Tetrasilane and digermane for the ultra-high vacuum chemical vapor deposition of SiGe alloys

John Hart a,⁎, Ramsey Hazbun a, David Eldridge a, Ryan Hickey a, Nalin Fernando b, Thomas Adam c, Stefan Zollner b, James Kolodzy a

aDepartment of Electrical Engineering, University of Delaware, 140 Evans Hall, Newark, DE 19716, United States
bDepartment of Physics, University of New Mexico, MSC 3D, P.O. Box 30001, Las Cruces, New Mexico 88003-8001, United States
cCollege of Nanoscale Science and Engineering, SUNY, New York 12203, United States

A B S T R A C T
Tetrasilane and digermane were used to grow epitaxial silicon germanium layers on silicon substrates in a commercial ultra-high vacuum chemical vapor deposition tool. Films with concentrations up to 19% germanium were grown at temperatures from 400 °C to 550 °C. For all alloy compositions, the growth rates were much higher compared to using mono-silane and mono-germane. The quality of the material was assessed using X-ray diffraction, atomic force microscopy, and spectroscopic ellipsometry; all indicating high quality epitaxial films with low surface roughness suitable for commercial applications. Studies of the decomposition kinetics with regard to temperature were performed, revealing an unusual growth rate maximum between the high and low temperature deposition regimes.

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1. Introduction
Silicon germanium is an important material system for many devices; specifically, it is the foundation of heterojunction bipolar complementary metal-oxide semiconductor (BiCMOS) devices and is used as stressors for Si channels in CMOS [1]. These technologies require high quality strained crystals with smooth surfaces. The growth temperature during silicon germanium epitaxy is an important variable for many reasons, including controlling dopant diffusion, growth morphology, alloy gradients, and strain. Lowering the deposition temperatures, however, presents problems with reduced epitaxial growth rates during chemical vapor deposition (CVD), due to CVD epitaxy being a thermally activated chemical reaction. The hydride gas sources typically used in industry for SiGe epitaxy are silane (SiH 4) and germane (GeH 4), for which the decomposition reaction transitions to reaction rate limited growth rate regimes at <670 °C and <350 °C, respectively [2,3]. Higher order precursors are an important avenue of current research because increasing the order, n, of the precursors, for example Si nH 2n+2 where n > 1, has been found to give a higher epitaxial growth rate at a given growth temperature [4,5]. The reason for this increase is thought to be caused by the lower bond strength between the IV—IV bonds than the IV—H bonds, for example in silicon the bond between Si—Si atoms is E Si—Si = 226 kJ/mol is lower than Si—H E Si—H = 318 kJ/mol. The lower bond strength allows for not only higher growth rates but also the capability to move to lower temperatures while maintaining growth rate and process throughput, believed to be from a deposition pathway through the hydrogen terminated Si surface during growth at low temperature [4]. Two such higher order molecules relevant to silicon germanium epitaxy are tetrasilane (Si 4H 10) and digermane (Ge 2H 6). In addition to the higher growth rates, there has been interest in utilizing these two precursors along with a Sn source to produce SiGeSn alloy films [6], a material with much interest for stressed CMOS [7], solar cells [8], and lasers [9]. Relatively low temperatures are needed for SiGeSn epitaxy to prevent Sn precipitation. These low temperatures are incompatible with typical lower order precursors due to the above mentioned reaction rate limitation, hence the emphasis on higher order precursors. There has been little work, however, on the kinetic decomposition of higher order precursors for SiGe alloy...
2. Experimental details

The epitaxy tool is an Oerlikon/Leybold Sirius CVD-300 ultra-high vacuum (UHV) CVD [10] with a turbo pumped base pressure of 1\texttimes10^{-7} Pa. The tool is a multi-wafer batch system with a double walled quartz tube deposition chamber and a gate valve separated load lock chamber. The tool has the capability of carrying up to twenty 200 mm diameter wafers with an additional five dummy wafers on either side of the boat for increased temperature uniformity. For this experiment, the Si wafer substrates were lightly boron doped (10–50 Ohm cm) <100> orientation, 125 mm in diameter. Only one target wafer was used at a time in this work and four dummy wafers were placed immediately adjacent to the growth wafer in the boat slots on each side of it. Before epitaxy, the wafers were prepared with a standard RCA clean [11] that ended with a 1:100 hydrofluoric acid (HF)/deionized water solution dip for 5 min before the solution was continuously diluted with 1 L/min of deionized water for 20 min. At this point the wafers were hydrophobic and hydrogen passivated [12], and were taken out of solution and immediately loaded into the CVD intro chamber within two minutes. No high-temp pre-bake of the wafers was used, such as to reduce any possible residual sub-oxide on the surface. The low temperature processing adopted here is in line with maintaining a low temperature budget for the entire epitaxial process. A typical interface oxygen contamination dose (O-dose) for this cleaning procedure was 7\times10^{13} atoms/cm², measured by secondary ion mass spectrometry (SIMS), close to that reported in [12] for a similar pre-epitaxial clean.

Once the load chamber reached a pressure of 1\texttimes10^{-5} Pa, approximately 5 min after the start of pump down, the wafers were inserted into the growth chamber using a magnetically coupled transfer rod, under a high flow of hydrogen. Hydrogen flow was ceased when the transfer rod was withdrawn and the intro chamber gate valve was closed, and tetrasilane/digermane flow proceeded immediately. Process gases were not mixed with an additional carrier gas and the total growth pressure during epitaxy was <0.1 Pa. The digermane and tetrasilane precursors were provided by Voltaix/Air Liquide Advanced Materials. The tetrasilane was a liquid source, and was delivered to the CVD chamber as a vapor from the cylinder through a mass flow controller without using a bubbler/carrier gas. The moisture and oxygen levels in the tetrasilane source were specified by the manufacturer to be less than 1 ppm. Further descriptions of the tetrasilane gas delivery are described elsewhere [13]. The germanium precursor is a 10% by volume digermane mix in H₂ gas, with a manufacturer specified moisture and oxygen level less than 0.1 ppm. The partial pressures noted in this work were individually measured at the growth temperatures by a gas independent capacitance manometer, and were corroborated with a hot cathode ion pressure gauge that was adjusted with a gas calibration factor for the particular gas. The total pressure in the chamber was dependent on the turbo-molecular pumping speed and the gas flow into the chamber; there was no use of a butterfly throttle valve or other means of adaptive pressure control. The tetrasilane flow rate was held constant at a SiH₄-calibrated mass flow controller reading of 7 sccm, the chamber pressure was measured to be 60 mPa with no other gases flowing. The digermane flow was varied from a nitrogen-calibrated mass flow controller reading of 0–25 sccm to generate different alloy compositions.

A series of characterization techniques were used to measure the properties of the deposited SiGe films, and to understand the relation between growth parameters and sample quality and crystallinity. X-ray diffraction (XRD) and reflectivity measurements were performed using a Philips/Analytical X'Pert MRD equipped with a high-resolution goniometer and a CuKα X-ray source (λ = 1.54056 nm). For diffraction measurements (XRD), a Bartels Ge (2 2 0) monochromator was inserted in the incident beam path (12 arc-sec divergence), while a three-bounce Ge (2 2 0) analyzer was inserted in the diffracted beam path. Film thicknesses and alloy composition of the SiGe layers were also determined by variable angle spectroscopic ellipsometry (VASE) data. Spectra were acquired using a J.A. Woollam VASE with a computer controlled Berek waveplate compensator. The ellipsometric angles were fitted using a three-layer model consisting of the Si substrate, the SiGe layer, and native SiO₂. The optical constants for all layers were taken from the literature [14], and the SiGe and SiO₂ thicknesses as well as the Ge concentration were fitting parameters. Atomic Force Microscopy (AFM) measurements were performed to evaluate the surface roughness and morphology of epitaxial films, using a Veeco/Bruker Dimension 3100 operating in tapping mode and captured with the Nanoscope V interface and software. AFM image handling was performed using Gwyddion AFM software [15].

3. Deposition kinetics

Symmetric (004) θ-20 XRD curves were used to measure the alloy composition and film thickness, and thus the film growth rate. As the digermane gas pressure increased, the germanium film composition increased, as shown in Fig. 1a for different growth temperatures. The relationship between gas composition and alloy composition is roughly linear with a higher slope for the higher substrate temperatures. As the temperature of the substrate was increased from 400 °C to 550 °C, proportionally less digermane gas was needed to achieve the same germanium concentration in the film. Growths with trisilane exhibit the same trend [5], whereas mono-silane chemistry exhibits the opposite trend, namely an increase in germanium concentration in the film.
with decreasing temperature [16]. Fig. 1b shows the growth rates of alloys from Fig. 1a. For the alloy compositions grown, the measured peak growth rate at temperature is 525 °C for alloys with germanium content <8% and 500 °C for larger germanium contents.

The data from Fig. 1 is separated by alloy composition and shown as an Arrhenius plot in Fig. 2. Above about 500 °C, pure Si films have a weak dependence on temperature. This weak temperature dependence is a hallmark of the mass flow limited regime, in which the precursor molecule reacts as soon as contact is made with the wafer and the growth rate in this region is highly dependent on precursor flux. For growths at 550 °C, the growth rate of silicon–germanium alloys decreases as the Ge concentration increases, which is typical for the mass flow limited regime in CVD for silicon–germanium and is seen in many reports [3,17,18]. The sharp falloff in growth rate as the temperature is increased in this region will be discussed in further detail in Section 5.

At temperatures below 500 °C for Si, the growth rate was strongly dependent on temperature with an activation energy of around 1.4 eV, which is similar to the activation energies reported in the literature for silicon films; of 2.1 eV for silane in an identical hot wall UHV/CVD [18], and 1.86 eV for trisilane in a reduced pressure CVD (RPCVD) [5], as well as an activation energy of 1.3 eV for germanium films grown with digermaine in H₂ ambient by RPCVD [19], and 1.56 eV for Ge grown by gas source molecular beam epitaxy (GSMBE) [20]. At low temperatures, the reaction rate limited regime may be caused by a surface hydrogen desorption limit, because the precursor molecule is inhibited from reacting with surface sites that are filled and passivated with hydrogen, so that deposition is limited by hydrogen desorption in this regime [21]. The SiGe alloy films grown here show similar, low temperature growth rate dependence, supporting the picture of a hydrogen-limited regime. Hydrogen desorbs from the germanium surface at a much lower temperature than silicon, leading to a higher amount of available sites on the SiGe alloy surface compared to a pure Si surface and thus a higher deposition rate for higher Ge content alloy films at the lower temperatures [22]. In this work, for the SiGe alloys (<19% Ge), the temperature dependence of the deposition rate in the reaction rate limited region has the same activation energy of approximately 1.4 eV as for pure Si.

It is interesting to compare the growth rates for alloys from tetrasilane and digermaine precursors to the growth rates from the traditional precursors silane and germane in a similar hot wall UHV-CVD tool. At higher temperatures, the growth rates from tetrasilane and digermaine are of the same order of magnitude as that of the traditional precursors [18]. For 500 °C, the growth rates of all alloy compositions grown with tetrasilane and digermaine are 2–3× higher than that of silane and germane, which confirms the expectation that higher order precursors provide increased growth rates at lower temperatures than traditional precursors.

A peak can be seen in the growth rate at 500 °C–525 °C for all alloy compositions, excluding pure Si. This peak in growth rate becomes more exaggerated with increasing germanium composition, with almost an order of magnitude increase in deposition rate than the rate at 550 °C. The peak deposition rate shifts to lower temperatures with increasing germanium composition, following the changing transition temperatures from the reaction rate limited to the mass flow limited regime. Further discussion on the growth rate peak is in Section 5.

4. Film characterization

In order to assess the quality of SiGe thin films grown with tetrasilane and digermaine, a representative set of three similar layers grown at three different temperatures were characterized in a growth temperature analysis study: Sample A at the lowest growth temperature of 450 °C, Sample B at an intermediate growth temperature of 515 °C meant to correspond to the growth rate peak, and Sample C at a higher temperature of 550 °C. A summation of the data obtained for the three samples in this growth temperature study is shown in Table 1.

The growth rate and composition of the films were measured using symmetric (004) ω-2θ XRD scans in the Panalytical X’Pert system described in Section 2, and modeled using Panalytical Epitaxy software. The ω-2θ XRD curves show a clear layer peak and fringing, shown in Fig. 3, indicative of high crystalline quality. Slight variations in the peak width and fringe separation were attributed to variations in the film thickness and composition between samples. The (004) ω- full width at half maximum (FWHM) for the SiGe layers was found to be similar to that of the underlying Si substrate, showing no detectable broadening, suggesting that there was no significant contribution to the layer peak due to dislocations, tilt, or twist relative to the substrate.

Further analysis on the epilayers by direct counts of etch pit defects using a dilute Secco etch [23] yielded threading defect densities (TDD) on the order of 10⁵ TDD/cm². For 21% germanium SiGe alloy layers grown by a combination of di-silane and digermaine, a relationship was measured between SIMS interface doses of oxygen and the TDD [24], in which dislocation densities of 10¹³ cm⁻² were measured for SIMS O-dose greater than 3 × 10¹⁵ atoms/cm². Similar numbers for TDD (3 × 10⁹ cm⁻²) and SIMS O-dose (7 × 10¹⁴ atoms/cm²) were measured in this work, and indicate that the material grown by tetrasilane and digermaine is at least no more defective than material grown by industry standards disilane and germane.

The surfaces of films grown for commercial devices typically require root mean square (RMS) roughness <1 nm in order to maintain a planar structure during device manufacture, and thus it is important to consider the surface morphology aspects of growth. In order to assess the roughness of samples grown with tetrasilane and digermaine, AFM was performed, as shown in Fig. 4 for the samples of Table 1. Sample
were found, as shown in Table 1. Excellent agreement between data and model for thickness and composition (data not shown here), with the system as described in Section 2. Excel-
served in other work [25].

seen here did not resemble the roughness of gas phase particles ob-
the low pressures maintained in these experiments (≈0.1 Pa total) with alloy composition, rather than happening at a particular
rate peak in growth rate for the growth of germanium on both silicon and Ge substrates. There was also a small increase in growth rate for the transition temperature region (between the mass-flow and the reaction-rate limits) at T ≈ 700 °C in the growth rate data reported by Greene et al. [17] utilizing disilane and digermane for 20% Ge layers by GSMBE, but this peak in growth rate was not discussed by the authors. For similar SiGe alloys grown by CVD, however, we found that the growth rate increased by almost an order of magnitude from the mass transport (high temperature) region to the growth rate peak temperature, as in Fig. 2. It is worth noting that all observations of such a growth rate peak, both here and in literature, occurred in reactions of higher order precursor molecules, specifically digermane.

The peak growth rate occurred at approximately 525 °C for 5% Ge, at 500–525 °C for 8% Ge, at 500 °C for 14% Ge, and somewhere between 450 and 500 °C for 19% Ge; as can be seen in both Figs. 1b and 2. The temperature of the growth rate peak appears to follow the transition temperature from rate limited to mass flow limited, and thus shifts with alloy composition, rather than happening at a particular fixed temper-
ure. The shift of the growth rate peak in temperature, as the Ge composition is changed, leads credence to the idea that the growth rate peak is a phenomenon associated with the growth of the alloy itself and not a gas phase phenomena, because the temperature at which the precursor gasses decompose would be fixed for a given molecule. With the longer mean free path, gas phase reactions are also not expected to have a large contribution in UHV-CVD. Bramblett et al. [20] observed a peak in growth rate for the growth of germanium on both silicon and germanium substrates using digermane, and linked it to an increased film roughness at the growth rate peak temperature. The roughness shown in sample B, Fig. 4, grown at the growth rate peak, however, is much different than the sharp (133) facet profile seen in ref. [20]. The roughness observed in the Bramblett work had a periodicity of ≈1 μm and a height of roughly 30% of the total film thickness whereas the lat-
eral size observed in this work was on the order of ≈100 nm with a height of roughly 10% of the film, exhibiting much different scales. As the morphological characteristics of Ge films grown in ref. [20] and the SiGe films shown in this work are different, it cannot be determined if the features are the result of the same phenomena.

In strained SiGe alloy layers, it is possible to have an energetically fa-
orous or 3D surface, in a very similar way to Ge growth on Si, as the strain due to pseudomorphic growth can be relieved through sur-
face corrugations [27]. No reason was given in [20] as to a cause for the reported 3D growth in germanium on germanium growths, and there is no strain in this system. Hydrogen is known to provide an ad-
antage to germanium growth on silicon as it acts as a surfactant in

5. Discussion of growth rate peak

An unanticipated result of this work was the sharp growth rate peak observed in Fig. 2, near 500 °C. Deposition of germanium films from digermane alone has previously shown this peak in growth rate in two reports; films grown by RPCVD [19] and by GSMBE [20] on both Si and Ge substrates. There was also a small increase in growth rate for the transition temperature region (between the mass-flow and the reaction-rate limits) at T ≈ 700 °C in the growth rate data reported by Greene et al. [17] utilizing disilane and digermane for 20% Ge layers by GSMBE, but this peak in growth rate was not discussed by the authors. For similar SiGe alloys grown by CVD, however, we found that the growth rate increased by almost an order of magnitude from the mass transport (high temperature) region to the growth rate peak temperature, as in Fig. 2. It is worth noting that all observations of such a growth rate peak, both here and in literature, occurred in reactions of higher order precursor molecules, specifically digermane.

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A, grown at the lowest temperature of 450 °C, is the smoothest sample with an RMS roughness of 0.1 nm. An RMS roughness of 0.1 nm was also measured for a clean Si wafer, not shown here, implying that the roughness measured for Sample A is at the accuracy of the AFM system setup and that its roughness is comparable to an epitaxial wafer. The roughness of the SiGe samples in Fig. 4 was non-monotonic with temperature. Sample B, grown at 515 °C, showed a roughness value higher than at temperatures above and below. This increase in roughness was small, about 0.9 nm RMS for sample B which corresponds to an increase in the maximum height differential, Rmax, of ≈7 nm. A similar roughness vs. temperature trend was observed for all alloy concentrations, with the lower temperature growth of films resulting in smoother layers, and with higher temperature growths resulting in rougher layers, and growths at intermediate temperatures corresponding to the growth rate peak resulting in the largest roughness values. The surface for the roughest sample (B) seemed to exhibit small hills of material across the surface with no apparent orientation of the hill pattern. The hills were approximately 100 nm wide with a height of 3–6 nm, or up to 10% of the film thickness.

There have been reports on the increased likelihood that higher order precursors have gas phase reactions which deposit observable particles on the wafer surface. This phenomena was not expected at the low pressures maintained in these experiments (<0.1 Pa total) due to the large mean free path at this pressure, which would tend to re-
duce the chance for gas phase interactions. In addition, the roughness seen here did not resemble the roughness of gas phase particles ob-
erved in other work [25].

The set of three samples of Table 1 was also analyzed with VASE, (data not shown here), with the system as described in Section 2. Excel-
lent agreement between data and model for thickness and composition were found, as shown in Table 1.
the epitaxial growth process, smoothing films that would otherwise form 3D surface morphology due to strain buildup [26]. The smoothness of SiGe films grown in the low growth temperature, hydrogen limited regime, such as Sample A above, supports the hypothesis that hydrogen has a smoothing effect on SiGe alloy films. The smoothing of SiGe samples with reduced growth temperature has been reported before for the traditional precursors silane and germane as well [18,27]. It is possible that the roughness appearing at 515 °C in Fig. 4 as the growth temperature increased past the hydrogen limited regime was simply due to the decrease of the amount of hydrogen on the surface of the film and the subsequent reduction of the surfactant effect, resulting in strain-induced roughening.

The growth rate peak was observed to shift with alloy concentration following the transition from mass-flow limited to reaction rate limited temperature regimes, which happens at lower temperatures for increasing Ge concentration. In addition, the onset of 3D growth also decreases in temperature with increasing germanium concentration. The appearance of 3D surface morphology and the growth rate peak both correspond to the intermediate temperature region. Since this is also the temperature where H-termination is no longer governing the deposition kinetics, it is possible that the phenomena of H desorption and 3D growth are interlinked. While the tendency of SiGe films to rougthen with increasing growth temperatures is not unique to higher order precursors, the decrease in film growth rate as the temperature is further increased does appear unique to higher order precursors.

6. Conclusion

Tetrasilane and digermane precursors produced CVD layers that were shown by X-ray diffraction to have bulk-like crystalline quality, with higher growth rates and at lower temperatures than the traditional precursors silane and germane. The samples grown with tetrasilane and digermane at lower temperatures were found to be less defective with smoother surfaces than the samples grown at higher temperatures. A peak in growth rate was observed between the reaction rate limited low temperature regime and the mass flow limited high temperature regime. This growth rate peak has only been noted in germanium growth by digermane, and has not been previously reported in SiGe alloy growth. The peak growth rate temperature also corresponded to an increase in surface roughness.

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