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TEMPERATURE-DEPENDENT EVOLUTION OF CHEMISORBED DIGERMANE IN Ge THIN FILM GROWTH

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TEMPERATURE-DEPENDENT EVOLUTION OF CHEMISORBED DIGERMANE IN Ge THIN FILM GROWTH

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ABSTRACT

The formation and evolution of chemisorbed digermane layers in context with germanium thin film growth was investigated by time-resolved surface reflectometry. Modulation of the source gas supply made possible the separation and independent study of the temperature dependence of the adsorption and desorption processes. The regeneration of active sites by molecular hydrogen desorption was identified as the rate-limiting step at low substrate temperatures. A dynamic method of thin film growth was demonstrated by repetitively replenishing the active film growth sites regenerated between two successive source gas pulses. The film growth rate was shown to be related to the substrate temperature and the delay time between successive source gas pulses.

INTRODUCTION

The potential for thickness control at the monolayer level has inspired much new research into the understanding of surface chemical reactions of silicon and germanium-containing compounds [1,2]. Of particular interest are self-limiting growth mechanisms that can be externally monitored and controlled. Various diagnostic techniques that allow nonintrusive *in situ* probing are an integral part of the surface chemistry studies.

This paper describes time-resolved studies of hydrogen-covered semiconductor film growth surfaces conducted by utilizing a nonintrusive optical probe. The hydrogen coverage is a consequence of using hydrogenated source gas molecules for thin film growth. As a side product of the surface chemical reaction, hydrogen hinders further film growth by occupying the active surface sites. Since in conventional CVD growth techniques, hydrogen desorption occurs concurrently with film growth, steady state measurements are not adequate to study the desorption and the film growth processes. It is necessary to turn to a dynamic approach in which thin film growth is studied as a result of a time-varying flux of source molecules. An additional advantage of using a pulsed gas source is that homogeneous components to film growth are excluded because all unreacted gas is immediately pumped away.

Detection and monitoring of the adsorption layers is achieved by an optical technique that is based on the relationship between surface reflectance and the electronic structure of the surface. The changes in the optical absorption of the surface produced by chemisorption-induced bond formation are revealed through measurements of the intensity of reflected light. The laser light utilized as a probe is nonintrusive and is compatible with a wide range of growth environments.

We demonstrate for the first time a dynamic method of germanium thin film growth termed "digital epitaxy." Digital epitaxy is defined as thin film growth that occurs in sub-monolayer increments from a multiplicity of discrete source gas pulses. Thin film growth occurs in cycles on the fraction of the growth surface which is liberated of hydrogen between two successive gas pulses. The fraction of the surface that is available for film growth depends on the substrate temperature and the delay time between two source gas pulses.

EXPERIMENTAL

The experimental apparatus consisted of the growth chamber and the data collection system. The growth chamber was a cylindrical stainless steel chamber of 23-liter volume. The vacuum was maintained by a turbo-molecular pump in the low 10^{-7} Torr region. During film growth the pressure was typically in the 10^{-4} Torr range. The time constant of the pumping system was 0.25 sec. A home-built pulsed molecular beam valve with water-cooled housing was used for generating gas pulses of 3 millisecond duration that had a rapid rise and fall time. The gas pulses were used in the free jet form (no skimmers or collimators) with repetition rates up to 3 Hz. The source gas was a 5% mixture of digermane in helium. At a reservoir pressure of 20 psia an average flux of 2.5×10^{17} cm^{-2} sec^{-1} of digermane molecules was estimated from a fast ionization gauge signal. The time profile of a helium pulse, identical with that of the gas mixture containing the source gas, is shown in Fig. 1. The substrate was attached to a molybdenum holder that was radiatively heated by a graphite resistance heater encapsulated in pyrolitic boron nitride. The sample temperature was monitored by an IR radiation thermometer.

The kinetics of adsorption layer formation (and consequently thin film growth) was monitored by time-resolved reflectometry at a fixed wavelength. The angle of incidence of a high stability He-Ne laser (632.8 nm) with 0.02% rms amplitude noise was 37.5 degrees. The specularly reflected laser light from the growth surface was detected by a silicon photodiode, amplified, digitized by a fast analog-to-digital 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 $\Delta R/R = c\theta$ [3]. ΔR is the differential reflectivity, R_{ads} and R are the reflectivities associated with the adsorbate-covered and bare germanium surfaces, respectively, θ is the surface coverage and c is a constant that includes the wavelength of the probe light and the complex dielectric constants of the germanium film and the adsorption layer. Since the normalized reflectivity change is proportional to the amount of chemisorbed digermane fragments remaining on the surface at any time, it was utilized to monitor the kinetics of digermane chemisorption and germanium film growth. The differential reflectivity signal, as illustrated by Fig. 1, reached its maximum value during the digermane pulse, and began to decrease immediately after the gas pulse was turned off. Because the maximum value of the differential reflectivity change was only 0.5%, signal averaging was performed to improve the signal-to-noise ratio when small coverage changes were measured. A digital delay generator was used to synchronize the gas pulses with the data collection cycles.

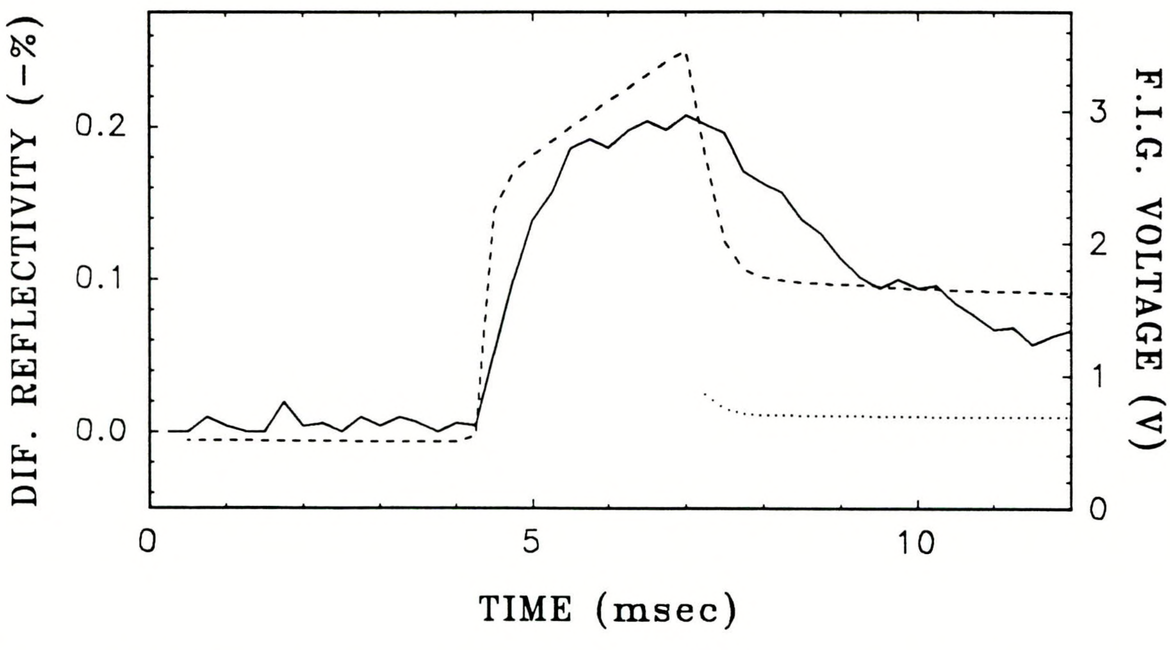

Fig. 1. The fast ionization gauge (FIG) signal represented by the dashed line shows the time profile of a helium pulse identical with the gas mixture pulse. The corresponding digermane flux is 2.5×10^{17} molecules/cm^2 sec. The residual digermane background following the gas mixture pulse is illustrated by the dotted line. The differential reflectivity signal obtained from digermane chemisorption at a substrate temperature of 540°C is shown by the solid line.

RESULTS AND DISCUSSION

The transient adsorption layers produced by the source gas pulses were monitored by time-resolved reflectometry. As illustrated by Fig. 2, the rate of adsorption layer formation was independent of the substrate temperature. The adsorption layers were of the monomolecular layer type best approximated by the Langmuir isotherm. A rate constant of $k_a = 780\ \mathrm{sec}^{-1}$ was determined from the data on Fig. 2 for the rate of change of surface coverage at a fixed pressure. The temperature dependence of the surface coverage shown on Fig. 2 is the consequence of the adsorption rate being overtaken by hydrogen desorption with increasing substrate temperatures.

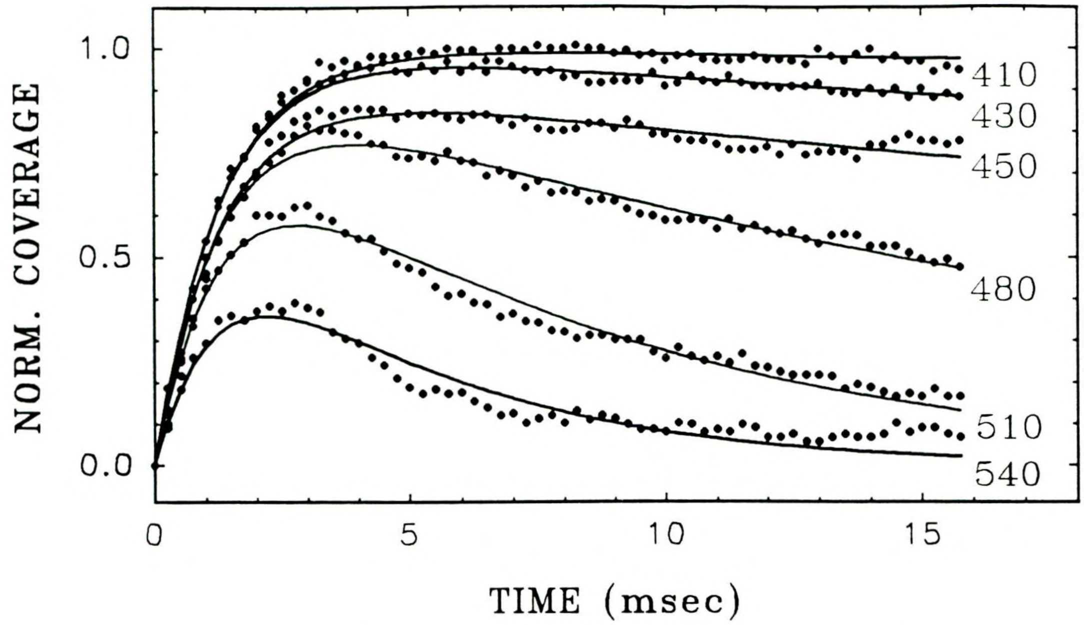

Figure 2. The hydrogen coverage on a Ge (100) surface resulting from digermane chemisorption is shown for several different substrate temperatures. The solid lines represent a fit to the experimental data shown by the solid dots. The fitting model is described in [4].

The decaying part following the maximum in the time-resolved reflectometry signal corresponds to the isothermal desorption spectrum. The isothermal desorption spectrum represents the evolution of the chemisorbed digermane layers into germanium thin films. The adsorption layers evolved by a single step first-order process throughout the entire substrate temperature range. An Arrhenius fit to the temperature-dependent rate constants gave $A = 1.6\times10^{13}\ \mathrm{sec}^{-1}$ for the pre-factor, and an activation energy of $E = 1.7 \pm 0.1$ eV. The rates used for the Arrhenius fit were determined from the slope of the decay curves during the first 10-20 msec of the desorption process (see Fig. 2). This was necessary because during pumpout time the residual source gas molecules from the unreacted scattered gas were replenishing the adsorption layer. The gas kinetic collision rate during the pumpout time was at least an order of magnitude lower than the flux from the jet, but the integrated effect was significant because the pumpout time constant is much longer than the pulse duration. Full isothermal desorption spectra at 406°C and 486°C are shown on Figs. 3 and 4, respectively. The solid lines show a model fit [4] to the experimental data represented by the solid dots. The model calculates the transient signal for a gas pulse of negligible duration compared with the pumpout time constant. The effect of the residual background is manifested as the difference between the single exponential decay curves given by the dashed lines and the experimental data. Figure 4 shows that at higher substrate temperatures the contributions to the adsorption layer from the short gas pulse (rapid exponential decay) and the residual background (slow exponential decay) can clearly be discerned.

The chemical nature of the first-order process is narrowed down to molecular hydrogen, or hydrogenated germanium fragment desorption. Since the time-resolved reflectometry signal only detects the absence of hydrogen from the growth surface, it is not specific to the mechanism

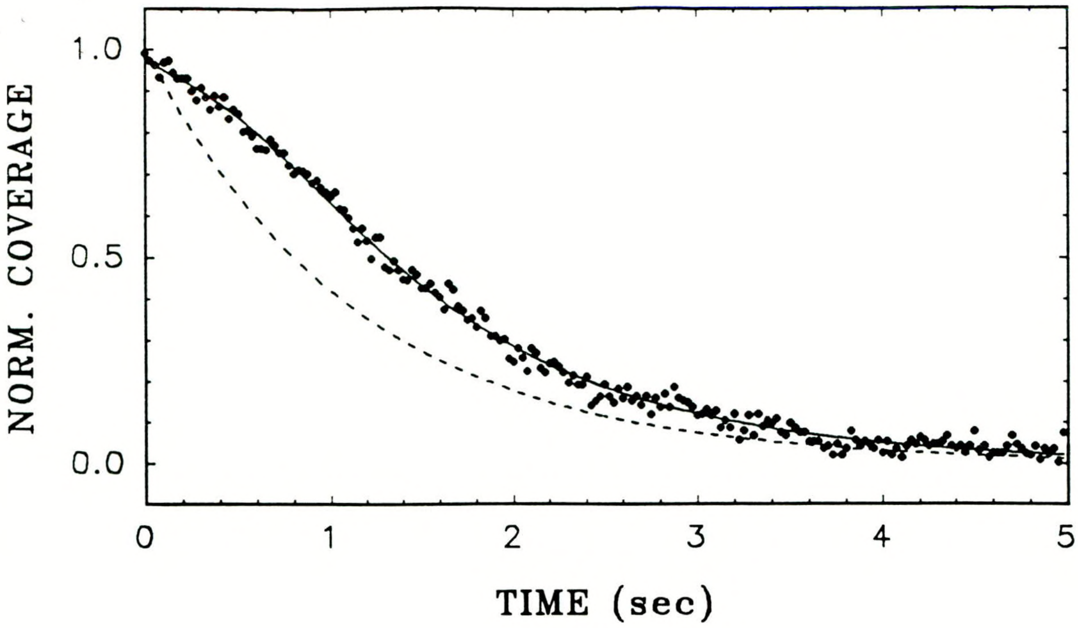

Figure 3. The solid dots represent the evolution of the hydrogen surface coverage on Ge(100) at 406°C, following a digermane pulse shown of Fig. 1. The dashed line illustrates first order desorption with Arrhenius parameters of E = (1.7 ± 0.1)eV and A = 1.6 × 10^{13} sec^{-1}. The solid line is a model calculation of first-order desorption that includes the contributions from the residual background during the pumpout time.

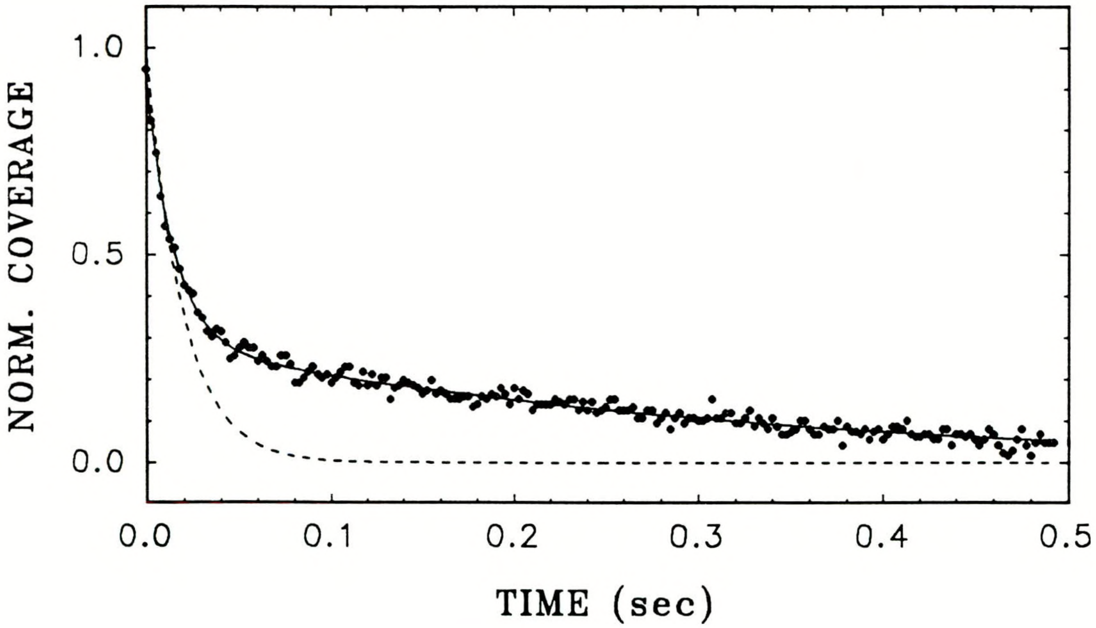

Figure 4. The solid dots represent the evolution of the hydrogen surface coverage on Ge(100) at 486°C, following a digermane pulse shown of Fig. 1. The dashed line illustrates first order desorption with Arrhenius parameters of E = (1.7 ± 0.1)eV and A = 1.6 × 10^{13} sec^{-1}. The solid line is a model calculation of first-order desorption that includes the contributions from the residual background during the pumpout time.

of the hydrogen loss. However, the high germanium film growth rates suggest that desorption of hydrogenated germanium fragments is negligible. Support for the conclusion that the first-order process represents molecular hydrogen desorption comes from the following thermochemical analysis of the activation energy of the first-order process. The heat of adsorption (Q) of hydrogen on a germanium surface is Q = 2D(GeH)-D(H-H). In the absence of an adsorption barrier, the heat of adsorption is equal to the desorption energy. Using 1.7 eV for the desorption energy and D(H-H) = 4.5 eV [5] for the bond energy of hydrogen, D(Ge-H) = 3.1 eV is obtained for the germanium-hydrogen bond energy. The 3.1 eV value gives a satisfactory agreement with the published upper limit of 3.3 eV [6] for the germanium-hydrogen bond energy. Observation of first-order kinetics for hydrogen desorption from hydrogenated Si (100) surfaces [7] further supports our assignment of the first-order process to molecular hydrogen desorption.

Comparison of the desorption rates at two different substrate temperatures presented in Figs. 3 and 4 shows that at low substrate temperatures the film growth rate was limited by the slow desorption of molecular hydrogen. Under these conditions the surface remained hydrogenated for several seconds after the source gas supply was turned off. At high substrate temperatures, hydrogen desorption was rapid, and the surface was essentially bare during film growth. The contribution from the residual background on Fig. 4 vividly illustrates that at high substrate temperatures the film growth rate is governed by the rate of source gas supply.

The rate-limiting nature of the hydrogen coverage at low substrate temperatures presents a possibility for using this process as a self-limiting control mechanism of thin film growth. In the absence of source gas, the growth surface would be regenerated by hydrogen desorption at a rate determined by the substrate temperature. Accordingly, if the source gas supply is modulated, the hydrogen coverage will also oscillate at the modulation frequency. The amplitude of the hydrogen coverage oscillations at a fixed modulation rate depends on the substrate temperature. The coverage oscillations were realized by periodic source gas pulses which repetitively saturated the active sites liberated between successive pulses. The hydrogen coverage oscillations on a (100) surface are related to germanium film growth by the following equation:

$$G = (a_0/4)(1/t)\theta_0[1-\exp(-kt)].$$

G represents the growth rate (in nm/min), a_0 is the lattice constant of germanium, and t is the delay time between two successive source gas pulses (in sec). θ_0 is the hydrogen surface coverage at saturation. It has a fixed value between 0 and 1 depending on the experimental conditions. k (in sec^{-1}) is the hydrogen desorption rate constant calculated from the previously determined rate parameters by the Arrhenius equation.

Digital epitaxy of Ge on various semiconductor surfaces was achieved by external modulation of the source gas supply. In situ monitoring of the surface coverage was utilized for real-time control of the growth conditions. Thin films of up to 150 nm thickness were grown from a multiplicity of successive source gas pulses. The average film thickness increase per source gas pulse was a function of the substrate temperature and the delay time between successive pulses. Preliminary results indicate that the thickness increment per pulse also depends on the chemical nature of the substrate and its crystallographic orientation.

CONCLUSIONS

Modulation of the source gas supply was utilized independently to study the kinetics of the elementary steps of germanium film growth from digermane by a surface reaction. The rate of digermane chemisorption was found to be independent of the substrate temperature. The active sites on the growth surface were regenerated by a temperature-dependent first-order molecular hydrogen desorption process. Because of the large activation energy, the hydrogen desorption process was rate limiting at low substrate temperatures. With increasing substrate temperatures, the fixed-rate adsorption process was overtaken by the desorption process and it became rate limiting. The temperature dependence of the hydrogen desorption process was utilized as a self-limiting mechanism in a germanium thin film growth technique. Hydrogen coverage oscillations were produced by pulsed delivery of digermane. Thin film growth occurred on the fraction of the growth surface that was regenerated by hydrogen desorption between two successive source gas pulses. Consequently, the film growth rates were found to be proportional to the amplitude of the hydrogen coverage oscillations. The amplitude of the hydrogen coverage oscillations was a function of the substrate temperature and the delay time between two successive digermane pulses.

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