



## Reduced-Pressure Chemical Vapor Deposition of Epitaxial Ge Films on Si(001) Substrates Using GeCl<sub>4</sub>

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A comparative study of the quality and growth kinetics of Ge films grown epitaxially on Si through a reduced-pressure chemical vapor deposition was conducted using GeCl<sub>4</sub> and GeH<sub>4</sub> as the Ge precursor. The growth rates of Ge films produced both by GeH<sub>4</sub> and GeCl<sub>4</sub> precursors were nearly constant in the 500–750°C temperature range, indicating that the growth was mass-transport limited. The films produced using the two precursors showed similar crystallinity, however, GeCl<sub>4</sub> Ge showed improved surface roughness. GeCl<sub>4</sub> also had better growth selectivity on oxide-patterned Si substrates.  
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The growth of heteroepitaxial Ge layers on Si(001) is of considerable interest due to the importance of its potential applications: high-performance Ge p-channel metal-oxide-semiconductor field-effect transistors<sup>1,2</sup> and as a path for integrating optoelectronic devices with Si complementary metal-oxide-semiconductor technology.<sup>3</sup> Challenges in Ge heteroepitaxy on Si include reducing both the high surface roughness resulting from the film's tendency toward island growth and the high dislocation densities of 10<sup>8</sup>–10<sup>9</sup> cm<sup>-2</sup> resulting from the 4.2% lattice mismatch. Further, for certain applications, robust selective growth conditions are desirable.

For Ge heteroepitaxy on Si, germane (GeH<sub>4</sub>) has been the standard precursor gas for gas source molecular beam epitaxy (MBE) and ultrahigh vacuum (UHV) and reduced-pressure (RP) chemical vapor deposition (CVD). Numerous studies have detailed the growth mechanisms, crystalline quality, and electrical properties of Ge films using GeH<sub>4</sub> precursor.<sup>4–12</sup> In comparison, very little has been reported for Ge films produced through a germanium tetrachloride (GeCl<sub>4</sub>). Cave and Czony attempted to deposit Ge epitaxial layers using a GeCl<sub>4</sub>–H<sub>2</sub> gas system,<sup>13</sup> and Miller and Grieco reported that growth and etching of Ge films occur depending on the GeCl<sub>4</sub>/H<sub>2</sub> molar ratio at 880°C.<sup>14</sup> Ishii and Takahashi also showed that growth and etching of Ge films occur depending on GeCl<sub>4</sub> partial pressure at 490–565°C and proposed that the growth reaction takes place through GeCl<sub>2</sub> adsorption on the surface directly from GeCl<sub>4</sub>.<sup>15</sup> However, the qualities of Ge layers produced through GeCl<sub>4</sub> have not been studied in detail.

In this article, the growth and characteristics of heteroepitaxial Ge layers on Si grown by GeCl<sub>4</sub> have been investigated using an industrial production RP CVD system. A comparison was made between GeCl<sub>4</sub> and GeH<sub>4</sub> at the same growth conditions. Growth kinetics, crystallinity, surface roughness, and growth selectivity using both precursors were examined.

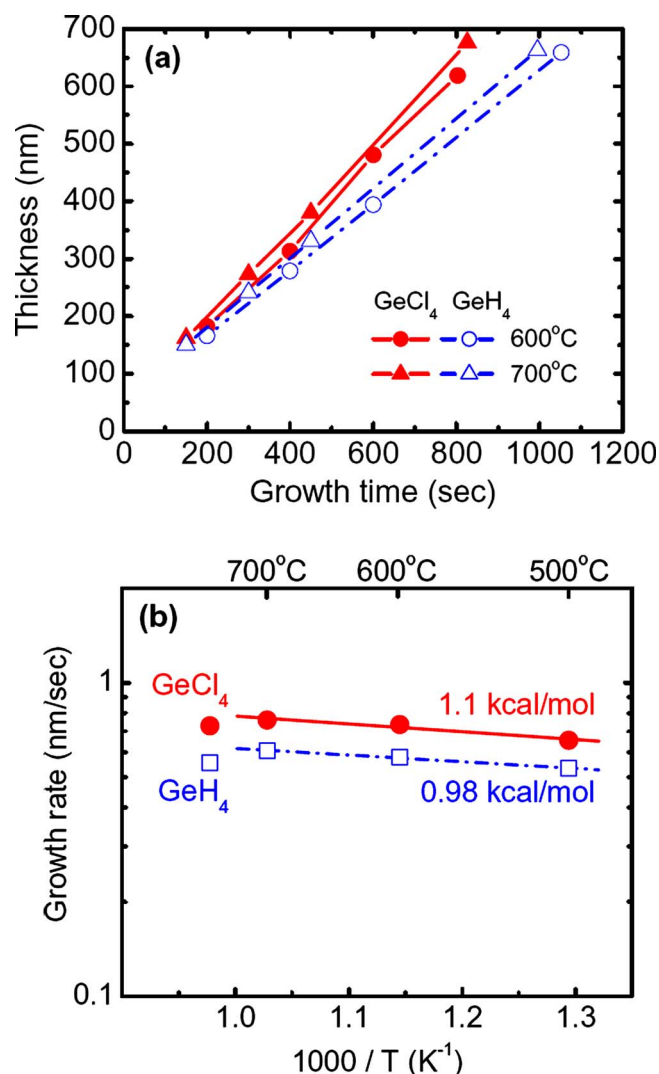
Epitaxial Ge layers were grown on p-type Si(001) substrates of ~0.02 Ω cm resistivity and 200 mm diameter in an industrial-type epitaxy reactor (ASM Epsilon E2000), horizontal, coldwall, single wafer load-locked with a lamp-heated graphite susceptor in a quartz tube. The substrates were cleaned in a diluted HF solution and deionized (DI) water rinsed followed by an in situ bake at 870°C under H<sub>2</sub> and at growth pressure for 1 min. In order to conduct a comparative study of the growth of the film by differing precursors without the potential confounding effects of the nucleation process, a two-step approach was made.<sup>12</sup> The first step for all the experiments included the growth of a 55 nm thick Ge buffer at 400°C for 540 s using GeH<sub>4</sub>. Because the Ge nucleation behavior using GeH<sub>4</sub> is well known compared to GeCl<sub>4</sub>, the initial buffer was grown using GeH<sub>4</sub>. Experimental conditions were explored during the sec-

ond step where either GeH<sub>4</sub> or GeCl<sub>4</sub> was used to produce thick films in the temperature range of 500–750°C. In order to compare growth rates, the molar flow of the two source gases was equalized: 30 sccm GeH<sub>4</sub> diluted at 25% in H<sub>2</sub> and a corresponding 334.8 μmol/min of liquid vapor GeCl<sub>4</sub> (partial pressure 3 × 10<sup>-2</sup> Torr). The GeCl<sub>4</sub> flow was produced by flowing hydrogen through a bubbler of liquid GeCl<sub>4</sub> and utilized a liquid vapor controller. A 20 slm hydrogen was used as a diluent gas for both GeH<sub>4</sub> and GeCl<sub>4</sub>. Growth pressure was fixed at 80 Torr in all the growth runs. Ge thickness was measured by spectroscopic ellipsometry using a SOPRA GES5 ellipsometer and confirmed by a scanning electron microscopy using a Zeiss Supra25 and by glancing-angle X-ray reflectivity using a Panalytical X'Pert diffractometer. X-ray diffraction and tapping-mode atomic force microscopy (AFM) using a Veeco Dimension 3100 AFM were used for the characterization.

Figure 1a shows the thickness of Ge layers deposited at 600 and 700°C using the two precursors as a function of growth time. Ishii et al. reported that the GeCl<sub>4</sub>–H<sub>2</sub> gas system (GeCl<sub>4</sub> partial pressure from 9.0 × 10<sup>-4</sup> to 1.3 × 10<sup>-2</sup> Torr) showed homoepitaxial Ge growth at low GeCl<sub>4</sub> partial pressure below 3 × 10<sup>-3</sup> Torr, but Ge etching occurred at its higher partial pressure with the temperature range of 490–565°C and at 6.5 Torr.<sup>15</sup> However, in our experiment, Ge thickness was linearly increased with growth time up to about 700 nm, and etching was not observed.

In Fig. 1b, the Ge growth rate is plotted as a function of an inverse growth temperature. GeCl<sub>4</sub> showed slightly higher growth rate than GeH<sub>4</sub>, while the slopes of the two curves were nearly parallel. From this data, the activation energy of Ge growth using GeCl<sub>4</sub> and GeH<sub>4</sub> was found to be fairly similar, 1.1 and 0.98 kcal/mol, respectively (1 kcal/mol = 0.0434 eV/molecule). In contrast, Ge layers grown by GeH<sub>4</sub> MBE showed an activation energy of 39 kcal/mol below 350 °C, the high value being ascribed to the effect of hydrogen desorption.<sup>16</sup> In UHV CVD at 3–5 mTorr, Ge growth using GeH<sub>4</sub> was reported to be reaction-rate limited below 450°C, with an activation energy of 22.6 kcal/mol.<sup>17</sup> Another study at 20 mTorr growth showed that between 300 and 375°C the growth is limited by a GeH<sub>4</sub> decomposition reaction at the Ge surface with an activation energy of 33 kcal/mol and that above 375°C it is controlled by diffusion and adsorption on the gas phase.<sup>5</sup> At RP CVD conditions, activation energies of 8.75 kcal/mol (500–600°C, 6 Torr)<sup>18</sup> and 6.9 kcal/mol (400–750°C, 20 Torr)<sup>10</sup> were reported. The latter was claimed to be in a mass-transport-limited regime in comparison with an activation energy of 4.2 kcal/mol of Si homoepitaxy in the same regime from SiH<sub>4</sub> or SiH<sub>2</sub>Cl<sub>2</sub>. The low activation energy value of ~1 kcal/mol calculated in the current study for both the GeCl<sub>4</sub> and the GeH<sub>4</sub> experiments indicates that the growth was mass-transport limited. Given that the Ge growth is controlled by mass-transport of reaction gas, not by its chemical reaction, it is conjectured that the slightly higher growth rate of GeCl<sub>4</sub> might be associated with an enhanced diffusivity of GeCl<sub>4</sub> in the gas phase.

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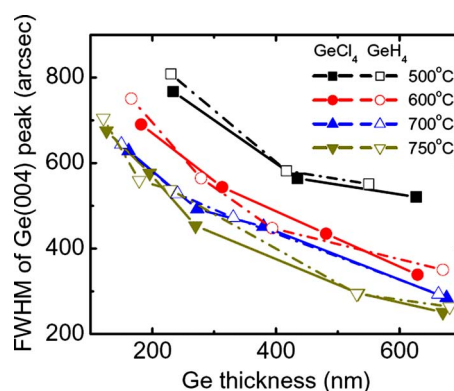


**Figure 1.** (Color online) (a) Thickness of Ge layers grown by GeCl<sub>4</sub> or GeH<sub>4</sub> at 600 and 700°C, including a 55 nm thick Ge buffer, and (b) inverse growth temperature vs growth rate. Activation energy obtained from the slope is indicated.

Regarding the slight reduction of growth rate at 750°C, a similar behavior was reported in Ge (using GeH<sub>4</sub> at over 500°C and at atmospheric pressure)<sup>19</sup> and Si (using SiH<sub>4</sub> at 110°C at UHV)<sup>20</sup> homoepitaxy and it was ascribed to the depletion of source gas and Si evaporation from the surface, respectively. However, it is not clearly understood and further study is underway for clarification.

Figure 2 shows full width at half maximum (fwhm) values of  $\omega$ -scan Ge(004) peaks (i.e., rocking curve) of the Ge layers grown at different temperatures and thicknesses using GeCl<sub>4</sub> or GeH<sub>4</sub>. The fwhm of Ge layers at all the temperatures decreases with increasing their thickness. This can be attributed to the peak broadening associated with localized strain induced by threading dislocation,<sup>21</sup> and its density is inversely proportional to the thickness of the epitaxial layer.<sup>22</sup> In addition, Ge layers grown at higher temperature showed lower fwhm at the same thickness. In all the growth temperature and thickness trials, the Ge layers using GeCl<sub>4</sub> or GeH<sub>4</sub> showed similar levels of fwhm values, indicating a corresponding similarity in crystallinity.

Figure 3a shows root-mean-square (rms) roughness of the Ge layers using GeCl<sub>4</sub> or GeH<sub>4</sub> at different temperatures as a function of thickness. Generally, the surface became less rough with thicker Ge layers. However, this effect showed indications of eventually



**Figure 2.** (Color online) FWHM values of  $\omega$ -scan Ge(004) peaks of GeCl<sub>4</sub> or GeH<sub>4</sub> Ge layers at different growth temperatures as a function of thickness.

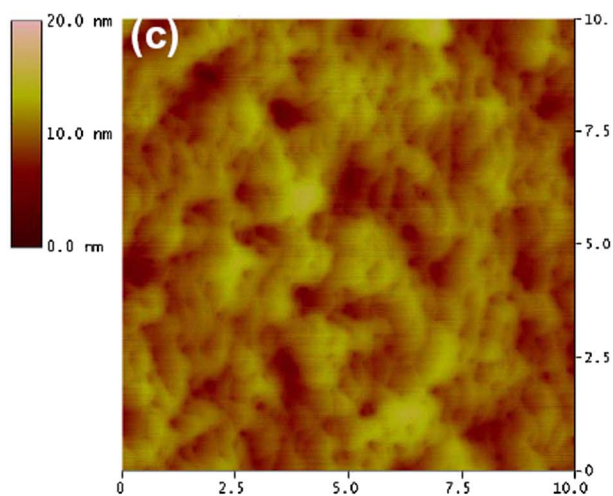
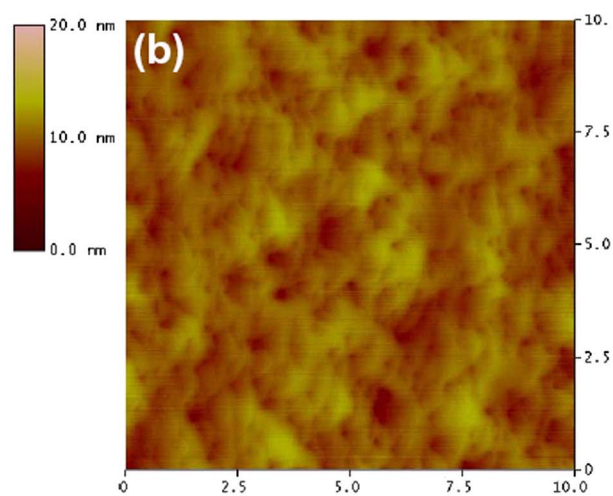
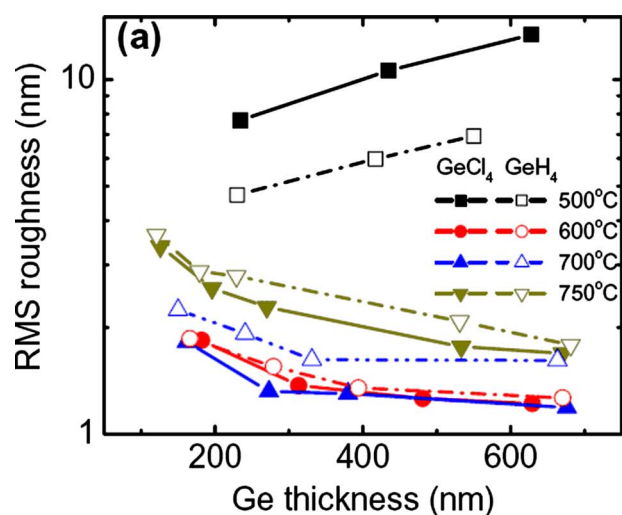
leveling off, most notably seen for the 600°C growth curve. Of the films produced using GeH<sub>4</sub>, the 600°C runs showed the lowest roughness, about 1.2 nm. As growth temperatures were increased above 600°C for GeH<sub>4</sub>, the surface roughness increased appreciably. More detailed study on the evolution of the surface roughness of GeH<sub>4</sub> Ge layers is reported elsewhere.<sup>12</sup> The GeCl<sub>4</sub> Ge layers exhibited a similar level of surface roughness with GeH<sub>4</sub> at 600°C, but the surface roughness achieved its lowest value for 700°C growths. In contrast to the GeH<sub>4</sub> growth runs, comparison of the surface roughness curves for GeCl<sub>4</sub> at 600 and 700°C indicates a fairly broad process window for achieving low surface roughness.

The moderately lower surface roughness of films produced using GeCl<sub>4</sub> relative to those of films produced using GeH<sub>4</sub> can be associated with the presence of Cl on the growing surface for the GeCl<sub>4</sub> runs. Exposure of the growth surface to Cl can lead to surface Ge dangling bonds becoming saturated with Cl, leading to a change in relative surface energy or to inhibited Ge surface diffusion.<sup>23,24</sup> It was further reported that HCl gas introduced during the growth of Ge islands on Si impeded island development due to the reduced Ge surface diffusion.<sup>24</sup> Because the surface diffusion is a thermally activated process, growth temperature is one of the primary variables in determining the surface morphology.<sup>5,17</sup> We believe that a reduced Ge surface diffusion related to Cl radicals bonding with the Ge surface dangling bonds explains why the GeCl<sub>4</sub> Ge layers in this study became smoother at elevated temperatures while the GeH<sub>4</sub> Ge layers became rougher at elevated temperatures (i.e., greater than 600°C).

Figures 3b and c show the AFM images of about 670 nm thick GeCl<sub>4</sub> and GeH<sub>4</sub> Ge layers grown at 700°C, respectively. The rms roughness measured for the GeCl<sub>4</sub> sample shown in Fig. 3b was 1.2 nm, while the rms roughness measured for the GeH<sub>4</sub> sample shown in Fig. 3c was 1.6 nm.

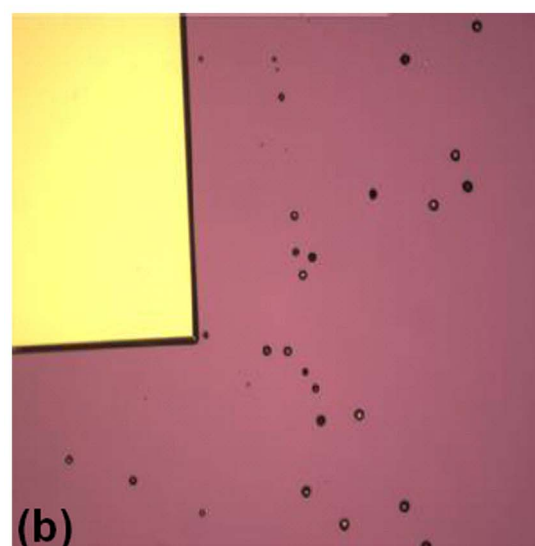
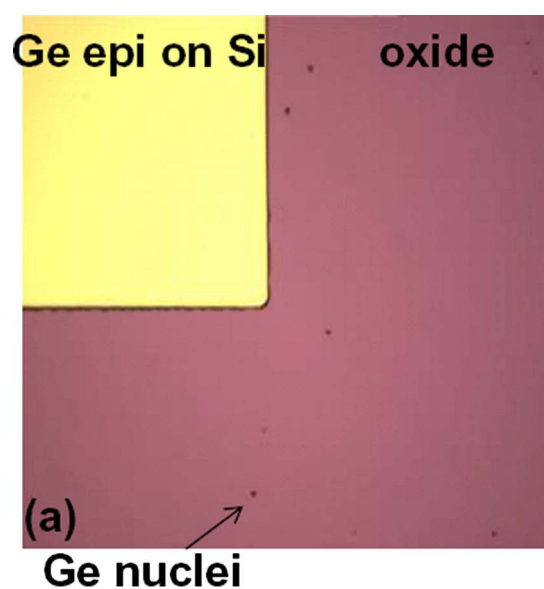
The defect density of a 650 nm thick GeH<sub>4</sub> Ge layer grown at 600°C was estimated to be about  $8.0 \times 10^8$  cm<sup>-2</sup> from plan-view transmission electron microscope images. The comparison of etch pit density (EPD) of about 670 nm thick GeH<sub>4</sub> and GeCl<sub>4</sub> Ge layers grown at 600 and 700°C was made using the AFM images after iodine defect etching (HF/HNO<sub>3</sub>/CH<sub>3</sub>COOH = 5:10:11 with 30 mg I<sub>2</sub> dissolved) and the EPD was roughly estimated to be  $5 \times 10^8$  to  $1 \times 10^9$  cm<sup>-2</sup> without a noticeable difference between GeH<sub>4</sub> and GeCl<sub>4</sub>. In order to get the trends of correlation of defect density with surface roughness and the fwhm of the X-ray peak, more experiments and in-depth studies are necessary.

Figures 4a and b show an optical microscope image of Ge layers selectively grown on oxide-patterned Si substrates using GeCl<sub>4</sub> and GeH<sub>4</sub>, respectively, at 600°C. The GeCl<sub>4</sub> Ge growth showed fewer and smaller-sized Ge nuclei on oxide compared to GeH<sub>4</sub> growth, indicating that GeCl<sub>4</sub> has better growth selectivity. As the studies of



**Figure 3.** (Color online) (a) Rms roughness from  $10 \times 10 \mu\text{m}$  AFM images of Ge layers at different thicknesses and growth temperatures using GeCl<sub>4</sub> and GeH<sub>4</sub>.  $10 \times 10 \mu\text{m}$  AFM images of 670 nm thick Ge layers grown at 700°C using (b) GeCl<sub>4</sub> and (c) GeH<sub>4</sub>.

Si and Si<sub>x</sub>Ge<sub>1-x</sub> selective epitaxy showed that the addition of HCl to the reactor during growth suppressed nucleation on the oxide,<sup>25,26</sup> it follows that the presence of Cl in the growth of Ge films using GeCl<sub>4</sub> should similarly lead to better growth selectivity.



**Figure 4.** (Color online)  $525 \times 437 \mu\text{m}$  bright-field optical microscope images of Ge films produced from (a) GeCl<sub>4</sub> and (b) GeH<sub>4</sub> grown on oxide-patterned Si substrates. They were grown at 600°C for 1830 and 2400 s using GeCl<sub>4</sub> and GeH<sub>4</sub>, respectively, which correspond to 1.37  $\mu\text{m}$  thick Ge growth on 55 nm thick Ge buffer on blanket Si substrates in both cases.

In summary, the growth kinetics and characteristics of RP CVD Ge epitaxy on Si using GeCl<sub>4</sub> have been investigated and compared with Ge epitaxy on Si using GeH<sub>4</sub>. Ge growth using GeCl<sub>4</sub> showed a nearly constant growth rate between 500 and 750°C without noticeably etching the Ge surface. Both precursors showed a mass-transport-limited growth in this temperature range with an activation energy of about 1 kcal/mol. The GeCl<sub>4</sub> Ge layers showed a similar level of crystallinity to that of the GeH<sub>4</sub> films at the same thickness while exhibiting lower surface roughness. GeCl<sub>4</sub> also showed a wider temperature process window than GeH<sub>4</sub> in producing films with low surface roughness. This is believed to be due to the reduced surface diffusion of Ge in the presence of Cl. Additionally, GeCl<sub>4</sub> Ge layers had better growth selectivity on oxide-patterned Si substrates.

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