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Heterogeneous Reaction Mechanisms and Kinetics Relevant to the CVD of Semiconductor Materials

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HETEROGENEOUS REACTION MECHANISMS AND KINETICS RELEVANT TO THE CVD OF SEMICONDUCTOR MATERIALS

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ABSTRACT

This report documents the state of the art in experimental and theoretical techniques for determining reaction mechanisms and chemical kinetics of heterogeneous reactions relevant to the chemical vapor deposition of semiconductor materials. It summarizes the most common ultra-high vacuum experimental techniques that are used and the types of rate information available from each. Several case studies of specific chemical systems relevant to the microelectronics industry are described. Theoretical methods fo calculating heterogeneous reaction rate constants are also summarized.

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I. INTRODUCTION

Heterogeneous reactions determine deposition rates, deposition uniformity, and utilization of reactant species. Any numerical model that calculates quantities such as these must contain some description of heterogeneous reactions. Information about the heterogeneous reactions at the deposition surface and at other solid walls provide boundary conditions on chemical species concentrations in a CVD reactor simulation. The information about heterogeneous reactions required to construct a numerical model for use in a CVD equipment simulation can range from simple reactive sticking coefficients (probabilities) to very detailed, elementary surface reaction mechanisms.

The experimental and theoretical methodologies for studying gas-phase chemical reaction mechanisms are quite mature and well-established. However, much less is known about heterogeneous surface reactions, and the techniques to study them are not in as mature a state. This white paper summarizes the experimental, theoretical and numerical modeling approaches that can be used to develop heterogeneous reaction mechanisms needed in semiconductor equipment models.

II. SURFACE SCIENCE EXPERIMENTS

A. Background

Aside from purely academic interest, most of the early surface science research was aimed at understanding the fundamental chemistry and physics of heterogeneous catalysis [1-3]. However, in the past ten or so years the scope of surface science research has broadened significantly and now includes such diverse topics as CVD, electrochemistry, tribology, corrosion, and plasma-surface interactions. In recent years, the surface science approach has led to a dramatic increase in our knowledge of the surface chemistry and kinetics of some key CVD processes related to silicon microelectronics. Some of the work regarding CVD surface science has been summarized in reviews and book chapters [4-5]. The processes that have been studied using a surface science approach include the CVD of semiconductors (e.g. Si, Ge, GaAs), metals (e.g. W, Cu, Al), and insulators (e.g. SiO_2). The information gained from these studies may be both mechanistic and kinetic in nature. We briefly discuss some examples later in this section. It is first important to understand the nature of the surface science approach.

B. Approach

The general philosophy behind the surface science approach is to study a surface or surface process in a well characterized and controlled environment, whenever feasible. This usually (but not always) requires that the study (or a portion of the study) be performed in an ultra-high vacuum (UHV) system. The surface science approach can yield both mechanistic and kinetic information about surface chemical processes. A wide variety of surface science diagnostics exist, but a detailed description of these techniques is clearly beyond the scope of this paper. A large number of books and review articles have been written discussing the merits and limitations of these techniques [1-3,6-23]. Some of the most commonly used surface science diagnostics are listed in Table 1. These techniques tend to fall into two broad categories. The first category of techniques (e.g. AES, XPS, LEED, etc.) directly probe some characteristic of the surface using charged particles and/or photons. These techniques generally yield elemental, chemical, or structural information. The second category of techniques (e.g., TPD) monitor neutral atoms, radicals, or molecules that have desorbed or scattered from the surface. These techniques yield information regarding the surface chemical reaction kinetics and mechanisms. In addition to temperature programmed desorption (TPD), there are a wide number of variations of techniques aimed at examining surface reaction kinetics and mechanisms, ranging from sophisticated modulated molecular beam scattering techniques to simple reactant gas backfilling or flow experiments at pressures of 10^{-9}-10^{-5} Torr. The techniques for measuring and modelling surface reaction kinetics have also been reviewed in detail elsewhere [13,16-18,24-31].

It is generally accepted that no one surface science technique is sufficient to perform a detailed surface chemistry study of CVD, catalysis, etc. For this reason most researchers incorporate several complementary techniques into a single UHV chamber. In the traditional surface science approach the surface chemistry and physics are examined in a UHV chamber at reactant pressures (and sometimes surface temperatures) that are normally far from the actual conditions of the process being investigated (e.g., catalysis, CVD, corrosion, etc.). This so-called "pressure gap" has been the subject of much discussion and debate for surface science studies of heterogeneous catalysis [3], and most of the critical issues are also relevant to the study of CVD. It is worth noting that the "pressure gap" for surface science studies of LPCVD reactions may actually be only a few orders of magnitude, e.g., 10^{-2} Torr (LPCVD) vs. 10^{-6} Torr (surface science experiment). While the effect of the "pressure gap" should always be considered when interpreting results, it does not *a priori* invalidate the surface science experiments. Indeed, there are a number of valid reasons for studying surface chemical processes at low pressures (and sometimes low temperatures). When approaching a complex chemical problem it is often advantageous to simplify the problem by dividing it into manageable pieces, and then study each

piece in a well-controlled environment. (This philosophy is certainly not unique to surface science.) By going to lower pressures and temperatures it is sometimes possible to isolate reaction intermediates and perform a stepwise study of a surface chemical mechanism. Also, reaction kinetics (particularly unimolecular kinetics) measured at low pressures often extrapolate very well to LPCVD or "real-world" conditions. Two such examples discussed below are Si deposition from silane and Al deposition from triisobutylaluminum (TIBA).

There are often some important chemical issues that cannot be addressed solely by low pressure studies and the traditional surface science approach. For these situations the capability of exposing the surface to realistic or near realistic pressures is needed. This is normally achieved by transferring the sample (under vacuum) from the UHV analysis chamber into a separate chamber that can be operated at higher pressures. This is sometimes referred to as a "model" study since it attempts to closely model the actual CVD (or catalysis, etc.) conditions. Since most surface science techniques cannot operate at these conditions, the surface may only be examined before and after the high pressure exposure. Another descriptive term for this method is the "Cook and Look" technique. Since this method is not truly *in situ*, it is mainly useful for studying adsorbates that may form too slowly to be seen under low pressure conditions. One example of this method as applied to the study of selectivity loss during tungsten CVD, as described below. One final point we wish to emphasize is that, in addition to the knowledge obtained from any of the surface science techniques, it is very desirable to have a reliable set of growth rate data that accurately represents the surface chemical kinetics at, or near, actual growth conditions. This allows reliable comparison of the reaction kinetics measured at low pressures ("surface science kinetics") to the growth rates measured at typical operating conditions (LPCVD kinetics). This information is sometimes not available (or of dubious quality) since measurements are often obtained in commercial reactors operated at conditions where the growth rate is dominated by mass transport rather than surface kinetic effects.

C. Surface Science Case Studies

1. Silicon

Silicon has received extensive interest from the experimental and theoretical surface science community, and it is one of the best understood surfaces of CVD interest. The kinetics of H_2 desorption from Si(100) and Si(111) have been measured in great detail by George [32], Yates [33], Heinz [34], and others, using a variety of surface science techniques. An early controversy arose regarding the reaction order of H_2 desorption from the monohydride adsorption state on Si(100). The reaction apparently exhibits first-order (rather than the expected second-order) kinetics with respect to the hydrogen coverage (at least for coverages > 0.1 ML). Now there is a

general consensus that H_2 desorption from Si(100) is indeed first order, and the reaction rate constant (activation energy and prefactor) has been accurately measured. The "unusual" first order kinetics have also been explained by a pre-pairing mechanism where the monohydride species tend to pair up due to energetic reasons. Boland [35] obtained direct experimental evidence for Si-H prepairing using STM, while Carter [36] used quantum mechanical calculations on small Si clusters to show that Si-H pairing was energetically favored over two isolated Si-H species. D'Evelyn [37] developed a statistical mechanical model for recombinative reaction kinetics that accounts for adsorbate pre-pairing (or attractive interactions). This model predicts a change to second-order kinetics at very low hydrogen coverages, and is in quantitative agreement with the experimental data of Heinz [34].

The desorption of H_2 from Si(100) is understood in great detail, but how is that information useful? For many conditions silicon CVD from silane (SiH_4) and other silicon hydrides proceeds primarily by H_2 desorption from the silicon surface. This is especially true for LPCVD of polycrystalline silicon, where the deposition rate is almost entirely governed by surface, rather than gas-phase chemistry. Moreover, Gates [38] showed that the critical adsorption state produced by silane (and disilane) dissociative chemisorption is the same adsorption state (i.e., the monohydride) studied in great detail by surface scientists (where the monohydride state was created by H-atom adsorption). Therefore, everything learned about H_2 desorption from silicon is directly relevant to the LPCVD of silicon from silane. Breiland, et al. [39] developed a simple silicon CVD mechanism which uses the H_2 desorption rate constant determined by surface science experiments as a key component. This mechanism is used in the SEMATECH model for polysilicon CVD, and gives quantitative agreement with growth rates measured in a commercial LPCVD horizontal furnace by Badgewell [40].

2. Tungsten

Tungsten CVD for microelectronic metallization has received a great deal of interest in the past decade [41]. It was found that the $H_2 + WF_6$ CVD process could be selective in that deposition occurred rapidly on many metals and semiconductors, but not on insulators such as silicon dioxide. The selective nature of the deposition process created much interest in that it significantly reduces the number of steps in the metallization process. Unfortunately, selective CVD is difficult to maintain and deposition eventually occurs on the oxide surface.

Creighton [42] investigated the mechanism of selectivity loss primarily using the "Cook and Look" surface science approach. In these studies an oxide coated silicon sample could be directly transferred from LPCVD conditions into a UHV chamber for surface analysis. Using this approach, Creighton found that the intrinsic cause of selectivity loss was due to the formation of a

volatile tungsten subfluoride (i.e. WF_5) which is formed by the interaction of WF_6 with the growing tungsten surface. The volatile WF_5 species could then adsorb on the oxide surface and disproportionate into elemental tungsten. Once elemental tungsten appears on the oxide surface, the hydrogen reduction of WF_6 proceeds and selectivity is lost. Creighton measured the formation rate of WF_5 using several methods [42] in order to verify that the amount of WF_5 formed could account for the degree of selectivity loss typically observed.

3. Aluminum

Aluminum CVD by triisobutylaluminum (TIBA) pyrolysis was examined for its potential as metallization for microelectronics [43,44]. A very nice example of the application of the traditional surface science approach to a CVD system is the work of Bent and coworkers [5,45]. They examined the surface chemistry of TIBA on Al surfaces using primarily TPD and low pressure beam scattering. TIBA was found to dissociatively chemisorb on the Al surface by ligand transfer to the surface Al atoms. The primary growth mechanism was found to proceed by β-hydride elimination from the adsorbed isobutyl groups, which forms isobutene (which immediately desorbs) and adsorbed atomic hydrogen (which immediately recombines and desorbs as H_2). The rate constant for this reaction was very accurately measured using TPD. A simple unimolecular CVD mechanism was developed which used the rate constants measured from the TPD experiments. This model was tested against effusive molecular beam experiments where TIBA impinged on single crystal Al surfaces at high temperature. Agreement between the simple unimolecular model and experiment were generally excellent. The model results were extended to LPCVD conditions and found be in good agreement with the results of Cooke [44]. Predicted absolute growth rates were about a factor of 2 too low (probably due the higher surface area of the polycrystalline deposit under LPCVD conditions) but the activation energies of the model and LPCVD measurements agreed within experimental error. One reason for the excellent agreement between model and experiment is that the kinetics of Al deposition is effectively in the "high pressure limit" at pressures above 10^{-5} Torr, for typical deposition temperatures. Under these conditions the surface is saturated with adsorbates, i.e. isobutyl groups. Therefore, the deposition rate under LPCVD conditions is determined solely by the rate constant of β-hydride elimination of the adsorbed isobutyl groups, and this rate constant was accurately measured by TPD. In summary, the TIBA/Al surface science study by Bent et al. [45] is a one of the best examples where the traditional surface science approach was used to obtain both mechanistic and kinetic information about a CVD process.

4. Other Examples

We briefly mention a few other examples where the surface science approach is being used to study the fundamental chemistry of CVD process. Crowell [46] and Vohs [47] used the traditional surface science approach to study the initial stages of SiO_2 deposition on silicon using the precursor TEOS. For the TEOS CVD system the precursor reactivity on oxide surfaces is very low and the traditional surface science approach has limitations. In this case the "Cook and Look" approach or an *in situ* methodology (e.g. using FTIR) may be more productive [48]. The TEOS/SiO_2 system is also an example where the relative importance of gas-phase vs. surface chemistry is still being actively investigated.

Other metal CVD systems, such as copper, have received a great deal of interest from the surface science community [49,50]. Aluminum deposition from hydride precursors (e.g. trimethylamine-alane) has also been studied [51].

In addition to studies of silicon surfaces, there has been considerable interest in the surface chemistry of germanium [52] and of compound semiconductor CVD. GaAs has been the most studied of the compound semiconductors [53], although some research on ZnSe [54] has also been reported.

D. Other methods for surface kinetic measurements

There are several methods of obtaining surface kinetic information that are probably not considered to be a subset of "surface science". One class of measurements involves determination of the deposition topology on top of (or inside of) small features intentionally fabricated on (or in) a surface. This information is compared to models of growth using various proposed chemical mechanisms and rate constants (or sometimes simply sticking probabilities). This technique of "feature-scale" modelling has been used by Cale [55] and McVittie [56] in order to "back out" surface kinetic parameters for some CVD reactions.

A perhaps more mundane, but extremely valuable method, is to simply measure the growth rate under well characterized and varied deposition conditions. By operating a reactor in the so-called "differential" mode, the effect of reactant depletion can be minimized. Then by independently varying the surface to volume ratio and/or the precursor residence time it may be possible to assess the relative importance of gas-phase vs. surface chemistry on the growth rate. A reliable and well characterized set of growth rate measurements can then serve as a data base for which any proposed chemical mechanism must be consistent.

The Sandia group has developed two molecular beam / surface scattering methods for measuring the reactivity of stable molecules [57] and radical intermediate species [58,59] at a

deposition surface. In the first type of experiment the reactive sticking coefficient (probability) for silane and disilane was determined. The reaction probability has a complex dependence upon both the surface temperature and the flux of the molecules at the surface. This flux dependence explains some seemingly inconsistent low-pressure CVD deposition rate data in the literature.

In the second type of experiment, denoted IRIS [58,59] (Imaging of Radicals Interacting with Surfaces), a molecular beam of a radical intermediate species is produced from a plasma, and these radicals impinge upon a surface. Spatially resolved laser-induced fluorescence (LIF) is used to monitor the difference in the incident and scattered fluxes of a species, and thus determine the fraction which reacts at the surface of the growing film. Although it is commonly assumed that radicals should be very reactive at a surface, the measured reactivities ranged from ~0.95 for SiH on an amorphous hydrogenated silicon surface [58] to essentially zero for SiO [59] and NH [60] on silicon oxide and nitride surfaces, respectively.

Table 1: Commonly Used Surface Science Techniques

Surface Science Technique	Incident particle	Detected particle	Information
Auger Electron Spectroscopy (AES)	e^-	e^-	Elemental composition Chemical information (sometimes)
X-Ray Photoelectron Spectroscopy (XPS)	X-ray	e^-	Elemental composition Chemical environment
Low Energy Electron Diffraction (LEED)	e^-	e^-	Surface crystallography, adsorbate geometry
High Resolution Electron Energy Loss Spectroscopy (HREELS)	e^-	e^-	Surface vibrations, Chemical structure, Bonding orientation
Surface Infrared Spectroscopy (SIRS)*	IR photon	IR photon	Surface vibrations, Chemical structure, Bonding orientation
Static Secondary Ion Mass Spectroscopy (SSIMS)	ion	ion	Chemical composition
Temperature Programmed Desorption (TPD)**	none	reactant & product molecules	Desorption kinetics, Coverages Reaction mechanisms and kinetics Adsorption kinetics (indirectly)
Molecular Beam Scattering or low pressure reactant exposure	reactant molecule	reactant & product	Adsorption kinetics, Reaction mechanisms and kinetics, Desorption kinetics

*Can be performed in transmission mode, external reflection mode (known as infrared reflection-absorption spectroscopy, i.e. IRAS, or reflection-absorption infrared spectroscopy, i.e. RAIRS), or internal reflection mode (known as attenuated total reflection spectroscopy, i.e. ATR, or multiple internal reflection, i.e. MIR). Most studies today use a Fourier transform infrared (FTIR) spectrometer.
**There are a large number of acronyms for this technique and its derivatives, including thermal desorption spectroscopy (TDS), thermal desorption mass spectrometry (TDMS), temperature programmed reaction spectroscopy (TPRS), etc.

III. THEORETICAL APPROACHES

A wealth of theoretical techniques have been established to calculate thermochemical information and reaction rates for homogeneous gas-phase reactions. These techniques include ab initio electronic structure calculations and various semi-empirical approximations, transition state theory, RRKM theory, quantum mechanical reactive scattering, and the classical trajectory approach. Although still computationally intensive, such techniques have proven themselves useful in calculating reaction energetics, pathways, and rates. Some of the same approaches have been applied to surface kinetics and thermochemistry, but with necessarily much less rigor.

Ab initio electronic structure calculations are applied using a "cluster" approximation; the properties of an entire surface are assumed to be mimicked by a much smaller cluster of atoms. However, it can be difficult to show that the small size of the cluster does not introduce gross errors ("edge effects") in the calculations. As an example, the mechanism for H_2 desorption from the Si(100)2x1 H surface has been studied by several groups using electronic structure calculations [36,37,61-63]. Unfortunately, different levels of theory and other assumptions in these calculations lead to fundamentally different conclusions about the desorption mechanism. Edge effects can be eliminated by applying periodic boundary conditions to a slab of surface atoms. This approach was taken, for example, in a theoretical study of the GaAs(100) reconstructed surface. Much more work is needed to develop electronic structure theory into a routine tool for understanding the chemistry at semiconductor surfaces.

Molecular mechanics force-field calculations [65] may provide an alternate approach to calculating energetics of surface reactions. These calculations use analytical expressions for bonding interactions between neighboring atoms, such as bond stretching energy, bending energy, torsional energy, etc., for each type of bond in the system. A computer code like MM3 computes the equilibrium structure of the collection of atoms by minimizing the total energy. These calculations can thus be employed to calculate the energetics of making and breaking bonds, and to calculate thermochemical properties such as heats of formation and entropies. Molecular mechanics has been very useful in understanding the elementary steps in the CVD of diamond [66,67]. We are not aware of this approach having been used in semiconductor systems, as of yet.

The classsical trajectory approach has been applied to calculation of reaction rate constants on Si surfaces. For example, Raff, Thompson, and co-workers have used classical trajectories to study the dissociative chemisorption of H_2 [68] and SiH_2 [69] on Si(111). Classical trajectory calculations are subject to several limitations. These calculations can only be as good as the empirical potential energy surface employed. Trajectory studies of gas-phase reactions usually use analytical fits to accurate ab initio calculations of the intermolecular potential. For surface

reactions, such ab initio potentials are impossible as of yet. Thus, the potential energy surfaces employed in gas-surface trajectory calculations are usually quite uncertain. In trajectory studies the random thermal fluctuations in a semi-infinite lattice of surface atoms must be simulated with a finite-sized slab of atoms. Approaches to the simulation of thermal motion include a generalized Langevin approach [70] and a velocity-reset method [71]. The classical equations of motion can only be integrated for timescales up to 10's or 100's of picoseconds, due to limitations of computer time. Often, however, chemical events of interest will only occur on much longer timescales. In these cases, statistical treatments, such as transition state theory, are usually employed. This approach has been used to simulate the diffusion of H [72] and Si [73] atoms on a Si(111) surface, and recombinative desorption of H_2 from Si(111) [74].

IV. NUMERICAL MODELING OF CVD SYSTEMS

The relative importance of gas-phase versus heterogeneous chemistry varies from CVD system to system. Yet, ultimately there will always be heterogeneous reactions that produce the deposited material. In constructing a numerical model of a CVD process for semiconductor equipment design or optimization it will always be necessary to supply some information about the heterogeneous (deposition) chemistry. Even if the chemistry is not specified in a very elementary manner, one still must ensure that the surface reactions specified "balance" in a chemical sense, in order that mass in the system will be conserved. The information about heterogeneous reactions required to construct a numerical model for use in a CVD equipment simulation can range from simple reactive sticking coefficients (probabilities) to very detailed, elementary surface reaction mechanisms.

Although use of sticking coefficients as the description of heterogeneous chemistry is the simplest approach possible, there can still be a great deal of information required from the modeler as input to the simulation. For every gas-phase species, ranging from just a few species (in the case that detailed gas-phase chemistry is not included) up to dozens (when detailed gas-phase chemistry is considered), one must specify the probability that the species will react upon collision with a surface. Moreover, the surface reaction probability will often depend upon the surface temperature, or perhaps, the pressure. It may also depend upon the coverage of other species on the surface, i.e., site-blocking. For each species surface sticking (reaction) probability, the user must also specify what byproducts are produced by the reaction and whether the reaction proceeds reversibly. Describing surface reactions via sticking probabilities is by far the most common method employed in CVD models.

Heterogeneous reaction rates are often expressed in terms of a Langmuir-Hinshelwood mechanism. The analytical functional form of the rate expression obtained accounts for the

competition for open reactive sites on a surface. It often provides the correct dependence upon reactant partial pressures. Representative examples using such analytical rate expressions include references [75] and [76] for Si deposition, and references [77] and [78] for Si_3N_4 deposition.

An alternate approach would be to specify an elementary chemical reaction mechanism at the surface. In this case one can have reactions between gas-phase species and surface species, or reactions between adsorbed species. At this level of specification, surface reaction mechanisms often become very complex, including dozens of elementary reactions. Such complex surface chemistry reaction mechanisms have been used in models for GaAs MOCVD [79-81], tungsten CVD [82], SiO_2 deposition from TEOS [83], and diamond CVD [67,84-86], for example.

For each reaction in a surface chemistry mechanism, one must provide a temperature dependent reaction probability or rate constant for the reaction in both the forward and reverse directions. (The user may specify that a reaction is irreversible or has no temperature dependence, which are special cases for the above, general statement). In order to simulate the heat consumption or release at a surface due to heterogeneous reactions, the (temperature-dependent) endothermicity or exothermicity of each reaction must be provided. In developing a surface reaction mechanism, one may choose to specify independently the forward and reverse rate constants for each reaction. An alternative would be to specify the change in free energy (as a function of temperature) for each reaction, and compute the reverse rate constant via the reaction equilibrium constant.

The Surface Chemkin formalism and software [87,88] were developed to aid in the integration of complex surface reaction mechanisms into chemically reacting flow simulations. In addition, it can provide a common (standard) format for surface reaction data exchange.

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