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Probing the silane, disilane and germane adsorption kinetics on the silicon (0 0 1) surface

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Abstract

In this paper, we make use of the hydrogen passivation concept to demonstrate that the pyrolysis of disilane (Si_2H_6) results in two silicon atoms and all six hydrogen atoms remaining on the surface and silane (SiH_4) produces one silicon atom and four hydrogen atoms on the surface. The dominant reaction pathways are identified and implications for Si film growth are discussed. The adsorption kinetics and subsequent dissociation of silane, disilane and germane during gas source molecular beam epitaxy on the Si(0 0 1) surface are studied in situ using modulated beam mass spectrometry (MBMS), temperature programmed desorption (TPD) and reflection high-energy electron diffraction (RHEED). These were also combined with the growth of various epitaxial layers involving repeated cycles of silane or disilane adsorption and hydrogen desorption with the layer thicknesses determined ex situ using X-ray diffraction (XRD) rocking curve measurements and computer simulations. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The initial stages of pyrolysis of disilane have been studied at relatively low temperatures ($<250^{\circ}C$) by a variety of techniques [1–9] and a number of reaction pathways have been proposed [1–5,7,10] but the identification of the dominant reaction pathway at higher temperatures corresponding to those used for film growth ($>400^{\circ}C$) remains unresolved. The growth of Si and SiGe films from hydride precursors such as silane (SiH_4), disilane (Si_2H_6) and germane (GeH_4) in gas source molecular beam epitaxy (GSMBE) is found to occur via a surface pyrolysis reaction and it is generally recognised that the growth rate is limited by the rate of desorption of the reaction product molecular hydrogen [11]. However, the mechanisms and reaction pathways of adsorption and dissociation of the precursors are not well understood and the studies reported here serve to clarify many of the mechanistic details of the growth process.

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2. Experimental procedure

The studies were performed using in situ modulated molecular beam mass spectrometry (MBMS), temperature programmed desorption (TPD), reflection high-energy electron diffraction (RHEED), and ex situ thickness measurement of layers grown by a temperature cycling technique involving low-temperature disilane adsorption and high-temperature hydrogen desorption. The kinetic measurements and layer growth were carried out in a double ended GSMBE system whose basic configuration has been described previously [12]. The mass spectrometer used in MBMS and TPD is a VG Quadrupole SXP300 with a synchronous motor-driven modulator located just in front of the ioniser. In TPD studies, the modulator is left in a stationary (open) position and the same electronics and multi channel scalar (MCS), as used for MBMS, are used for data collection. The RHEED measurements were obtained using a VG LEG110 electron gun operating at 15 keV and a k-space data collection system. The ex situ layer thickness measurements were made using a Philips high-resolution X-ray material research diffractometer.

3. Results and discussion

Placing the mechanical modulator in the line of sight from the sample to the mass spectrometer makes it possible to differentiate the signal of the desorbing or scattered beam from that of the background since in the ideal case the background will have no time-varying component. By measuring the magnitude of the first harmonic in data collected by the MCS as a function of substrate temperature, the rate of desorption of possible reaction products over the range from 400°C to 700°C was measured. The desorbing signal at mass/charge 31 was found to have no temperature dependence but at mass/charge 2 the signal was clearly thermally activated with an activation energy of 1.8 eV. The results suggest that the pathway of disilane pyrolysis on the Si(0 0 1) surface is very different from the Si(1 1 1) surface since silane production has been observed from growth on the Si(1 1 1) surface. The activation energy for hydrogen is in agreement with the silicon growth rate at various temperatures measured from RHEED intensity oscillation measurements (1.9 eV).

An accepted route for the pyrolysis of disilane is a sequential decomposition process where hydrogen is transferred from the adsorbed silicon hydride to the surrounding active sites. Under the growth conditions considered here it is assumed that the initial adsorption process and subsequent dissociation from the trihydride phase to the dihydride phase is not rate limiting in the overall growth process.

Two pathways have been proposed for the decomposition of the SiH_2 intermediates to the monohydride SiH phase

$$2\underline{Si}\text{–}H_2 \rightarrow H_{2(g)} + 2\underline{Si}\text{–}H, \quad (1)$$

$$2\underline{Si}\text{–}H_2 + 2\underline{Si}\text{–} \rightarrow 4\underline{Si}\text{–}H, \quad (2)$$

where $\underline{Si}$- is an active site for adsorption and $\underline{Si}$–X represents an adsorbed species X. Accepting that surface passivation occurs by hydrogen terminating the Si dangling bonds, a clear distinction between the two dihydride decomposition reaction pathways (1) and (2), can be drawn by measuring the amount of Si deposited while producing a fully hydrogen passivated surface. This was probed experimentally by performing a repetitive sequence of clean surface exposures to disilane at a temperature where negligible recombinative desorption of hydrogen takes place from the monohydride phase, followed by a high-temperature annealing to reproduce the clean surface for the next cycle. In this way the process can be said to be a variant of atomic layer epitaxy (ALE) which we have termed temperature cycled growth (TCG). All the samples grown consisted of an intial 6.8 nm SiGe marker layer followed by a 6.7 nm Si buffer, the TCG layers, another 6.8 nm SiGe marker layer and finally a 3.9 nm silcon cap. The resulting layer thicknesses were measured ex situ using XRD. Using this technique the amount of silicon deposited during each exposure cycle could be studied as a function of substrate temperature and flux. Exposing a clean Si surface to disilane with a beam equivalent pressure (BEP) $= 9 \times 10^{-6}$ mbar at growth temperatures of 430°C resulted in $\frac{1}{3}$ of a monolayer of silicon being

deposited per cycle. This is consistent with a complete sequential decay of the adsorbed silicon hydrides to form a surface completely covered in hydrogen. In this case, each disilane molecule would produce the two silicon atoms and all the six hydrogen atoms for passivation of the dangling orbitals on the surface. The resulting surface will be almost exclusively monohydride and under this circumstance, the overall pyrolysis of disilane can be given by Eq. (3):

$$Si_2H_{6(g)} + 6\underline{Si} - \rightarrow 2\underline{Si}\text{–}SiH + 4\underline{Si}\text{–}H. \quad (3)$$

For lower temperatures of about 250°C, $\frac{1}{2}$ ML of Si was deposited per cycle and this would suggest that the passivated surface is formed by a less complete sequential decay of the disilane. The number of disilane molecules, which give rise to $\frac{1}{2}$ ML of deposited Si, would again provide all the hydrogen required for passivation of the dangling bonds on the surface. In this case, the fully passivated surface will contain an equal amount of monohydride and dihydride units, and the pyrolysis process can be given by Eq. (4):

$$Si_2H_{6(g)} + 4\underline{Si} - \rightarrow 2\underline{Si}\text{–}SiH_2 + 2Si\text{–}H. \quad (4)$$

TPD experiments were also performed on hydrogenated Si surface to complement the TCG investigations. The hydrogenated surfaces were prepared by adsorption of disilane on a clean surface at the dosing stage of the TCG growth. Fig. 1 shows the TPD spectra of hydrogen resulting from a monohydride and a monohydride + dihydride surface produced from disilane exposure at 430°C and 200°C, respectively, and also exposure to atomic hydrogen. Exposure at 430°C confirms that only the monohydride β_1 phase was present while below 250°C a dihydride β_2 phase was observed in coexistence with the monohydride phase. These observations are therefore consistent with silicon coverages achieved in the TCG experiment [13].

The adsorption of silane and subsequent dissociation has also been the subject of many studies and the consensus of opinion is that the subsequent dissociation of the silicon hydrides is sequential in

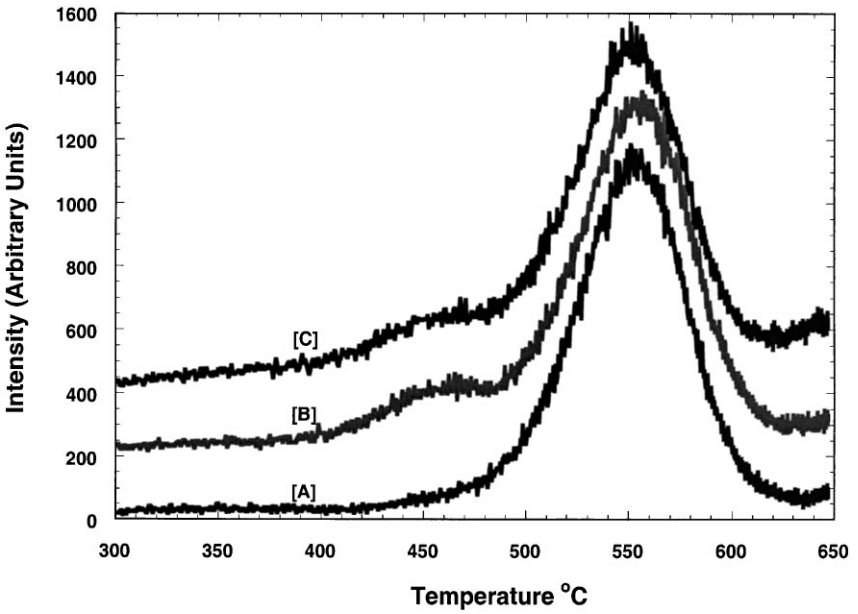


Fig. 1. TPD of hydrogen from the Si(0 0 1) surface. Curve [A] shows purely monohydride desorption from a surface produced from disilane exposure at 430°C on the clean surface, curve [B] shows monohydride + dihydride desorption from disilane exposure at 200°C. This is identical to curve [C] produced from atomic hydrogen exposure.

a similar way to that for disilane. Test structures similar to those described earlier for disilane were grown using silane as the growth precursor. For adsorption temperatures of 392°C and 313°C with 5 min exposures at a BEP of 2.7×10^{-5} mbar, 0.20 ± 0.05 ML/cycle were deposited in each case. For higher silane pressures (BEP $= 6.9 \times 10^{-5}$ mbar) for a 10 min exposure at 200°C a complete layer of hydrogen is detected from TPD and the amount of silicon deposited in the growth experiments is still found to be 0.20 ± 0.05 ML/cycle. This is consistent with each silane molecule depositing one silicon atom and four hydrogen atoms to give a maximum coverage of 0.25 ML/cycle which is just within our experimental uncertainty. Both TCG and TPD experiments imply that the dominant SiH_2 dissociation pathway for silane and disilane is that given by Eq. (2).

Germane adsorption was found to behave in a similar fashion to silane, however 100 cycles of germane TCG were not performed on silicon since the surface is likely to go 3D very quickly, it was therefore studied using TPD of hydrogen for the first 10 cycles only. Unlike disilane or silane, germane TCG on Si(0 0 1) with adsorption at 340°C results in a gradual shift in the monohydride β_1 peak towards lower temperatures with each cycle of deposition along with the appearance of other peaks at lower temperatures in the TPD temperature ramp. The resulting spectra are shown in Fig. 2. The shift in the β_1 peak has been considered by Ning and Crowell [14] and they postulated that the germanium modifies electronic structure weakening the silicon–hydrogen bond while Russell and Breiland [10] suggest a two-step desorption pathway via a germanium monohydride intermediate as the reason for the observed shift. The more likely reason, we believe, is that considered by Russell [15] where the shift is due to surface hydrogen diffusion to the germanium site before desorption. This diffusion will be more significant at higher temperatures in the TPD ramp and hence further desorption takes place from previously depleted sites beyond the initial peak at lower temperatures. The fact that more than 10 exposure cycles are needed to produce the single monohydride desorption peak from the surface implies that more than one monolayer of germanium

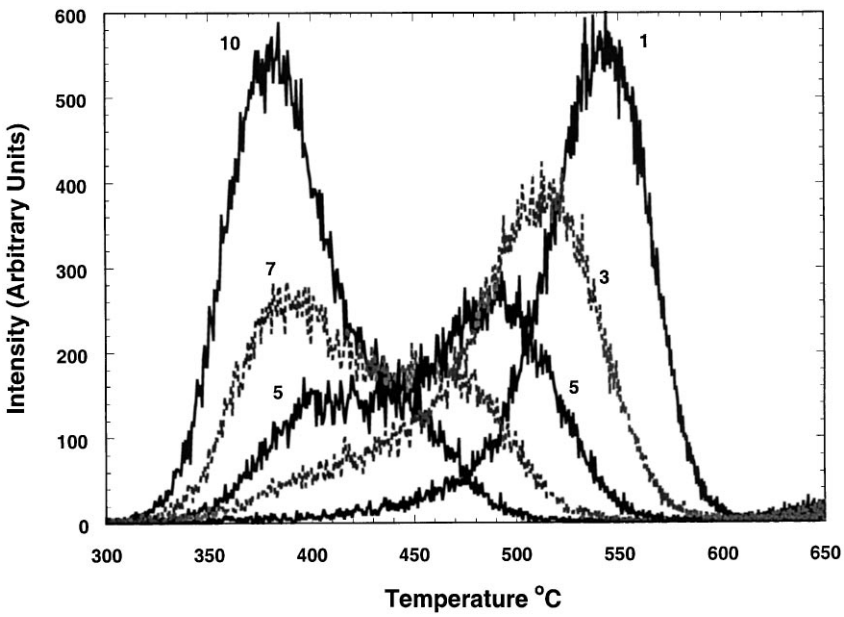


Fig. 2. TPD of hydrogen from cycled germane exposure on the Si(0 0 1) surface. The bold numbers refer to the number of germane exposures and annealing cycles.

is required for this to occur. More work is clearly required to clarify this reaction scheme.

One of the conclusions from the above result is the ability of a fully hydrogen covered surface to passivate further adsorption. This is clearly demonstrated by the invariance in the shape of TPD spectra when the monohydride surface is further exposed to disilane and also to germane fluxes. This behaviour is very different when a Si monohydride covered surface is exposed to atomic hydrogen. In this case, a β_2 dihydride peak is observed, which can only occur by a direct hydrogen insertion and the breaking of the Si–Si dimer bond to form the dihydride units. To complement these results, growth rate measurements from RHEED intensity oscillations during disilane deposition were also monitored. In the hydrogen desorption growth limited regime, any presence of a lower-energy channel to hydrogen desorption will increase the growth rate and this is indeed observed when germanium is present on the surface. The increase in growth rate can be monitored by RHEED oscillations and in this way can be used to monitor the presence of surface germanium. The monohydride surface exposed to germane showed no enhancement in growth rate whereas a clean surface exposed to germane clearly enhances the subsequent growth rate of silicon from disilane. It is therefore clear that dangling orbitals (active sites) have direct control over the kinetics of disilane, silane and germane chemisorption and subsequent dissociation.

4. Conclusions

In summary, the TCG thicknesses, RHEED oscillations and TPD measurements confirm that the Si(0 0 1) surface is passivated by hydrogen and it is clear that the dangling orbitals have direct control over the kinetics of growth. The decomposition of silane, disilane and germane provides the hydrogen which passivates these dangling bonds and they can only be re-generated (to allow further growth) by subsequent recombinative desorption of molecular hydrogen. However, recent studies [16] suggest a weak flux dependence of the growth rate even at temperatures as low as 400°C where the hydrogen coverage is close to unity and the growth is in the hydrogen desorption limited regime. This finding is considered to be due to the removal of hydrogen from the surface by disilane through a mechanism such as abstraction. This suggests that a closer examination of the degree of passivation of the silicon monohydride surface is needed. The dissociation of disilane molecules is found to occur sequentially without any release of molecular hydrogen or SiH_x species directly into the gas phase (see reaction (2)) and the major reaction products on the surface are SiH_2 and SiH. Silane has been shown to dissociate in a similar manner to disilane where a 'self-passivated' surface at 300°C consists of 1 ML of hydrogen and 0.25 ML of silicon. Germane behaves in a similar fashion to silane in that it produces 1 ML of hydrogen before the surface becomes passivated but creates a lower-energy channel to hydrogen desorption.

Acknowledgements

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