Nucleation and growth of silicon on SiO₂ during SiH₄ low pressure chemical vapor deposition as studied by hydrogen desorption titration

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We have developed a new approach to characterize the initial stages of nucleation and early growth of Si on SiO₂ from SiH₄ at low pressures. In a rapid thermal chemical vapor deposition reactor a sequence of alternating growth and hydrogen thermal desorption cycles using an in situ mass spectrometer is carried out. Desorption of hydrogen (a reaction product) is used to titrate the area of exposed Si surface on the SiO₂ surface after each growth step. A sensitivity of better than 10⁻¹⁵ monolayers (ML) is demonstrated. Nucleation and growth of Si islands is seen upon SiH₄ exposure under chemical vapor deposition conditions (500–700 °C). Once nucleated, the islands grow in size at rates consistent with those of Si epitaxial growth until they merge to form a polycrystalline film.

I. INTRODUCTION

Gases like SiH₄ have been used in the microelectronics industry for decades as precursor molecules for chemical vapor deposition (CVD) processes. Despite that, it is only recently that novel applications have brought enough research focus on CVD processes that a fundamental understanding of the underlying chemical reactions and their impact on reactor design and process parameters has begun to emerge.²⁻⁴ Especially the SiH₄ chemistry has recently been studied quite extensively, because of the success of ultrahigh vacuum CVD (UHV CVD),¹⁻³ which allowed fabrication of heterojunction bipolar transistors with record cutoff frequencies.¹⁻³ However, fundamental studies⁵⁻¹² have not analyzed process selectivity, a major advantage of CVD techniques over competing techniques, such as molecular beam epitaxy (MBE).

Characterizing the origins of selectivity and the loss of selectivity is a major challenge for surface analytical techniques. Generally, upon loss of selectivity one deals with a nonuniform surface coverage due to the formation of nuclei on the surface. The additional challenge is therefore to determine the nature of nucleation centers whose dimensions can be on the scale of a few angstroms. We have developed a technique, based on temperature programmed desorption (TPD), that allows characterization of the stage of nuclei formation and growth at total surface coverages of much less than a monolayer.

The technique has been applied to study the selectivity of SiH₄ growth on Si and SiO₂ surfaces. SiH₄ grows selectively on Si and not on SiO₂, although this selectivity is lost after an incubation time that is temperature and surface preparation dependent.²¹³¹⁴ We have studied specifically the growth of Si from SiH₄ on SiO₂. In a rapid thermal chemical vapor deposition (RTCVD) reactor,¹⁵ a sequence of alternating growth and hydrogen thermal desorption cycles using an in situ mass spectrometer is carried out. Desorption of hydrogen (a reaction product which decorates exposed Si surface sites) is used to titrate the area of exposed Si surface on the SiO₂ surface after each growth step. Nucleation and growth of Si islands is studied under UHV CVD conditions (500–700 °C). Islands grow in size at rates consistent with those of Si epitaxial growth until they merge to form a polycrystalline film. This approach provides new insights into the mechanisms which control selective growth and determine microstructure.

II. EXPERIMENTAL AND RESULTS

The growth experiments were carried out in a multicamera ultrahigh vacuum (UHV) system¹⁶ that integrates wafer precleaning, film growth, and surface analytical capabilities. Gas-phase reaction products were collected after each growth step using a differentially pumped mass spectrometer (Dycom). Samples used were 3.25-in.-diam double-side-polished As-doped (3×10¹⁸ cm⁻³) Si(100) wafers for growth and for TPD. RCA cleaned¹⁷ wafers were loaded into a glove box purged with ultrapure nitrogen (10-ppb purity) and the RCA oxide was etched with a HF gas-phase process. After clean the samples were first loaded through a load lock into a UHV sample-transfer chamber and then into the reactor. Prior to SiH₄ growth all wafers were oxidized in situ with dry oxygen at reduced pressures (10 Torr at 600 °C). Oxidation and SiH₄ CVD growth were carried out in a lamp-heated quartz-wall rapid thermal CVD reactor described previously.¹⁵¹⁸ The reactor is turbomolecular-pumped and reaches UHV base pressure. Total pressure during growth was measured with a baratron gauge and controlled in the pressure range from 10⁻⁴ to 10⁻⁵ Torr using flow controllers. Wafer temperature was controlled with an infrared pyrometer in the temperature range from 500 to 750 °C.

The experiment takes advantage of the difference in SiH₄ adsorption behavior on SiO₂ and Si surfaces. Clean Si(100), when exposed to SiH₄, will saturate with one monolayer of SiH species that give rise to a H₂ desorption signal upon TPD.¹⁵ In contrast, SiO₂ does not exhibit any surface adsorbate after SiH₄ exposure and does not give rise to any H₂ desorption signal upon anneal (as shown later). Thus any signal from an oxidized Si surface will...
come from Si islands or nuclei on the oxide and can be used to quantitatively titrate the number of exposed Si surface sites on SiO₂.

The starting surfaces were freshly prepared in situ oxidized Si(100) surfaces, with oxide thicknesses above 10–20 Å. The pressure/temperature pattern to accomplish Si growth and surface site titration is schematically represented in Fig. 1. The sequence can be broken up into a growth/passivation step and a titration step.

1. Growth/passivation: To initiate growth (or nucleation), a reactant pressure, typically ~1 mTorr SiH₄ is established. During growth the reactor ambient is never exposed to a lit filament to avoid reactant decomposition unrelated to the wafer surface. After pressure equilibration the temperature of the wafer is ramped up to reach the desired growth temperature, typically between 500 and 750 °C. Silicon is then grown for a time Tₜ₁ which is typically 5 min. After growth the surface is saturated with one monolayer of Si-H surface species. We know from previous studies that, at the pressures used here, a full monolayer will be established within less than a minute at any temperature at or below 500 °C. The Si growth stage is followed by a "passivation" stage at ~500 °C for 1 min, as shown in Fig. 1. After passivation, temperature and SiH₄ pressure are reduced rapidly. This "freezes in" the surface hydrogen. The amount of adsorbed hydrogen is proportional to the number of available surface Si surface sites.

2. Titration: A short (less than 1 min) pump step allows one to bring the reactor pressure into the low 10⁻⁶ Torr range, after which the valve to the mass spectrometer is opened. Subsequently, the amount of hydrogen desorbing from the surface is titrated using a 10-K/s thermal desorption ramp. The quantity of hydrogen is normalized by measurements taken from clean Si(100) surfaces (1 monolayer). Finally, after reaching the maximum temperature of the ramp, the sample is cooled down again and after reaching T < 500 °C, SiH₄ flow is reestablished to passivate the surface in order to prevent adsorption of residual contaminants.

This sequence of growth and titration is repeated until the TPD signal from the surface indicates that a full coverage of Si has been obtained.

A series of thermal desorption spectra taken from an oxidized Si(100) surface is shown in Fig. 2. Spectra are shown for SiH₄ growth at 560 °C and 1.3-torr total pressure (exclusively SiH₄) for various exposure times ranging from 5 min to 1 h. These spectra are compared to a spectrum taken from a clean Si(100) surface, as used for epitaxial Si growth. This spectrum is representative of a full monolayer of surface SiH. Additionally, the spectrum taken after 30-min growth on oxide is shown magnified 50× above the spectrum of the clean sample.

A clean SiO₂ surface does not show any appreciable H₂ desorption in the temperature range analyzed. For ex-
tended SiH₄ exposure times the desorption peak intensity from the oxide surface is seen to grow superlinearly with exposure time. The peak shape and position, however, are identical, within our resolution, to the peak measured for a clean Si(100) surface. Furthermore, the signal/noise ratio of the peak after 30 min gives an indication of the sensitivity of the technique. A sensitivity of down to 10⁻³ monolayers can be achieved easily and 10⁻⁴ is possible.

Figure 3 shows scanning electron microscope (SEM) pictures of samples from two stages during SiH₄ growth on SiO₂. These pictures correspond to the degree of coverage that gives rise to the TPD spectra after ≈40 and ≈75 min on the scale of Fig. 2. The nonuniformity of the surface coverage is clear.

Figure 4 shows the integrated peak intensity of the H₂ TPD for various conditions as a function of SiH₄ exposure time on a double-logarithmic scale. The data for SiH₄ exposure show a rapid initial intensity increase followed by a region in which the intensity rises proportionally to t². Essentially identical results are obtained for purified SiH₄. If plotted on a linear scale, the TPD signal intensity shown in Fig. 4 extrapolates to time zero, i.e., the first time SiH₄ exposure occurs at growth temperature. This implies that, under the conditions of this experiment, no incubation exists for formation of the first nuclei. We have also measured the time-to-full-coverage for growth temperatures between 500 and 750°C and, assuming zero incubation time, determined its activation energy to be >30 kcal/mol, consistent with the apparent activation energy of SiH₄ decomposition on Si(100) in the same temperature range.

We have found that three experimental parameters are critical to the reproducibility of curves like the ones in Fig. 4. The final temperature of the TPD ramp has to remain as low as possible, i.e., below ≈600°C, to prevent surface reactions of Si nuclei with the exposed SiO₂. Second, the state of the starting surface is critical to the density of nuclei at the surface, where thicker oxides generally exhibit fewer nuclei. Ultrathin oxides (10–20 Å) are expected to exhibit pinholes through the oxide which should facilitate initial nucleation. Finally, the total SiH₄ pressure and the residence time of the gas in the reactor impact growth rate and nucleation rate and have to be controlled accurately for reproducibility.

### III. DISCUSSION

The surface species during SiH₄ CVD has been identified previously as SiH. The single peak in the thermal desorption spectra is thus due to H₂ desorption from Si–H surface species. Figure 2 demonstrates clearly the two extreme situations that characterize the experiment. A clean (or HF-cleaned and thus SiH₄-passivated) Si(100) surface exhibits H₂ desorption from one monolayer of SiH₄ species after even a short exposure to SiH₄ to any temperature below 500°C (and above room temperature). In contrast, the clean SiO₂ surface does not exhibit H₂ desorption after even extended exposures under such conditions. SiH₄ does not react with SiO₂ and thus does not leave any reaction products at the surface after pump-down that could be detected with TPD. Any signal from a SiO₂ surface is thus expected to come from areas of exposed Si on the SiO₂ surface. Thermal desorption can then be used to titrate the amount of Si surface sites on the SiO₂.

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surface and can thus be used to characterize the initial stages of nucleation and growth of polycrystalline Si on SiO₂.

The sensitivity of the technique is demonstrated here to be better than 10⁻³ monolayers. With an improved experimental setup further enhancements are expected. For near-ideal systems, such as SiH₄ on SiO₂, where the SiO₂ substrate does not contribute an appreciable signal that could interfere with the signal from the Si nuclei, ultimate sensitivities much better than 10⁻⁴ monolayers should be attainable. We think that the application of the surface site titration technique to problems of nucleation and growth can contribute significantly to our understanding of the underlying mechanisms of selectivity and loss of selectivity, as well as to the characterization of the early stages of nuclei growth.

The following discussion gives a few examples of the potential of this technique. The spectra in Fig. 2 show that the spectral shape and position of the desorption peak remain the same over the entire coverage range accessible. This allows the conclusion that the surface species under equilibrium conditions is SiH even at the early stages of growth, i.e., when the surface coverage is less than 2% of a monolayer. At this stage of growth the nuclei are expected to be ~500–1000 Å in diameter and a significant number of surface sites should already be edge atoms (Fig. 3). Studies with increased sensitivity and using room temperature exposure might be able to identify contributions of edge or corner sites, which might exhibit species like SiH₂ or SiH₃.

The TPD intensity versus exposure time plot in Fig. 4 shows a r² dependence for longer SiH₄ exposures. A r² dependence can be explained by the growth characteristics of SiH₄ on Si(100). SiH₄ growth on Si(100) does not exhibit an incubation time and is linear in time. The same is expected for the surface of a Si nucleus. Assuming a roughly hemispherical nucleus shape (Fig. 3) and assuming the nucleus diameter grows linear in time, then its surface area will grow with a r² dependence. Formation of additional nuclei cannot contribute significantly to the intensity for this growth dependence to dominate. A r² dependence is thus expected for the growth of a few, large Si nuclei. This is indeed the situation for SiH₄ exposures, as demonstrated in Fig. 3. This nuclei stage of growth is thus characterized by the decomposition of SiH₄ on existing nuclei and the growth of Si on a Si surface. The growth kinetics follows the temperature dependence found for SiH₄ growth on Si(100) surfaces, as seen from the measurement of the activation energy.

In the initial stages of SiH₄ selectivity loss one distinguishes a region with steeper growth kinetics. In this growth regime the signal expected from a small number of nuclei that grow with time (the r² dependence) is superseded by a strong increase in the number of nuclei with time. The total time dependence is thus expected to be steeper than r².

The TPD signal saturates once it reaches ~1 monolayer. The number of surface sites does not increase any further once the entire surface is Si covered. Small differences between the signal intensity after saturation and the signal from a clean Si(100) surface are attributable to the surface morphology, which is rougher on polycrystalline surfaces than on single crystalline surfaces (larger surface area).

Although the signal/noise ratio does not allow measurements below 10⁻³ to 10⁻⁴ monolayers, extrapolations to even earlier stages of nuclei growth can be made. The TPD signal intensity shown in Fig. 4 extrapolates to time zero, i.e., the first time SiH₄ exposure occurs at growth temperature. The oxide thicknesses used for these experiments was in the range of ~20 Å. We can infer from this finding that for the relatively thin oxides used, Si nucleus formation occurs immediately after SiH₄ exposure commences. For very thin oxides this is not a surprise, as the oxide is known to have micropores which expose the underlying Si thus enabling formation of a Si seed that extends to the oxide surface. Under such conditions an incubation time before growth does not exist. It would be interesting, however, to check the validity of this statement for a wider range of oxide thickness.

Summarizing, we have demonstrated a technique that enables characterization of selectivity loss of CVD reactions, and the nucleation and the early growth stage of nuclei. For the particular case of SiH₄ on SiO₂, we have found no evidence for an incubation time for loss of selectivity on ultrathin oxides, which is likely caused by microchannels that exist in such oxides. We have also shown that, after formation of nuclei, the subsequent growth stages are controlled by the growth kinetics of SiH₄ on the nuclei surfaces. For the very early stage of nucleation, however, we conclude that the growth kinetics is dominated by ongoing formation of additional nuclei. This new approach provides new insights into the mechanisms which control selective growth and determine microstructure.

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