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Real-time monitoring of a surface reaction in germanium film growth

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Epitaxial germanium film growth by a surface reaction was investigated using a pulsed molecular jet. Time-resolved reflectometry was utilized for *in situ* monitoring of both the formation and the evolution of a chemisorbed layer of digermane. The rate of chemisorption was independent of temperature. Evolution of the adsorption layers occurred by a temperature dependent first-order process, believed to be molecular hydrogen desorption. Digital growth of germanium films was demonstrated by periodically refilling the active surface sites liberated by molecular hydrogen desorption between two successive gas pulses. Epitaxial germanium films over 150 nm thick were grown on Si (100) substrates.

The use of germanium in the growth of strained layer superlattices, lattice matching buffer layers, and SiGe alloys has focused new interest on germanium growth techniques and various issues concerning lattice-mismatched epitaxy of germanium.¹ Improved understanding of the surface reactions of germanium containing compounds² is of great significance in the development of silicongermanium based atomic layer epitaxy.³ Since thin-film growth is almost exclusively conducted at fixed substrate temperatures, isothermal desorption experiments seem tailor-made for their investigation. An additional advantage of desorption experiments carried out at fixed substrate temperature is that the reaction order of surface processes can be obtained directly.⁴

Despite these advantages, desorption experiments are not widely used for thin-film growth monitoring because their implementation can seriously interfere with the growth environment. In this letter we report on a method of studying adsorption layer formation and thin-film growth by a combination of pulsed molecular jets and time-resolved surface reflectometry. The adsorption layers were produced by pulsed molecular jets of digermane. The advantage of this technique over steady-state growth experiments is that contributions from homogeneous gas phase reactions are excluded by immediately pumping away the unreacted source gas and any reaction products that scattered off the growth surface. The time dependence of the light intensity specularly reflected by the growth surface was used to study the formation (the adsorption isotherm) and the evolution (the isothermal desorption spectrum) of the adsorption layer. The laser light used in this technique provides a nonintrusive surface probe and is fully compatible with a wide range of growth environments. Finally, digital epitaxy (i.e., growth of a thin-film in discrete submonolayer increments) was demonstrated by growing germanium films of finite thickness from a multitude of digermane pulses.

The experiments were conducted in a standard stainless-steel vacuum chamber of 23 liter volume that was pumped by a turbomolecular pump. The time constant of the pumping system was 0.25 s. The pressure prior to growth was in the low 10^{-7} Torr region. The samples were

attached to a molybdenum holder that was radiatively heated by a graphite resistance heater encapsulated in pyrolytic-boron-nitride. The sample temperature was monitored by an infrared radiation thermometer. A home-built pulsed molecular beam valve⁵ with water cooled housing was used for generating gas pulses of 3 ms duration that had a short rise and fall time. The gas pulses were used in a free jet form with repetition rates up to 3 Hz at a distance of 4 cm from the substrate. The source gas consisted of 5% digermane mixed with helium. At a stagnation pressure of 20 psia in an average flux of 2.5×10^{17} cm⁻² s⁻¹ of digermane molecules was estimated from a fast ionization gauge signal. A time profile of a helium pulse identical with the source gas pulse is shown in Fig. 1.

Time-resolved reflectometry at a fixed wavelength was used to probe the growth surface. The angle of incidence of a high stability He-Ne laser (632.8 nm) with 0.02% rms amplitude noise was 37.5°. The laser beam sampled a 2 mm diam spot size near the center of the $22 \times 22 \text{ mm}^2$ substrates. Parallel-polarized light was used because the sensitivity was higher than with perpendicular polarization.⁶ The specularly reflected laser light was detected by a silicon photodiode, amplified, digitized by a fast analog-todigital converter, and stored by a microcomputer. In surface reflectometry the adsorbate-induced change $\Delta R/R$ $=(R_{ads}-R)/R$ at a fixed wavelength is linearly proportional to the surface coverage, $^{6} \Delta R/R = c\Theta$. ΔR is the differential reflectivity, R_{ads} and R are the reflectivities associated with the adsorbate covered and bare germanium surface, respectively, Θ is the surface coverage, and c is a constant that includes the wavelength of the probe light and the complex dielectric constants associated with the germanium film and the adsorption layer. Since the differential reflectivity is proportional to the amount of chemisorbed digermane fragments remaining on the surface at any time, it was utilized to monitor the digermane chemisorption and desorption kinetics. The differential reflectivity signal, as illustrated by Fig. 1, reached its maximum value at the end of the digermane pulse, and began to decrease immediately after the gas pulse was turned off. Because the largest differential reflectivity was only 0.5%, signal averaging was performed to improve the signal-to-



FIG. 1. The solid line represents adsorption layer formation and the early stage of hydrogen evolution from a digermane pulse of 2.5×10^{17} mol/ cm² s at 813 K. The dashed line shows the profile of a 3 ms duration helium pulses measured by a fast ionization gauge (FIG), that is identical with the source gas pulse. The dotted line represents the residual digermane background in the chamber.

noise ratio. A digital delay generator was used to synchronize the gas pulses with the data collection cycles.

The time-resolved reflectometry signal includes information about both the formation (the adsorption isotherm) and evolution (the isothermal desorption spectrum) of the chemisorption layers as a function of time, as illustrated in Fig. 1. The adsorption was of the monomolecular layer type that was best approximated by the Langmuir isotherm. The chemisorption layers reached surface equilibrium for the given conditions during the source gas pulse. Multiple pulsing of source gas with variable delay time between the pulses did not change the level of the saturation signal, or the shape of the adsorption isotherm. The rate at which the active surface sites were filled (i.e., chemisorption rate) by the molecular jet was rapid $(k=850 \text{ s}^{-1})$ and independent of the substrate temperature.

The isothermal desorption spectrum is represented by the decaying part of the reflectometry signal. Full isothermal desorption spectra on Ge (100) surfaces are shown for 679 and 759 K substrate temperatures in Figs. 2 and 3, respectively. Analysis of the isothermal desorption spectra by model calculations shows that the digermane adsorption layers evolved by a single step first-order process throughout the entire substrate temperature range. The decay curves in Figs. 2 and 3 are not single exponentials because the residual scattered gas was replenishing the adsorption layers during pumpout time. However, when the pumping speed dependent contributions by the background were subtracted, single exponential decay curves were obtained (note the dashed line on Figs. 2 and 3). Detailed discussion of the modeling of various aspects of the adsorption layer formation and evolution will be given elsewhere.⁷ Evolution of the adsorption layers took several seconds at low and intermediate substrate temperatures (673-773 K). With increasing substrate temperature the lifetime of the adsorption layers became shorter than the pulse



FIG. 2. Evolution of the hydrogen surface coverage on Ge (100) at 679 K, following a digermane source gas pulse shown in Fig. 1. The dots represent experimental data averaged from 16 pulses. The dashed line illustrates first-order desorption for a rate constant $k_d=0.85 \text{ s}^{-1}$. The solid line is a model calculation of first-order desorption that includes the contributions from the residual background during the pumpout time. The inset shows experimental hydrogen coverage oscillations from digermane chemisorption on a Si (100) surface at 743 K substrate temperature and 0.333 s pulse period. The tick marks in the inset are at 1 s intervals. Phenomenological interpretation of these oscillations by a first-order model is given by the dotted curve.

duration. At 850 K the existence of the adsorption layers could no longer be conclusively confirmed. An activation energy of $E_d = (40 \pm 2)$ kcal/mol and a frequency factor of $A = 1.6 \times 10^{13}$ s⁻¹ were obtained for the first-order decay process on Ge (100) surfaces. According to the equation $2E_{\text{Ge-H}} = Q + E_{\text{H-H}}$ which represents the process of hydrogen adsorption with no activation barrier ($Q = E_d$), a heat of adsorption of Q = 40 kcal/mol, and a molecular hydrogen bond strength of $E_{\text{H-H}} = 103$ kcal/mol⁸ would give a value for the Ge—H bond strength of 71.5 kcal/mol. This



FIG. 3. Evolution of the hydrogen surface coverage on Ge (100) at 759 K, following a digermane source gas pulse shown in Fig. 1. The dots represent experimental data averaged from 16 pulses. The dashed line illustrates first-order desorption for a rate constant $k_d = 50 \text{ s}^{-1}$. The solid line is a model calculation of first-order desorption that includes the contributions from the residual background during the pumpout time.

value for the germanium-hydrogen bond strength is in good agreement with the 65 kcal/mol in the existing literature.⁹ It is concluded that the chemical nature of the firstorder process is molecular hydrogen desorption. The conclusion is further supported by experimental observations of first-order desorption from hydrogenated (100) Si surfaces.¹⁰ However, based on the available experimental data, desorption of hydrogenated germanium fragments cannot be ruled out.

Digital epitaxy is based on the idea of using the hydrogen desorption process, which is relatively slow at low and intermediate substrate temperatures (much slower than digermane chemisorption), in combination with pulsed source gas delivery as an externally controlled self-limiting mechanism. The hydrogen coverage resulting from chemisorption of digermane terminates further chemisorption after completion of a monolayer. The portion of the gas pulse that is not chemisorbed is rapidly pumped away before new active sites are regenerated by hydrogen desorption. Only those active sites that are regenerated during the delay time between two pulses (pulse period) can chemisorb new source gas molecules from the next pulse. The corresponding hydrogen coverage oscillations on a (100) surface are related to germanium film growth rates by the following equation:

$$G = \left(\frac{a_0}{4}\right) \left(\frac{1}{t}\right) \Theta_0[1 - \exp\left(-k_d t\right)]. \tag{1}$$

G (nm/s) represents the growth rate, a_0 is the lattice constant of germanium, and t (s) is the pulse period. Θ_0 is the hydrogen surface coverage at the end of the pulse. Θ_0 has a fixed value between 0 and 1 depending on the experimental conditions. k_d (s⁻¹) is the hydrogen desorption rate constant. The growth rate $G = (a_0/4)\Theta_0k_d$ for continuous digermane supply is obtained as a limiting case of Eq. (1) for infinitely small $(t \rightarrow 0)$ pulse periods.

For a particular substrate the amplitude of the hydrogen coverage oscillations was found to depend on the substrate temperature, the source gas pulse period, and the pumpout time constant. The interference caused by chemisorption of background digermane can be reduced or eliminated by increasing the pumping speed of the apparatus. For a particular material, the amplitude of the oscillations depends on the crystallographic orientation of the substrate. Other experimental parameters may also influence the amplitude of the oscillations. In addition to Ge (100), hydrogen coverage oscillations were also observed on GaAs (100), Si (111), and Si (100). Experimentally measured hydrogen coverage oscillations are illustrated in the inset of Fig. 2. The oscillations are produced on a Si (100) surface at 743 K substrate temperature from a burst of digermane pulses with a pulse period of 0.333 s. Stopping the pulsation results in depletion of the surface, as illustrated by the full decay following the oscillations. The dotted curve in Fig. 2 is an illustration of the oscillations by a model (zero background) first-order hydrogen desorption process with a rate constant $k_d = 0.85 \text{ s}^{-1}$ for a pulse period of 0.333 s.

The Ge films grown on Si (100) substrates from 1300 digermane pulses were typically 150 nm thick. The digermane reactive sticking probabilities were hydrogen coverage dependent, with a bare surface limit of 0.07 estimated from the high-temperature growth rates. The films were epitaxial in the substrate temperature range between 670 and 850 K. The epitaxial quality was investigated by Rutherford backscattering spectrometry (RBS), and x-ray double crystal diffractometry (DCD) measurements. The x-ray DCD measurements indicate that the Ge films were partially relaxed with a half-maximum width of 1454 arcsec corresponding to a $D=10^9$ cm⁻² density of 60° dislocations.¹¹ The RBS minimum yield of 4%, and the rising dechanneling probability towards the Si/Ge interface¹² corroborate the x-ray DCD results.

In conclusion, a dynamic method for thin-film growth and *in situ* monitoring has been devised by combining time-resolved surface reflectometry and a modulated source gas jet. Separate investigation of the elementary steps (adsorption, desorption) of a complex film growth process was conducted by measuring the response to a rapid source gas pressure jump at the growth surface. The experimental results indicate that hydrogen coverage of the growth surface terminates chemisorption of digermane until active sites are regenerated by a substrate temperature dependent hydrogen desorption process. The self-limiting hydrogen coverage provides a potential for external control of the thin-film growth process at the submonolayer level by adjustments of the substrate temperature and the delay time between source gas pulses.

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