Silicon vapor phase epitaxial growth catalysis by the presence of germane

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Experiments involving the epitaxial growth of $Ge_x Si_{1-x}$ films by chemical vapor deposition have shown that the addition of germane greatly enhances the growth rate, compared to that seen with dichlorosilane alone. Careful analysis shows that the increase is not accounted for by summing the individual growth rates, but clearly indicates that the silicon growth rate is catalyzed. The magnitude of the effect increases at lower temperatures, with a two orders of magnitude increase seen at 625 °C.

Silicon-germanium alloys have recently demonstrated great promise for the growth of such devices as heterojunction bipolar transistors.[1] We have extensively investigated the growth of these $Ge_x Si_{1-x}$ alloy films grown by a chemical vapor deposition process, and in this letter report that the presence of a small amount of germane causes a very large increase in the growth rate of the films (over 50 times that seen with dichlorosilane alone). This effect is too large to be accounted for by the additional Ge growth but indicates a catalytic effect on the Si growth due to the presence of germane. The implications of a simple growth model, where the rate-limiting step is the adsorption of silicon (and Ge) containing species to a surface predominantly covered with adsorbed hydrogen, are then compared with our experimental results.

The epitaxial films were grown in a limited reaction processing reactor[2] at temperatures of 700 °C or less using dichlorosilane (Si source) and germane (Ge source) in a hydrogen carrier gas. The system is a combination of chemical vapor deposition and rapid thermal processing in which the wafer is suspended on quartz pins in a horizontal quartz tube containing the process gas flow. The wafer is heated by high-power tungsten-halogen lamps which are located external to the process tube. Thus the only hot portion of the reactor is the silicon wafer itself. The system pressure was maintained at 6.0 Torr with a hydrogen flow of 3.0 slpm. The dichlorosilane flow was held at 26 sccm while the germane flow was varied from 0 to 3.0 sccm. All the films were grown on a Si (100) substrate. Thickness measurements and Ge concentrations were determined via secondary-ion mass spectroscopy or Rutherford backscattering.

The growth rates of silicon alone (with 26 sccm $SiCl_2H_2$) and germanium alone (with 3.0 sccm germane) were measured over the temperature range of interest (500–700 °C) and plotted in Fig. 1. The Arrhenius plot shows an exponential dependence of the growth rate on temperature for both silicon and germanium which is indicative of reaction-rate limited growth. The activation energies associated with the growth processes are 1.9 eV for silicon (dichlorosilane) and 0.38 eV for germanium (germane).

The addition of 2.5 sccm germane to the dichlorosilane flow at 700 °C resulted in a ten times increase of the total growth rate with a final film composition of $Ge_{0.25} Si_{0.75}$ (Fig. 2). At lower temperatures this growth rate enhancement is even more pronounced. The growth rate at 625 °C jumps from < 3 Å/min (extrapolated from the data in Fig. 1) for silicon alone to over 200 Å/min with the addition of 3.0 sccm germane, the final film composition being $Ge_{0.32} Si_{0.68}$ (Fig. 3). In these figures the growth rates are broken down into the effective growth rates of the silicon and germanium constituents of the film. From this one sees that not only does the Ge growth rate component increase with increasing germane flow as one would expect, but that the silicon growth rate component increases drastically as well. At 625 °C this increase is from < 3 Å/min to over 170 Å/min, roughly a two orders of magnitude increase. Thus the germane has an enormous catalytic effect on the growth rate of silicon at low temperatures. Other work with silane (as opposed to dichlorosilane) and germane sources has shown a much smaller growth enhancement ($\approx 10\times$).[3,4] In that work, the catalytic effect was found to be consistent with increased hydrogen desorption from germanium sites on the growth surface, allowing increased adsorption of the growth species and hence an enhanced growth rate.

We now attempt to account for our growth rate data with such a model, in which the growth rate is limited by the availability of adsorption sites at the crystal surface. The adsites are assumed to be predominantly blocked with ad-
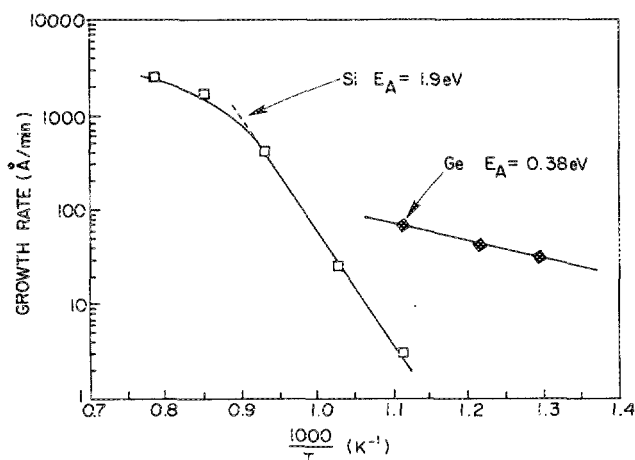

FIG. 1. Arrhenius plots for the growth rate of epitaxial silicon (26 sccm) and epitaxial germanium (3.0 sccm) at 6.0 Torr in the 500–1000 °C temperature range. Activation energies associated with the growth rate are 1.9 eV for silicon and 0.38 eV for germanium.
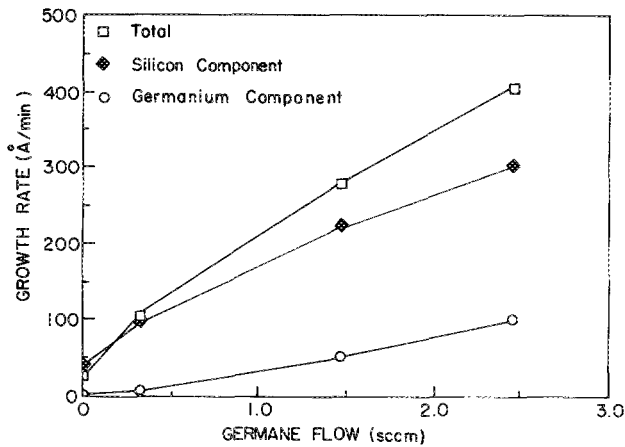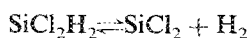
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FIG. 2. Total and component growth rates for Ge_xSi_{1-x} epitaxy at 700 °C as the amount of germane introduced to the gas flow is changed. The growth pressure was 6.0 Torr and the dichlorosilane flow was 26 sccm.

sorbed hydrogen. The growth rate enhancement, seen with germane addition, is postulated to result from a decreased surface coverage of hydrogen due to the weaker Ge—H bond (comparing the $+90.79$ kJ/mol enthalpy of formation for germane to the $+32.64$ kJ/mol value for silane).[5] Additional (simplifying) assumptions are as follows:

(1) Only one type of adsorbing species is important for Si and Ge growth and these result from simple decomposition reactions which we will take to be (the exact mechanism is not critical to the derivation):

$$SiCl_2H_2 \rightleftharpoons SiCl_2 + H_2$$

and

$$GeH_4 \rightleftharpoons GeH_2 + H_2. \tag{1}$$

(2) All the adsorbing species (GeH_2, $SiCl_2$, and H) compete for the same type of adsorption site.

(3) All Si and Ge containing species that adsorb contribute to the growth rate, i.e.,

$$R_{growth} = GR_{adsorption}$$

or
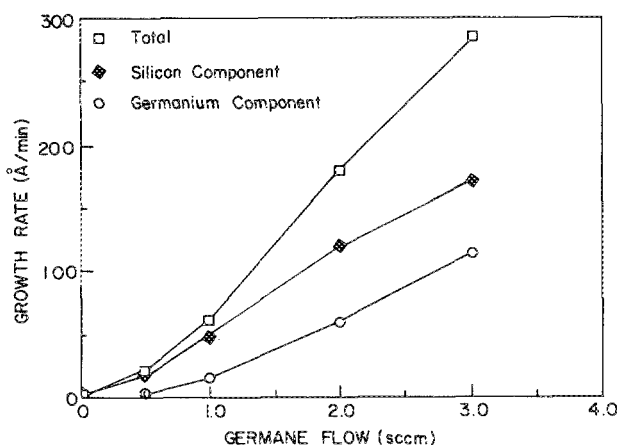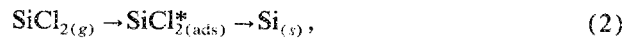

FIG. 3. Total and component growth rates for Ge_xSi_{1-x} epitaxy at 625 °C as the amount of germane introduced to the gas flow is changed. The growth pressure was 6.0 Torr and the dichlorosilane flow was 26 sccm.

$$SiCl_{2(g)} \rightarrow SiCl_{2(ads)}^* \rightarrow Si_{(s)}, \tag{2}$$

where R_{growth} and $R_{adsorption}$ are the growth and adsorption rates, respectively, and G is a geometric factor. Since the adsorption rate is assumed to be rate limiting, the gas phase decomposition reactions will be in equilibrium so that

$$P_{SiCl_2} = K_{Si} P_{SiCl_2H_2}$$

and

$$P_{GeH_2} = K_{Ge} P_{GeH_4}, \tag{3}$$

where P_{SiCl_2}, P_{GeH_2}, etc., are the partial pressures of the respective gas species and K_{Si} and K_{Ge} are the equilibrium constants. The adsorption rate for each species is assumed to be of the nondissociative Langmuir form[6] which may be written

$$R_{adsorption} = (1 - \phi)e^{-(E_a/kT)}R_{collision}, \tag{4}$$

where $(1 - \phi)$ is the fraction of available sites, E_a is the activation energy for adsorption, and $R_{collision}$ is the collision rate of the adsorbing species with the surface. The collision rates are given by the kinetic theory of gases as

$$R_c(Si) = K_s P_{SiCl_2H_2}, \tag{5}$$

$$R_c(Ge) = K_G P_{GeH_4}, \tag{6}$$

and

$$R_c(H) = K_H (P_{H_2})^{1/2}, \tag{7}$$

where K_s is $(2\pi m_{SiCl_2} k_b T)^{-1/2}$ and K_G and K_H are similarly defined. The hydrogen adsorption and desorption is equal under steady-state growth conditions. The Polanyi–Wigner equation[7] for a first-order desorption process is

$$R_{desorption}(H) = vN\phi e^{-E_d/kT}, \tag{8}$$

where v is the frequency factor, N the number of sites cm^{-2}, ϕ the fraction of filled sites, and E_d the activation energy for H desorption. We modify the equation as follows, to account for the proposed enhanced desorption of H due to the addition of Ge to the surface, by replacing $e^{-E_d/kT}$ by $F(x) = [xe^{-E_{dg}/kT} + (1 - x)e^{-E_{ds}/kT}]$, where $x = $ Ge fraction in the epitaxial film, and E_{dg} and E_{ds} are the activation energies of hydrogen desorption from Ge and Si, respectively. We assume that $E_{dg} < E_{ds}$ because of the weaker Ge—H bond so that the desorption rate increases as the germanium fraction (x) increases. If we set the H adsorption and desorption rates equal using Eqs. (4), (7), and (8) and solve for the fraction of open sites, we obtain

$$(1 - \phi) = vNF(x)/[vNF(x) + K_H (P_{H_2})^{1/2} e^{-E_a/kT}]. \tag{9}$$

This shows that as the Ge fraction of the film increases the number of available sites increases through the dependence of $F(x)$. The component growth rates of Ge and Si may be written

$$R_g(Ge) = GK_g P_{GeH_4} (1 - \phi)e^{-E_g/kT}$$
$$R_g(Si) = GK_s P_{DCS} (1 - \phi)e^{-E_s/kT}. \tag{10}$$

Since the growth rates both contain the common terms $(1 - \phi)$ we may write

$$(1 - \phi) = \frac{R_g(\text{Ge})e^{E_g/kT}}{GK_g P_{\text{GeH}_4}} = \frac{R_g(\text{Si})e^{E/kT}}{GK_s P_{\text{DCS}}}$$

or (11)

$$\frac{R_g(\text{Ge})}{R_g(\text{Si})} \frac{P_{\text{DCS}}}{P_{\text{GeH}_4}} = \frac{K_g}{K_s} e^{(E_s - E_g)/kT} \equiv J.$$

The parameters on the left-hand side of Eq. (12) are known for a set of growth conditions at 625 °C and the value of J, which should be constant for a given temperature, is calculated for each. It is clearly seen from Table I that the value is not constant, as predicted by the model, but falls off with increasing P_{GeH_4}.

This suggests that the growth rate in our experiments using dichlorosilane and germane sources is not limited by the adsorption of the growth species, as proposed, but may be limited instead by some other factors, such as gas phase kinetics, surface nucleation, oxygen desorption (we are not growing in an ultrahigh vacuum system), or the influence of the chlorine from the dichlorosilane. It is also possible that a more complicated adsorption scheme could be devised which accurately describes the growth phenomena. Experiments are under way in an attempt to distinguish between the different mechanisms which might explain the observed growth rate enhancement.

In summary, we have found that in low-temperature vapor phase epitaxy, a small addition of germane can increase the effective growth rate of silicon by two orders of magnitude. Although the exact mechanism responsible for the catalysis is not known, this effect is very fortuitous because it enables one to obtain reasonable growth rates for the $\text{Ge}_x \text{Si}_{1-x}$ films (100 Å/min) at low temperatures without the use of lasers, plasmas, or other exotic growth enhance-

ment techniques. An understanding of the catalytic effects in $\text{Ge}_x \text{Si}_{1-x}$ will hopefully lead to a means of enhancing the growth rate of pure silicon at low temperature as well.

TABLE I. Growth model parameter J calculated for various germane flows at 625 °C.

GeH$_4$ flow (sccm)	J
0.5	10.7
1.0	8.1
2.0	6.3
3.0	5.7

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