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Probing the disilane adsorption kinetics: An alternative approach

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The adsorption kinetics and subsequent dissociation of disilane during gas source molecular beam epitaxy on Si(001) surface is studied *in situ* using modulated beam mass spectrometry, thermal desorption spectroscopy, reflection high energy electron diffraction and growth of epitaxial layers involving repeated cycles of disilane adsorption and hydrogen desorption. The dissociation of disilane molecules is found to occur sequentially and the major intermediate reaction products are SiH_2 and SiH. At temperatures above 400 °C, disilane dissociates readily to give two silicon atoms and all six hydrogen atoms and forms the monohydride $(2\times1)+(1\times2)$ surface. The formation of a Si-monohydride surface also passivates against further adsorption and dissociation of disilane. The main reaction pathway for the decomposition of SiH_2 to SiH is identified and studied as a function of incident flux and growth temperature. This process is found to be controlled by the number of unsaturated dangling orbitals. [S0163-1829(99)50708-X]

The growth of Si and SiGe films from hydride precursors such as disilane (Si_2H_6) and germane (GeH_4) in gas source molecular beam epitaxy (GSMBE) involves a surface pyrolysis reaction.[1,2] It is generally recognized that the growth rate is limited by the rate of desorption of molecular hydrogen (a reaction product) from the surface[3] and this limitation arises from the hydrogen-coverage-dependent sticking coefficients of the hydride precursors. However, the mechanisms and reaction pathways of adsorption and dissociation of the precursors are not well understood. The initial stages of pyrolysis of disilane have been studied at relatively low temperatures (<250 °C) by a variety of techniques[4–8] and a number of reaction pathways have been proposed,[4,6,9] but the identification of the dominant reaction pathway at higher temperatures corresponding to those used for film growth (>400 °C) remains unresolved. In this paper, we make use of the hydrogen passivation concept to demonstrate that the pyrolysis of Si_2H_6 results in two silicon atoms and all six hydrogen atoms remaining on the surface. The dominant reaction pathway is identified and implications for Si film growth are discussed.

The experimental results were obtained using *in situ* modulated molecular beam mass spectrometry (MBMS), thermal desorption spectroscopy (TDS), 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.[10] The *in situ* measurements were obtained with liquid-nitrogen-cooled panels in order to increase the beam-to-background ratio and pumping speed whereas the layer growth was performed with the cryopanel water cooled. The latter provides more than a tenfold increase in operating pressure but poorer beam-to-background ratio. The mass spectrometer used in MBMS and TDS is a VG Quadrupole SXP300 with a synchronous motor driven modulator located just in front of the ionizer. It is assumed to be an ideal density detector[11] and has direct line of sight to the sample through the modulator but it is not in the plane of incidence of the molecular beam. For MBMS measurements, the modulator is phase locked to a drive signal derived from a free running multichannel scaler (MCS). The electron multiplier of the mass spectrometer was operated in pulse counting mode, with its output fed into the MCS via a charge sensitive pre-amplifier, timing amplifier, and discriminator. The density of the detected neutral molecules/atoms entering the ionizer is assumed to be proportional to the amplitude of the harmonic at the modulation frequency obtained using fast Fourier transform. The detected flux is then obtained by scaling the neutral density by the square root of temperature of the substrate. In TDS studies, the modulator is left in a stationary (open) position and the same electronics and MCS described above 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. *Ex situ* layer thickness measurements were made using a Philips high-resolution x-ray material research diffractometer.

One of the consequences of the hydrogen passivation of the Si(001) surface against adsorption of disilane is that the rate of production of any reaction products during the pyrolysis of disilane will also be limited by molecular hydrogen desorption kinetics. The temperature dependence of the rate of formation of possible reaction products over the range from 400 °C to 700 °C was investigated by modulating the desorbing flux from the surface using MBMS. The desorption rate of molecular hydrogen ($m/e=2$) was found to follow the growth rate (i.e., increases with increasing temperature as expected) with an activation energy of 1.8 eV, but the signal corresponding to the hydride species (mass spectrometer fully deresolved to cover the range $m/e=29-32$) remained largely constant. This absence of any temperature dependence in a region where hydrogen coverage of the surface is known to change significantly[12] indicates that SiH_x and silane (SiH_4) do not desorb from the surface. The path-

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TABLE I. Sample structure.

Layer material	Growth method	Thickness
Si (cap)	Conventional	60 Å
SiGe (marker)	Conventional	120 Å
Si	TCL	See Table II
Si	Conventional	120 Å
SiGe (marker)	Conventional	120 Å
Si	Conventional	buffer and substrate

way of disilane pyrolysis on the Si(001) surface is thus very different from the Si(111) surface where SiH_4 production has been observed.[6,13]

Another route for disilane pyrolysis on a clean Si(001) surface is via the dissociative chemisorption of disilane to form SiH_3 on the surface and subsequent dissociation of SiH_3 and SiH_2 to the monohydride phase,[7] i.e., $Si_2H_6 \rightarrow 2SiH_3 \rightarrow 2SiH_2 \rightarrow 2SiH$. In this reaction scheme, the accepted view is that disilane chemisorbs dissociatively on the surface requiring two active sites. The SiH_3 formed in the process is relatively unstable and readily decomposes to SiH_2 at room temperature leaving an adsorbed hydrogen.[4,7] The mechanism by which the next hydrogen atom is lost from SiH_2 is, however, less clear and from low temperature studies[4,5,7] two reaction pathways have been proposed:

$$2SiH_2 \rightarrow H_2(g) + 2SiH, \tag{1}$$

$$SiH_2 + \underline{Si} \rightarrow 2SiH, \tag{2}$$

where $\underline{Si}$ indicates a Si atom with a dangling orbital. The difference between the two reaction pathways lies in the number of hydrogen atoms per disilane molecule which remain on the surface and passivate the Si dangling orbitals. Accepting that surface passivation occurs by the formation of Si monohydride, a clear distinction between the two reaction pathways can be drawn by measuring the amount of Si deposited while producing a full monohydride coverage on a clean surface. This can be probed experimentally using the following procedure. Epitaxial layers were grown by repeated cycles of sequential dosing on a clean Si(001) surface with disilane at a given temperature and annealing at 600 °C to desorb the hydrogen in the absence of a disilane flux. The dosing temperatures employed are sufficiently low to ensure negligible hydrogen desorption[12] such that any thickness due to normal continuous growth can be ignored. This cycle is repeated 100 times and the resulting layer forms the second part of a Si barrier between two SiGe quantum wells (see Table I). With the exception of the layer grown by this temperature cycling technique, the rest of the structure was grown at 500 °C using the conventional GSMBE technique. The inclusion of the first part of the Si barrier eliminates any effect of Ge surface segregation on the subsequent growth of the temperature cycled layer (TCL). The thickness of the layer is obtained by comparing *ex situ* x-ray rocking curve measurements and simulations based on the dynamic theory of diffraction. The details of growth condition and measured thickness of the TCL are given in Table II and the corresponding rocking curves are shown in Fig. 1. Sample BF690 had no TCL and served as a reference.

TABLE II. Sample information.

Sample	Dose Temp. (°C)	Dose Pressure (mbar)	Dose Time (s)	Cycled layer thickness (ML)
BF689	430	1×10^{-5}	20	33
BF690	NA	NA	NA	0
BF691	320	1×10^{-5}	60	39
BF695	430,320	1×10^{-5}	10,60	33
BF699	250–300	8×10^{-5}	60	49

Consider first the result for sample BF689, where dosing occurred at 430 °C, the TCL thickness is measured to be 33 monolayers (ML), and therefore 1/3 of a monolayer of Si was deposited per cycle. The surface maintained the $(2\times1)+(1\times2)$ monohydride surface reconstruction after dosing and previous reflectance anisotropy studies have shown that hydrogen desorption at this temperature is negligible during the dosing period.[12] An equivalent of one ML of hydrogen is therefore required for complete passivation of the surface. The number of disilane molecules which produce the 1/3 ML of deposited Si could only provide the equivalent of one ML of hydrogen if all the hydrogen atoms from the molecules participate in the passivation of dangling orbitals with no loss to the gas phase. This means that the dominant SiH_2 dissociation pathway is that given by Eq. (2), since if any significant amount of hydrogen were to desorb directly during pyrolysis of disilane to the Si-monohydride phase [i.e., via Eq. (1)], surface passivation would not be complete. Under these circumstances, it should be noted that full passivation via Eq. (1) would lead to growth of more than 1/3 ML per cycle, contrary to the experimental finding from BF689.

The surface reaction given in Eq. (2) requires a Si dangling orbital and is therefore in direct competition with the dissociative chemisorption of the incident disilane. For BF689, the dosing temperature is sufficiently high for the rate of the reaction [Eq. (2)] to be fast such that the resulting monohydride passivates the surface and prevents further dis-

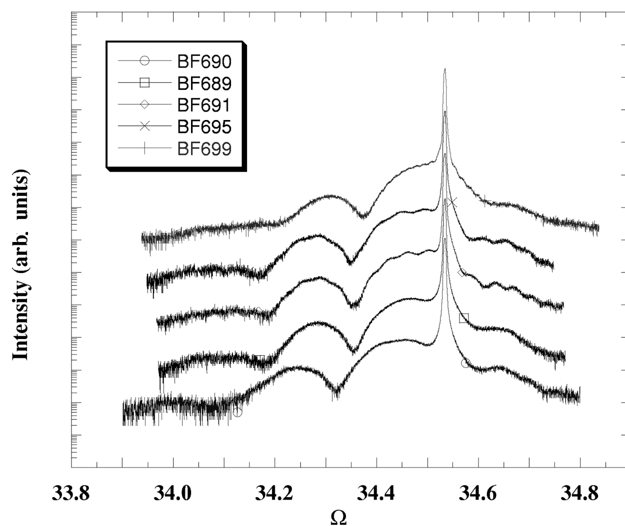

FIG. 1. X-ray rocking curves of (004) reflection from the grown structures in Table II.

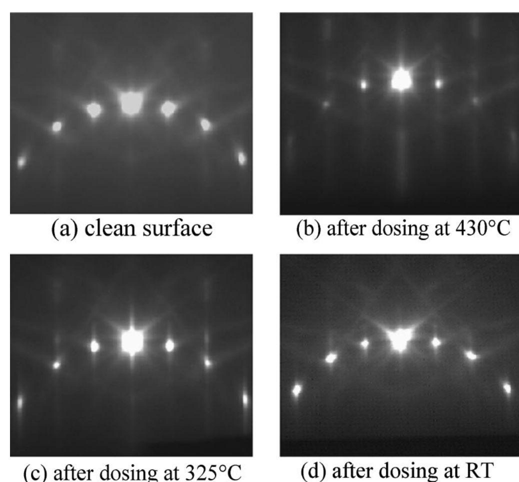

FIG. 2. RHEED pattern of a clean and hydrogenated Si(001) surface in the [110] azimuth.

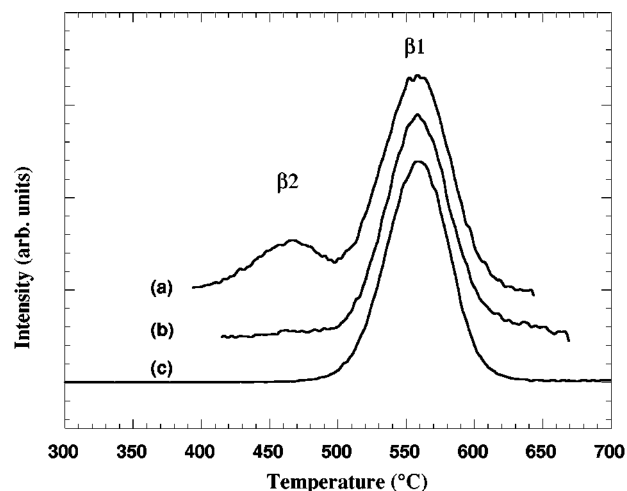

FIG. 3. H_2 TDS spectra from Si(001) surface dosed with disilane at temperature of (a) 150 °C, (b) 150 °C after first forming the monohydride at 430 °C (cf. BF695) and (c) 430 °C.

sociative chemisorption of disilane and the formation of any higher hydrides. This, however, may not be true when the dose temperature is lowered or the incident disilane flux is increased. In sample BF691, lowering the dosing temperature to 320 °C increased the TCL thickness to 39ML. Lowering the dosing temperature further (to 250 °C–300 °C) and increasing the disilane flux simultaneously resulted in a TCL thickness close to 0.5 ML per cycle as obtained for sample BF699. In addition to TCL thickness measurements, RHEED patterns were also obtained from surfaces after dosing at 430 °C, 325 °C, and room temperature (Fig. 2). All the patterns indicate the presence of dimers although the half order diffraction features have a lower intensity compared with the clean surface as the temperature was decreased. Both results suggest that the increase in the measured TCL thickness (BF691 and BF699) is due to the incomplete dissociation of SiH_2 and its co-existence with monohydride on the surface after dosing. This co-existence is anticipated as the monohydride phase is produced as a product of SiH_3 decomposition. Given that, if the decomposition process is sequential, one would expect a maximum of 0.5 ML per cycle if none of the SiH_2 further dissociate to the Si monohydride. The layer thickness of 1/2 ML per cycle obtained for sample BF699 means that the lower dosing temperature and higher incident flux favored the presence of SiH_2 given the faster rate of adsorption provided by the larger flux and slower rate of SiH_2 decomposition at the lower temperatures. The number of disilane molecules which give rise to 0.5 ML of deposited Si would again provide all the hydrogen required for passivation of dangling orbitals on the surface, where monohydride and dihydride coexist since no hydrogen desorption occurs. This would give a maximum hydrogen coverage of 1.5 ML.

The effect of the dangling orbital (or its absence) on the disilane dissociative chemisorption and formation of SiH_2 during disilane exposures is further investigated by first forming the monohydride surface before adsorption at lower temperature. In BF695, the adsorption cycle consists of a first dose with disilane at 430 °C to form the monohydride surface, followed by dosing at 320 °C as in BF691. The accumulated effect of the two doses is in fact the same as BF689 with a single dose at 430 °C producing only one third of a Si ML per cycle. In addition to epitaxial growth, evidence of surface passivation by monohydride was also obtained by TDS. The experiments were carried out in an analogous way to the dosing scheme employed in TCL growth. Figure 3 shows the H_2 TDS spectra for silicon surfaces dosed with a disilane beam equivalent pressure of 4.6×10^{-6} mbar for 30 mins at temperatures of (a) 150 °C, (b) 150 °C after first forming the monohydride at 430 °C (cf. BF695), and (c) 430 °C. The TDS spectra for (a) shows a double peak feature where β_1 and β_2 peaks are identified to be desorption from monohydride and dihydride phases respectively.[7,8,14] In contrast to (a), the spectra for (b) and (c), which are identical, shows only the β_1 peak. This indicates that only the Si-monohydride phase predominates and there is an absence of higher hydrides (SiH_3, SiH_2) on the surface. The initial dosing at 430 °C forms predominantly the monohydride phase which passivates the surface against further adsorption of disilane and the formation of the higher hydrides at lower temperature. This behavior is very different from that observed when a Si monohydride covered surface is exposed to atomic hydrogen. Exposure at this low temperature leads to the formation of dihydride, which can only occur by breaking the Si-Si dimer bond. Hence, disilane dissociative chemisorption does not occur via the same mechanism involving the breaking of the Si-Si dimer bond. Both the TCL thickness and TDS measurements therefore confirm that the Si(001) surface is totally passivated by Si-monohydride against further adsorption of disilane and it is clear that dangling orbitals (active sites) have direct control over the kinetics of disilane chemisorption and subsequent SiH_x decomposition.

The results presented here demonstrate that the principle route for SiH_2 dissociation during disilane pyrolysis occurs via Eq. (2) and that the formation of the monohydride phase is very effective in passivating the Si(001) surface against further adsorption/dissociation of disilane. At temperatures above 400 °C, adsorbed disilane molecules completely pyrolyse to give two Si atom and six hydrogen atoms on the surface. Under these conditions, the dissociation of disilane from a thermal beam source occurs sequentially, giving the resultant monohydride phase without producing directly any

gas phase H_2 or the desorption of any silane or hydride radicals. In conventional GSMBE, layer by layer growth of Si can only occur if active adsorption sites (i.e., the dangling orbitals) are present on the surface. The decomposition of disilane studied here provides the hydrogen atoms which passivate these active sites and they can only be regenerated by subsequent recombinative desorption of molecular hydrogen.[6] The MBMS result is therefore consistent with the understanding that the growth on the Si(001) surface is limited by the desorption of molecular hydrogen. The decomposition process detailed in Eq. (2) is not the rate limiting process in the overall growth reaction but its dominance over Eq. (1) is the only plausible explanation for the results of TCL. Lowering the adsorption temperature introduces higher hydride species and data shows that the decomposition of SiH_2 is controlled essentially by the availability of dangling bonds and is therefore a function of growth temperature and incident disilane flux. It should be noted that Eq. (2) does not provide an atomistic picture of the decomposition process but only reflects the final state of SiH_2 decomposition. The full passivation of the surface cannot be achieved without the diffusion of the hydrogen and/or silicon atom on the surface.[4]

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