, 3, or 2 eV for C, Si, or Ge, respectively) *directly to the CVD growth surface*. Reaction 7 creates the dangling bonds for reaction 6, and reaction 7 has been found to be a rapid and facile reaction.^{54,55} Halogen atoms probably exhibit similar abstractions/sticking chemistry but the practical use of halogens is limited by their corrosive action. Hydrogen is a clean, convenient, gas and is readily dissociated to H_{at} . We have studied the kinetics and mechanisms of H_{at} reactions on Si^{54} and diamond⁵⁵ surfaces. One objective was to clarify the roles of H_{at} in the CVD processes discussed below. We directly measured the rate and activation energy of reaction 7 using isotopic labeling ($\text{D}_{\text{at}} \rightarrow \text{H-X}$ and $\text{H}_{\text{at}} \rightarrow \text{D-X}$). Time-of-flight (TOF) scattering and recoil spectroscopy was used to follow the surface H and D coverages in real time by mass analyzing the recoiled H^+ and D^+ ion signals.^{54,55}

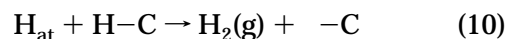
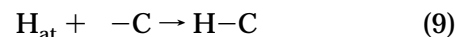
On both $\text{Si}(100)$ and $\text{Si}(111)$ surfaces, when only the monohydride species is present, the abstraction probability is ≈ 0.36 times the adsorption rate of H_{at} or D_{at} .⁵⁴ For $\text{X} = \text{Si}$, the rate of reaction 7 is $\approx 1/3$ the rate of reaction 6.⁵⁴ For $\text{X} = \text{Si}$ and C , the abstraction reaction 7 is very slightly activated by increasing surface T , (activation energies $\approx 0.5-1$ kcal/mol.^{54,55} A two-dimensional quantum mechanical model was used to interpret the results on Si .⁵⁴ According to the model, the activation energy is due to enhanced abstraction rates from the $\nu = 1$ vibrational states of the surface Si-H or Si-D bond. Reaction 7 may involve a direct reaction between the gas phase and adsorbed atoms, known as Eley-Rideal (ER) abstraction,⁵⁶ and the atomic H (D) may be accommodated into a "hot precursor" state, first proposed by Harris and Kasemo.⁵⁷ The H_2 or HD product containing excess translational energy has been detected on metals,⁵⁸ but not for semiconductor surfaces.

C. Diamond CVD Using Hydrocarbon Radicals and Atomic H

The chemistry of diamond thin-film growth using hydrocarbons and hydrogen was recently reviewed by Butler and Woodin.⁵⁹ We do not consider the combustion flame chemistry here, but focus on the

hot filament and plasma-driven diamond CVD chemistries. A general coverage of diamond growth was provided by Angus and co-workers,⁶⁰ who stated, "Atomic hydrogen plays a major role in mediating rates and in maintaining a proper surface for growth." The reactor conditions use an H_2 to CH_4 ratio on the order of 100/1, and a filament at $T \approx 2300$ °C or a plasma to dissociate the H_2 .^{59,60}

Gas-phase reactions of H_{at} include abstraction of H from CH_4 to make methyl radicals, and suppression of polycyclic C_n formation. On the surface, adsorbed H stabilizes the sp^3 C, preventing sp^2 C formation (preventing surface reconstruction) which leads to graphite formation. As emphasized by Gat and Angus,⁶¹ reaction 9 delivers chemical free energy to the diamond growth surface. Reaction 10 creates open sites (--C). These open, dangling bond, sites control the film GR by providing sites for CH_3 adsorption, and open sites also allow reaction 9 to proceed.



The steady state coverage of open --C sites must be kept very small to prevent surface graphite formation and is controlled by a delicate balance of the rates of reactions 9 and 10.

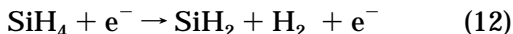
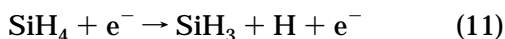
Our studies on diamond used polycrystalline films prepared in the Butler group at the Naval Research Laboratory.^{55,62} Using D_{at} , the rate of reaction 10 was 0.03 ± 0.01 times the rate of reaction 9,⁵⁵ roughly $1/10$ the rate observed on Si .⁵⁴ Abstraction proceeds at 0.03 times the rate of D_{at} sticking, and is characterized by an activation energy of order 1 kcal/mol (measured between 50 and 800 °C). An isotope effect was clearly observed. The rate of $\text{D}_{\text{at}} \rightarrow \text{H-C}$ was 3 times the rate of $\text{H}_{\text{at}} \rightarrow \text{D-C}$,⁵⁵ which can be explained in the E-R mechanism by more efficient momentum transfer from $\text{D} \rightarrow \text{H}$, than from $\text{H} \rightarrow \text{D}$. The first isothermal measurement of H_2 thermal desorption kinetics from diamond was also reported,⁶² and we expect these to be useful in models of diamond CVD.

D. Plasma-Enhanced CVD of Amorphous Hydrogenated Si (a-Si:H)

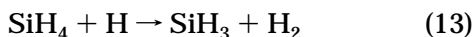
Amorphous hydrogenated Si (a-Si:H) films are routinely deposited using plasma-enhanced CVD (PE CVD) on glass and metal sheet substrates. In display fabrication the areas are ≈ 0.5 m², and solar cells based on a-Si:H are made over larger areas. The thriving flat panel display industry depends on PE CVD of a-Si:H and dielectric films. Low cost fabrication of $\approx 10^6$ a-Si:H transistors per display would be impossible without PE CVD. In the PE CVD system found in a modern display factory, a glass plate of area ≈ 0.3 m² is held at $T = 250-300$ °C in contact with a plasma at $P \approx 1$ Torr. The common feed gas is pure SiH_4 when the intrinsic (undoped) a-Si:H active layer of the transistor is deposited. Phosphine is added to deposit n-type a-Si:H for low-resistance contacts between the intrinsic layer and thin-film metal wires. The transistor dielectrics are grown as

amorphous Si–nitrogen alloys using a mixture of the gases SiH₄, NH₃, and N₂ in a process that is similar operationally, but different chemically.⁶³

The plasma chemistry of SiH₄ has been summarized briefly by Jasinski and Gates¹ and in great detail by Perrin.³¹ The homogeneous chemistry determines the species incident on the surface, as we illustrated in ref 1. The processes converting inert SiH₄ to reactive species are electron impact dissociation, ion–molecule reactions, and radical–molecule reactions. Electron impact produces mainly SiH₃ and SiH₂ through reactions 11 and 12.³¹



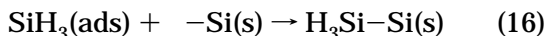
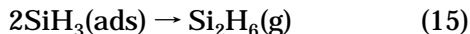
Some important radical–molecule reactions are reactions 13 and 14:



Here, we do not attempt a complete description of the growth mechanism as we neglect the ion flux to the surface which is strongly dependent on the SiH₄ partial pressure.³¹

In addition to reactions 11 and 12, electron impact produces smaller partial pressures of SiH, Si atoms, and atomic H.³¹ Different pathways analogous to reactions 13 and 14 produce Si₂H_x radicals. Many of the pertinent reaction state constants were measured by Jasinski, who helped put this chemistry on a quantitative foundation.^{64,65} One radical, SiH₃, is relatively unreactive with H₂, SiH₄, and other small molecules.⁶⁵ The highly reactive species SiH₂, SiH, and Si are converted to other species within 1 or 2 molecular collisions, so the flux to the surface is a mixture of SiH₃, SiH₄, and some Si₂H_x.^{1,31,64} The growth surface is H-terminated, and SiH₄ is unreactive with this surface.⁶⁶ The silyl radical, SiH₃ is the primary growth species according to most models,³¹ but Veprek has presented an alternative model with Si₂H₆ and Si₃H₈ as the primary growth species.⁶⁷

The surface reactions of SiH₃ have been the topic of many studies.^{68–70} A key observation, the formation of Si₂H₆ via reaction 15 strongly suggests that SiH₃ exists in a weakly adsorbed precursor state with surface mobility.⁶⁸



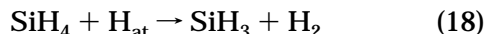
The major film growth reaction is schematically shown as reaction 16, requires a dangling bond ($_-\text{Si}(\text{s})$) on the surface, and similar reactions are envisioned for Si₂H_x species. The symbols (ads) and (s) denote weakly adsorbed species and the solid film, respectively. The coverage of dangling bond sites controls the growth rate. Some workers have attributed the production of these sites to reaction 17, where the SiH₃ can either be incident from the gas phase, *or* can be weakly adsorbed.^{31,71}



Our studies⁵⁴ of reaction 7 (see section III.B) and the slow rate of the bimolecular reaction of SiH₃ with SiD₄,⁶⁵ suggest that reaction 7 and reaction 17 must *both* be considered as channels producing open sites. The fluxes of SiH₃ and of atomic H reaching the growth surface, and the rate of reaction 17, will be necessary data to resolve this issue. The lack of accurate rate data for most of the surface reactions (including reactions 15–17 and others) hinders development of an accurate picture of the surface processes leading to film growth. Termination of the surface with H,^{31,71} and observations of reaction 15⁶⁸ and reaction 7 for Si,⁵⁴ are among the meager facts. The film is usually assumed to contain a “growth zone” near the top surface having an ill-defined thickness.^{31,71} In this zone, Si–Si cross-linking is thought to occur by elimination of H₂ and SiH₄.^{31,71} It would be interesting to observe any nonthermal behavior of these products, with Si–Si bond energy appearing in the internal energy of desorbing H₂ or SiH₄. The density of the film, and hence the electrical quality, is controlled by a balance of the rate of reaction 16 and analogous “sticking” reactions with Si–Si cross-linking. Suppression of SiH₂, SiH, and Si as growth species is also thought to be important.^{31,71}

E. Atomic H and a-Si:H

Atomic H is used in two ways to alter the short-range order in a-Si:H and even to produce microcrystalline Si films on amorphous substrates. These are addition of H₂ to the SiH₄ plasma^{52,72–74} and exposure of a-Si:H films to H_{at} after growth using an H₂ plasma.^{52,75–77} The latter procedure is called “chemical annealing”.^{75,78} During growth, addition of H₂ should simplify the plasma chemistry, *and increase the partial pressure of SiH₃* by reaction 18.



The reactions of H₂ with SiH₂ and SiH are fast, so these reactive species are depleted by H₂ addition. During growth, “annealing” of the surface by reactions 6 and 7 can occur, promoting Si–Si cross-linking. Etching of weakly bound SiH_x species is another active process.⁵² Electronic quality a-Si:H is deposited below 100 °C using H₂ dilution of the SiH₄ plasma.⁷²

The post-growth chemical annealing by H_{at} is also fascinating. Shimizu initially described the favorable action of H_{at} on a-Si:H.^{78,79} Recently, spectroscopic ellipsometry^{76,77} has been used to document the conversion of a-Si:H to a crystalline structure with small crystallite size (“microcrystalline Si”) by exposure to a-Si:H at 250 °C. Raman spectroscopy studies were especially convincing.⁵² Photoelectron spectroscopy has been used to study the effect at 50–100 °C.⁷⁵

IV. Modeling of CVD Processes Using Surface Kinetics

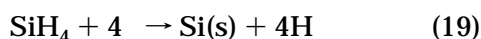
A. Introduction

We discuss here the use of surface reaction rate measurements to *predict* CVD film growth rates

(GR) and film stoichiometry.⁴⁶ Surface coverages of H^{80,81} or H and Cl⁸² on the dynamic CVD growth surface have been predicted for Si. These examples illustrate how surface chemistry and fundamental rate data contribute to optimizing practical CVD processes. We assume the reader is familiar with some basic concepts covered in ref 1, such as coupling of homogeneous and heterogeneous chemistry and control of film growth rate by the rate of product desorption via kinetic feedback.^{1,46,80,82} Under low T and P conditions, kinetics control the rate of film growth, and relatively simple models using measured desorption rates for the products, and precursor adsorption rates, can accurately describe the film growth rate and stoichiometry as a function of T .

B. Models for Si Epitaxial CVD

Gates and Kulkarni used a simple kinetic model to describe Si growth from SiH₄ for low P film growth. The key idea was to apply mass (atom) balance expressions to the *steady-state growth surface* at a selected T .^{80,81} When the reactor P is low, SiH₄ reaches the substrate intact and is the only active growth precursor. Under higher P conditions, homogeneous SiH₄ reactions producing more reactive species must be considered.¹ The key steps in the mechanism used to describe the low P growth are the adsorption of SiH₄, reaction 19, and the desorption of H₂, reaction 20. The symbol $_$ denotes a db on a surface Si atom.



Details of the surface decomposition of SiH₄ to adsorbed H have been discussed elsewhere^{1,37,66} and are omitted here, as these steps are faster than reaction 20 at low T , and faster than reaction 19 at high T .⁸⁰ Si growth rates from the literature for growth below 600 °C were accurately predicted using *only the rate of H₂ desorption* measured on Si single-crystal surfaces in UHV.⁸⁰ In 1991, the Yates group at the University of Pittsburgh had just reported the first-order H₂ desorption rate on Si(100)⁸³ (an observation confirmed by the George group⁸⁴), and these were used in the model. Between 600 and 1000 °C, the reactive sticking probability of SiH₄ was used as an adjustable parameter.⁸⁰ In addition to the Si GR, the model also *predicted the steady-state surface coverage of H*, and this was compared with *in situ* measurements of this coverage.⁸¹ Thus two very different measured quantities, H coverage and film GR, were predicted using only the rate of reaction 20 at low T , and using the rates of reactions 19 and 20 at high T .⁸⁰

Epitaxial Si growth below 600 °C is of interest in making abrupt dopant profiles in doped Si layers, and especially for the synthesis of Si_xGe_{1-x}/Si heterostructures with abrupt changes in Ge concentration between the Si_xGe_{1-x} and Si. Such heterostructures exhibit band-edge photoluminescence at liquid He T .^{85,86} and a variety of quantum effect devices including resonant tunneling diodes⁸⁷ have been demonstrated in the Si_xGe_{1-x}/Si system. As the Si from SiH₄

and Si from Si₂H₆ GR's are controlled by H₂ desorption below 600 °C, adding a coreactant that increases the rate of reaction 20 will increase the rate of film growth. This is observed in the case of GeH₄ addition to the Si from SiH₄ system,⁸⁸ and the observations of this effect were summarized by Greve.² Several workers have studied the rate of H₂ desorption from Si_xGe_{1-x} surfaces. Ning and Crowell reported that the activation energy for H₂ thermal desorption from Si(100) surfaces containing various concentrations of Ge decreased slightly as the Ge surface coverage increased.^{89,90} Some of the Si_xGe_{1-x} growth chemistry is discussed elsewhere in this volume by White and co-workers.⁹

A kinetic mass balance model was developed by Coon, Wise, and George to describe the growth of Si from SiCl₂H₂ at temperatures of 650–1200 °C.⁸² The successful *extrapolation* of kinetic parameters measured at low T (<600 °C) to the growth T was emphasized. The rate of SiCl₂H₂ adsorption and the rate of H₂, HCl, and SiCl₂ desorption were all reported in one study²² and extensive predictions of Si GR, and the H and Cl steady-state surface coverages were given in a separate paper.⁸² The rate of HCl thermal desorption was found to control the GR from 650 to 910 °C (similar to the Si from SiH₄ system at 400–600 °C). Above 910 °C, the rate of adsorption of SiCl₂H₂ limits the Si GR.⁸²

In section II.D, we sketched the chemistry of selective Si CVD in the Si/Cl/H system, and we used SiCl₄ and H₂ as our example (Figure 6). SiCl₂H₂ is also used for selective Si. Restricting our attention to $T > 910$ °C, the Si/Cl/H system illustrates an important distinction in CVD chemistry. As the Coon, Wise, and George model shows, the Si GR from SiCl₂H₂ is *kinetically controlled at low P*, the growth pressures being 0.01–0.1 Torr for the data modeled in this study.⁸² Selective Si CVD is practiced at higher P (>10 Torr), with Madar's calculations pertaining to 75 Torr, for example.⁴⁰ While thermodynamic equilibrium is not reached in a flow reactor, it is approached at high T and P . The selective Si CVD process is *thermodynamically controlled* to a good approximation due to the higher P used. This clear dichotomy arises from the dependence of gas-phase reaction rates on total P . The rate of collisionally activated homogeneous reactions (precursor pyrolysis, for example) can be proportional to the total P under CVD conditions.⁹¹ The surface science and film growth communities often neglect this fact.

C. Aluminum Films from Triisobutylaluminum

Bent, Dubois, and Nuzzo investigated the mechanistic chemistry of aluminum alkyls and Al surfaces.⁹² The intersection of different specialties, from organometallic chemistry and metal surface chemistry to CVD process design is seen in this exquisite series of investigations.⁹² The reactions of triisobutylaluminum (TIBA) on Al(111) and Al(100) surfaces were studied under UHV conditions, including identification of the H₂ and isobutylene products, and conditions for carbon free Al film growth.^{92,93} The rate-determining step in TIBA decomposition was found to be β -hydride elimination of isobutylene from the surface. The E_A for desorption of isobutylene and

the S^R of TIBA from the UHV studies were used to predict the GR of Al films at $P \approx 1$ Torr as a function of T .⁹³ This work was among the first demonstrations that kinetic parameters from low P , UHV, studies could be extrapolated over 6 orders of magnitude in P to predict a CVD growth rate to within a factor of 2–3.⁹³ At the total P of 1 Torr, homogeneous reactions may occur in the reactor, and this is probably the reason that the predicted GR (using only surface kinetics) was lower than the observed GR.

D. A Predictive Model for TiSi₂ Growth

Recently, Southwell and Seebauer have taken the kinetic modeling of CVD growth based on UHV kinetic measurements to a higher level.⁴⁶ The model concerns TiSi₂ growth from TiCl₄ and SiH₄, a system that can potentially be made selective for deposition on Si (see section II.D). These authors employ a microbalance to measure the TiSi₂ GR, and mass spectrometry is used to simultaneously measure product evolution under steady-state growth. The microbalance also served to calibrate the mass spectrometer product signals, in separate measurements. The GR of TiSi₂ could be measured independently from gravimetric data and mass spectrometry.

The model consisted of writing a mass balance equation for Ti, Si, and H, and two such equations for Cl (because Cl has two distinct reaction paths on the TiSi₂ surface). Product desorption and TiCl₄ and SiH₄ adsorption rates were measured previously under controlled UHV conditions.⁹⁴ The rates for each step were substituted into the mass balance equations, and the result was solved numerically. The Si/Ti ratio (film stoichiometry) was predicted and measured for a range of T and P conditions. The focus was *prediction of conditions for stoichiometric TiSi₂ deposition*, and the model suggests that lower TiCl₄ pressures will make the process easier to control.⁴⁶ This work indicates the future of this field—fundamental surface chemistry measurements connected to a practical CVD process. The examples discussed here emphasize that the connection takes the form of a kinetic model.

V. Atomic Layer Control over CVD Film Growth

A. II–VI Semiconductors and Metal Oxides

The atomic layer epitaxy (ALE) mode of CVD growth is a fascinating innovation that was patented in the 1980s and published in the 1990s.^{95–97} Originally, ALE was developed as a special mode of molecular beam epitaxy (MBE) growth in which the evaporative fluxes of two elements (Cd and Te, or Zn and Te) were *alternated*.⁹⁶ The substrate T was selected such that one monolayer (ML) of the element remained *chemisorbed* but subsequent layers evaporated to be pumped away. One cycle of growth consists of exposure to both elements. A growth rate of 1 ML per “cycle” is truly achieved, as a full layer of each element is deposited when the substrate T is properly selected. This growth mode is known as “type I” ALE in two noteworthy reviews of ALE.^{97,98} Later, the concept of *alternating pulses of two CVD precursor gases* became more widely used.^{99,100}

Chemical ALE (or type II ALE^{97,98}) is a special mode of CVD growth. Hereafter, we refer to chemical ALE simply as “ALE”, consistent with common practice.^{99,100} ALE can provide atomic layer thickness control, conformal growth over surface topography, and uniform growth over large areas. Stable, readily available molecules are typically used as precursors, which are delivered *as gas pulses in alternating fashion*. The substrate T and gas pressure are selected to allow one molecular layer of the precursor to chemisorb. Successful ALE chemistry is restricted to a handful of materials, such as metal oxides (for example Al₂O₃, Ta₂O₅, TiO₂) and the binary semiconductors ZnS and GaAs. Goodman and Pessa summarized the field as of 1986 in a significant review,⁹⁷ while Suntola has covered the field in noteworthy summary papers.^{99,100} The early 1990s produced new attempts to apply ALE concepts to elemental materials such as Si,^{101,102} SiC,^{101,103} and extension to mixed oxides including the superconducting YBa₂Cu₃O_x systems.^{101,103} The latest proceedings of the International Conference on ALE, in 1992¹⁰¹ and 1994¹⁰³ summarize the status of the field.

The basic chemical ALE strategy exploits a difference in adsorption energy between the first layer of chemisorbed molecules, E_1 , and the adsorption energy of subsequent molecular layers (approximately E_d in Figure 1). Such a difference in adsorption energy is well known for many systems from studies of the isosteric heat of adsorption and from temperature-programmed desorption.¹⁰⁴ The temperature is selected so that $E_1 > kT > E_d$. Excess reactant (not chemisorbed) is pumped away when the gas pulse is turned off, leaving one chemisorbed layer, an effect known as “self-limiting adsorption”. Due to steric crowding or other effects, the precursor coverage in this chemisorbed phase is submonolayer, and hence the growth rate is < 1 ML/cycle. The concept of building the solid in units of 1 atomic layer is approximated, but not fully achieved. Because the GR/cycle is very reproducible, the film thickness is proportional to the number of growth cycles, and fine control over thickness is readily achieved. A disadvantage is that ALE growth rates are quite low, but this is accommodated by processing 10–101 substrates simultaneously in a large batch reactor.¹⁰⁰

The film composition is determined by thermodynamics (the stable phase for the selected conditions), not kinetics, provided the duration of each gas pulse is long enough for complete reaction at the surface. Exothermic reactions give excellent ALE results,¹⁰² for example metal chlorides plus water to deposit high quality metal oxide films,^{105–107} or a metal chloride reacting with H₂S to deposit the metal sulphide (see below).^{97–100} In an earlier paper, we emphasized that a negative enthalpy change and a small entropy change are associated with the most successful chemistries for ALE.¹⁰²

ALE was developed in Finland to fabricate thin film electroluminescent (TF-EL) displays.^{99,100} The simple monochrome TF-EL structure consists of a light-emitting ZnS layer sandwiched between two dielectric layers (Al₂O₃). Both the ZnS and Al₂O₃ layers are made using “chemical” ALE, with the trilayer made in one deposition run. Monochrome

TF-EL panels have been made with ALE for several years.¹⁰⁵ The present challenge is to produce a *multicolor* TF-EL display with ALE, by deposition of ZnS doped with different metals sequentially in a stacked structure.¹⁰⁶ The Soviet literature contains a significant body of ALE work on oxides, and refers to this method as "molecular layering ALE", or ML-ALE. Recent work on SnO₂¹⁰⁷ and more complex oxides¹⁰⁸ by Drozd and co-workers provides a creative example of the ALE approach as applied to complex solids.

B. GaAs Growth by ALE

The deposition of GaAs by ALE has been widely studied, and the surface chemistry enabling atomic layer growth is quite well defined. Unwanted carbon doping of the GaAs films remains as a major problem that may limit the use of this method. Nishizawa and his co-workers first demonstrated a GR proportional to the number of gas pulse cycles by alternating the supply of Ga(CH₃)₃ and AsH₃.¹⁰⁹ The continuing efforts of this group were recently reviewed.¹¹⁰ Bedair and co-workers have investigated many aspects of GaAs ALE, emphasizing structural studies, reactor design,¹¹¹ and novel device structures.¹¹² Conformal covering of elaborate surface topography, combined with ALE growth, has been demonstrated for GaAs and InGaAs by this group.¹¹³ By using Ga(CH₃)₃, In(CH₃)₃, and AsH₃, conformal growth on trench sidewalls and on vertical wall structures was demonstrated.¹¹³

Surface decomposition of Ga(CH₃)₃ is thought to be the key to ALE growth of GaAs. Yu has discussed his model based on self-limiting adsorption of Ga(CH₃)₃ in detail¹¹⁴ and in abbreviated form.⁶ According to this scheme, during the Ga(CH₃)₃ precursor pulse a *steady-state fixed Ga coverage* is reached when the adsorption rate of Ga(CH₃)₃ is balanced by the desorption rate of Ga(CH₃)₃.^{6,114} When ethyl groups are substituted for methyl, ALE growth is not successful.^{6,114} Creighton has concluded that a simple picture of GaAs ALE consisting of alternate deposition of Ga and As layers is not correct.¹¹⁵ He introduced the role of surface steps acting both as "sources" and "sinks" for atoms and proposed that incomplete monolayers are present during GaAs ALE.¹¹⁵ An interesting approach to ALE was demonstrated for GaAs using *pulsed atomic H* exposure, and this may lead to novel chemistries for group IV elements and other materials.¹¹⁶

C. Extension of ALE to Group IV Semiconductors

The goal of atomic layer control over film thickness has motivated several studies using modified CVD growth of Si and diamond. With the elemental solids C or Si, the strategy using a difference between E_i and E_d is not employed. Exothermic film growth reactions are only possible at high T , or using radicals such as H_{at} to provide chemical free energy. Thus, the chemical mechanisms bear little resemblance to the ALE methods outlined above. Kinetic control over a surface exchange reaction may be used, the precursor exposure time and pressure must be controlled, and the T is adjusted to reproducibly deposit

1 or 1/2 or 2 ML of film in each growth "cycle". The growth surface should be continuously terminated with atoms (or larger ligands) to obtain abrupt interfaces. The surface free energy of Si, Ge, or diamond is reduced by this termination (relative to the bare surface), and adsorption of contaminants is minimized.

We employed the strategy of carefully selecting the substrate T and of alternating hydride and chloride reactants to approximate Si ALE growth.¹¹⁷ The two halves of an ALE "cycle" can be thought of as surface chlorination, and then reduction of the Cl layer using a source of H.¹⁰² The two reactants Si₂Cl₆ and Si₂H₆ were selected because of their relatively high reactivity compared to SiCl₄ and SiH₄.¹¹⁷ A Ge(100) substrate was used so that the thickness of thin Si layers could be quantitatively measured by medium energy ion scattering (MEIS) and by direct recoiling methods. At the optimum growth T of 465 °C, the chlorination step using Si₂Cl₆ is self-limiting because product desorption (SiCl₂) is extremely slow at this T .^{22,118} The reduction of the Cl layer using Si₂H₆ was not self-limiting, so the Si₂H₆ exposure step was adjusted for complete removal of surface Cl and a GR of 2 ML/cycle. Maintaining the growth surface terminated with H or Cl lowered the Si surface energy resulting in continuous Si overlayers on Ge, in contrast to the typical Si on Ge island growth mode.¹¹⁷

Alternative chemistries using H_{at} to reduce the surface Cl layer have been explored by us¹¹⁹ and others.¹²⁰ Chemical free energy is delivered by H_{at}, and all the of the discussion of section III should be considered. We believe that H_{at} induces mixing in the near surface region, making this chemistry incompatible with abrupt interfaces or dopant profiles, which are primary goals in Si ALE. This approach is compatible with reduced growth T , and with high-precision control of film thickness. The seminal work on ALE of Si by the Nishizawa group used relatively high temperatures (≈ 800 °C), and alternating pulses of SiCl₂H₂ and H₂.¹²¹ Self-limiting growth is observed for particular exposures to the two reactants, and the mechanism for this behavior at 800 °C has been a puzzle. We recently presented a kinetic model to help explain how self-limiting growth occurs at these high Si surface temperatures.¹²² The model predicts that the saturated growth surface is fully terminated with Cl, so the measured H coverage during SiCl₂H₂ exposure should be very small or zero.¹²²

VI. Summary

It is obvious that surface reaction steps are important to CVD film growth. The unique capabilities of CVD, and the active role of heterogeneous chemistry in defining these capabilities are not obvious. We have emphasized here the unique attributes of CVD and the surface chemistry that underlies these features. We have also discussed selected systems that reveal either novel chemical effects or very strong connections between fundamental surface kinetics studies and CVD growth. A few "take home messages" are listed below. (1) Conformal growth with uniform film thickness inside elaborate struc-

tures is possible with CVD and requires a low precursor sticking probability. (2) Surface mobility of the precursor in a weakly adsorbed phase contributes to uniform, smooth, films, and can assist in conformal coating for small-length scales. (3) Three basic strategies for *area-selective* CVD processes were outlined in section II.D, using either a coreactant or a combination of etching and deposition pathways.

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