

## The effect of hydrogen on the surface segregation of phosphorus in epitaxially grown relaxed Si<sub>0.7</sub>Ge<sub>0.3</sub> films by rapid thermal chemical vapor deposition

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The surface segregation of phosphorus in relaxed Si<sub>0.7</sub>Ge<sub>0.3</sub> epitaxial films grown on Si (100) substrates by rapid thermal chemical vapor deposition was investigated in this letter. The effect of the growth temperature on phosphorus segregation was studied experimentally and examined using a two-state model. As the growth temperature is reduced, phosphorus segregation is greatly suppressed, and we report an extremely sharp phosphorus turn-off slope of 6 nm/dec at 500 °C. The sharper slopes at low temperatures are explained by a modified two-state model which includes the effect of increased surface coverage of hydrogen at low temperatures. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4757123>]

As device dimensions are scaled down, a sharp profile of dopants is becoming a key factor to realize nano-scale semiconductor devices such as silicon tunneling diodes,<sup>1</sup> tunneling field effect transistors,<sup>2</sup> and two-dimensional electron gases (2DEGs) in a modulation-doped Si/SiGe heterostructure.<sup>3</sup> 2DEGs are of particular interest for quantum dot (QD) applications. A QD is usually fabricated on a 2DEG, with top metal Schottky depletion gates used to isolate a single electron in the underlying 2DEG layer. However, the strong surface segregation of n-type dopants in a relaxed SiGe epitaxial film can cause a high dopant concentration at the surface, resulting in high gate leakage current and ineffective gating. Therefore, a sharp turn-off slope of n-type dopants is necessary.

Although a turn-off slope of 2–3 nm/dec for antimony was reported in Si epitaxial films grown by molecular beam epitaxy (MBE),<sup>4</sup> it has been difficult to obtain such abrupt profiles for phosphorus and arsenic, the most common n-type dopants in chemical vapor deposition (CVD) systems.<sup>5</sup> Several works were reported to reduce phosphorus segregation in Si by *ex situ* cleaning (13 nm/dec)<sup>6</sup> or by introducing substitutional carbon atoms into Si epitaxial films (11 nm/dec).<sup>7</sup> However, the former approach requires a growth interruption, which may introduce contaminants into the growth interface. For the latter, the control over carbon atoms into substitutional sites is critical since the interstitial carbon could degrade device performance due to their midgap energy states.<sup>8</sup>

In this letter, we report an extremely sharp phosphorus turn-off slope of 6 nm/dec in relaxed Si<sub>0.7</sub>Ge<sub>0.3</sub> films without any *ex situ* cleaning step or introduction of carbon into the epitaxial films. We also investigated the surface segregation of phosphorus in strained vs. relaxed Si<sub>0.7</sub>Ge<sub>0.3</sub> films grown by rapid thermal CVD (RTCVD). We found that the hydrogen coverage on the surface during the growth plays an important role in the suppression of phosphorus segregation in the CVD process at low temperatures (500–600 °C). Finally,

a modified version of the two-state model (TSM) was used to model the effect of surface hydrogen on phosphorus segregation and its dependence on the growth temperature.

In this work, Si (100) substrates (for strained SiGe) and polished relaxed Si<sub>0.7</sub>Ge<sub>0.3</sub> virtual substrates with a graded Si<sub>1-x</sub>Ge<sub>x</sub> (0 < x < 0.3) buffer layer grown on Si (100) substrates (for relaxed SiGe) were used to study phosphorus segregation. Prior to being placed into the reactor, substrates were cleaned by the following steps: 5 min in diluted hydrofluoric acid (HF) (1%), 15 min in H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> (2.5:1), followed by 2 min in diluted HF (1%). Then, the samples were heated to 850 °C in a hydrogen carrier at 6 Torr to remove the residual oxide before the epitaxial growth starts. The gas precursors were diluted silane and germane in hydrogen for Si and SiGe growth, and a diluted phosphine in hydrogen was the doping gas. The test structure for phosphorus segregation is as follows: first, a 20-nm undoped Si<sub>0.7</sub>Ge<sub>0.3</sub> buffer layer was grown followed by a 10-nm n-type Si<sub>0.7</sub>Ge<sub>0.3</sub> layer doped with phosphorus of peak level between 10<sup>18</sup> and 10<sup>19</sup> cm<sup>-3</sup>. Both layers were grown at 575 °C and the growth rate was 5 nm/min. Then, an undoped Si<sub>0.7</sub>Ge<sub>0.3</sub> cap layer was grown at 500 °C–600 °C to study the effect of growth temperature on phosphorus segregation with its thickness between 30 and 150 nm. To investigate the effect of growth rate, we varied the growth rate of the Si<sub>0.7</sub>Ge<sub>0.3</sub> cap layers between 0.1 and 30 nm/min by adjusting the partial pressures of silane and germane. The Ge fraction in the SiGe cap layer was between 0.28 and 0.30. Last, a thin Si cap layer of 4 nm was grown at 625 °C with the growth rate of 2.5 nm/min. The films were subsequently characterized by secondary ion mass spectrometry (SIMS) to determine the phosphorus profiles and the growth rates.

Most prior works of phosphorus segregation in SiGe were done in compressively strained SiGe layers,<sup>9</sup> not in the relaxed SiGe layers required for a modulation-doped 2DEG, i.e., a higher conduction band in SiGe than in Si. Thus, we compared the phosphorus profiles in strained and relaxed SiGe films first. We found that the segregation is much worse in relaxed SiGe films than in strained SiGe films (Fig. 1(a)).

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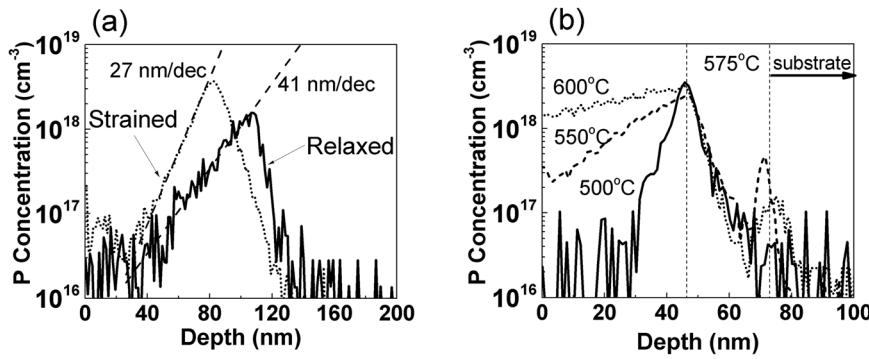


FIG. 1. Phosphorus profiles in (a) strained and relaxed  $\text{Si}_{0.7}\text{Ge}_{0.3}$  layers grown at  $575^\circ\text{C}$  and (b) relaxed  $\text{Si}_{0.7}\text{Ge}_{0.3}$  cap layers grown at  $500$ ,  $550$ , and  $600^\circ\text{C}$ .

For a growth temperature of  $575^\circ\text{C}$  and growth rate of  $5\text{ nm/min}$ , the turn-off slopes of phosphorus in strained and relaxed films are  $27$  and  $41\text{ nm/dec}$ , respectively. The fundamental reasons for this difference are unknown and a further study is required. We then focused on phosphorus segregation in the relaxed  $\text{Si}_{0.7}\text{Ge}_{0.3}$  films.

Phosphorus profiles measured by SIMS for relaxed SiGe layers grown at  $500$ ,  $550$ , and  $600^\circ\text{C}$  are shown in Fig. 1(b). At a depth of  $45\text{ nm}$ , the phosphine supply for the doped layer was turned off. As the growth temperature is reduced, the surface segregation is reduced with the phosphorus turn-off slope declining from  $127\text{ nm/dec}$  at  $600^\circ\text{C}$  to  $9\text{ nm/dec}$  at  $500^\circ\text{C}$ . By adjusting the gas flow rates of silane and germane at  $500^\circ\text{C}$ , an extremely sharp slope of  $6\text{ nm/dec}$  was obtained with the growth rate of  $0.08\text{ nm/min}$ , which we believe is the sharpest reported turn-off slope of phosphorus in relaxed SiGe films.

In our work, a matrix of Si and Ge atoms and surface hydrogen complicate the analysis of phosphorus segregation. In a simpler case of P in Si (100), a segregation energy of  $0.64\text{ eV}$  was first reported by Nützel and Abstreiter<sup>10</sup> from SIMS results. This work used a so-called TSM<sup>11</sup> of P atoms moving between the surface and the sub-surface layers in Si. Later, by temperature programmed desorption (TPD), Cho *et al.*<sup>12</sup> reported a segregation enthalpy of  $0.86\text{ eV}$ , which is defined as free energy of phosphorus in surface and bulk layers, essentially the same as the segregation energy defined in the TSM. The P coverage in their study was larger than  $0.1$  monolayer (ML) and the major Si surface structures with P surface coverage  $> 0.1$  ML were previously proposed by Yu *et al.*<sup>13</sup> as a mixture of Si-Si, Si-P, and P-P dimers. Sen *et al.*<sup>14</sup> used density functional theory to predict the different favorable sites for surface P atoms at a coverage above and below  $0.13$  ML. Thus, the work of Refs. 12 and 13 might not be directly relevant to our experimental results since the integrated P doses in our samples are at most  $5 \times 10^{12}\text{ cm}^{-2}$  ( $\sim 0.01$  ML). Other works on Sb,<sup>10</sup> As,<sup>15</sup> and Ge<sup>16,17</sup> surface segregation in Si have also been modeled by using a TSM. In addition, those works all ignored any temperature dependence of attempt frequency and used the segregation energy to reflect all temperature effects. Thus, in this letter, we also use a modified TSM to investigate phosphorus segregation in the more complicated structure of relaxed  $\text{Si}_{0.7}\text{Ge}_{0.3}$  layers.

TSM describes the dopant segregation as an exchange process of P atoms and host atoms (Si or Ge in this study) between the surface layer and the sub-surface layer (Fig. 2). The rate equations governing this exchange process between those two layers are

$$\frac{dn_1}{dt} = -r_{12}n_1(1 - n_2) + r_{21}n_2(1 - n_1), \quad (1)$$

$$\frac{dn_2}{dt} = -r_{21}n_2(1 - n_1) + r_{12}n_1(1 - n_2), \quad (2)$$

$$r_{12} = \nu e^{-\frac{E_1}{kT}}, \quad (3)$$

$$r_{21} = \nu e^{-\left(\frac{E_1 + \Delta E_{surf}}{kT}\right)}, \quad (4)$$

where  $n_1$  and  $n_2$  are the normalized concentrations of phosphorus in the sub-surface layer (layer 1) and the surface layer (layer 2),  $r_{12}$  and  $r_{21}$  are the jumping rates of phosphorus from the sub-surface layer to the surface layer, and vice versa.  $E_1$  is the activation energy barrier facing phosphorus in the sub-surface layer,  $\Delta E_{surf}$  is the segregation energy, which represents the difference of activation barriers, and  $\nu$  is the attempt frequency (Fig. 3). We assume a single attempt frequency independent of temperature as previous reports suggested for phosphorus segregation in Si.<sup>10-12</sup> It is assumed that P atoms below the sub-surface layer are trapped and cannot diffuse during the time scale of the growth. Assuming  $n_1$  and  $n_2 \ll 1$ , the differential rate equations can be solved and the turn-off slope of phosphorus  $x_0$  (nm/dec) is

$$x_0 = \frac{a_0 \ln 10}{4} \frac{1}{\ln\left(1 + e^{-\frac{\Delta E_{surf}}{kT}}\right) - \ln\left[1 - e^{-\left[r_{12} + r_{21}\right] \frac{a_0}{4GR}}\right]}, \quad (5)$$

where  $a_0$  is lattice constant and  $GR$  is the growth rate.

According to the TSM, the surface segregation occurs because P atoms in the sub-surface layer tend to jump to the surface layer due to the lower energy level in the surface

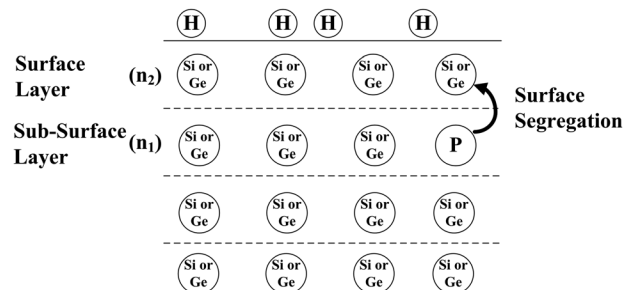


FIG. 2. A simplified schematic of phosphorus segregation as occurring via exchange of P atoms in the sub-surface layer with Si and/or Ge atoms in the surface layer with finite coverage of surface hydrogen.

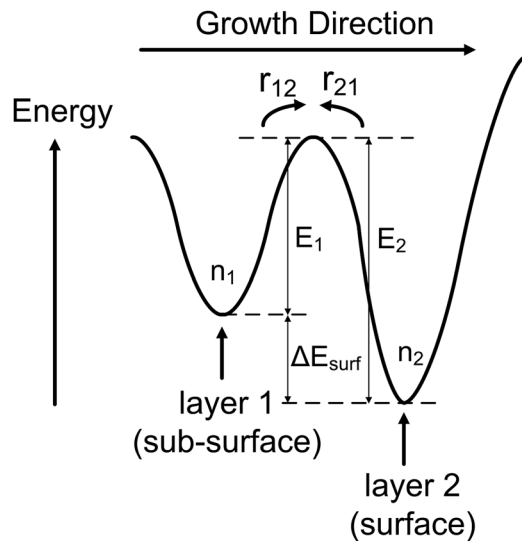


FIG. 3. Schematic of the two-state model of phosphorus energy near the surface during the growth. Layer 2 represents the surface layer and layer 1 is the next atomic layer below the surface.

layer (Fig. 3). In thermal equilibrium (low growth rates), the surface segregation is determined by the ratio of the phosphorus concentrations at the surface and sub-surface layers ( $n_2/n_1$ ), which only relies on the temperature and the segregation energy ( $\Delta E_{surf}$ ) through the first term in the denominator of Eq. (5). At lower temperatures, if still in equilibrium, more P atoms are trapped in the surface layer than in the sub-surface layer due to the lower energy state of the former, so the segregation is stronger. On the other hand, in the kinetic-limited regime of high growth rates, P atoms in the sub-surface layer cannot reach equilibrium with those in the surface layer. Therefore, phosphorus will be trapped in the sub-surface layer and the limiting factor is its activation energy barrier  $E_1$ . As the temperature is reduced, the probability of phosphorus jumping across the barrier to the surface layer is smaller because of the lower kinetic energy of phosphorus. As a result, phosphorus segregation is reduced. This physical limit has been applied to reduce phosphorus segregation in Si (100) grown by MBE at temperature below  $500^\circ\text{C}$ <sup>10</sup> and the best turn-off slope (4 nm/dec) for P in Si was reported by room-temperature growth.<sup>18</sup>

Our experimental data (points) of phosphorus turn-off slope vs. growth rate at different temperatures ( $500^\circ\text{C}$  to  $600^\circ\text{C}$ ) and theoretical curves based on the TSM are shown in Fig. 4. At  $600^\circ\text{C}$ , the segregation is near the transition between thermal equilibrium and kinetic-limited regimes. Thus,  $\Delta E_{surf} = 0.47\text{ eV}$  can be fitted by assuming the experimental results were in the regime of thermal equilibrium. Furthermore, as Nützel and Abstreiter<sup>19</sup> suggested that the attempt frequency be between  $10^{11}$  and  $10^{13}$  Hz, we selected  $\nu = 1 \times 10^{12}$  Hz to fit the data at  $600^\circ\text{C}$  and found  $E_1 = 1.84\text{ eV}$ . Despite a good match between the experimental data and the theoretical curve at  $600^\circ\text{C}$ , there is a large discrepancy between the experimental results and the model at lower temperatures ( $500^\circ\text{C}$ – $575^\circ\text{C}$ ). The low dependence of the segregation on growth rate suggests the data at low temperatures were in the equilibrium regime, not kinetically limited. However, the phosphorus slope was much sharper at lower temperatures, in contrast with what would be expected

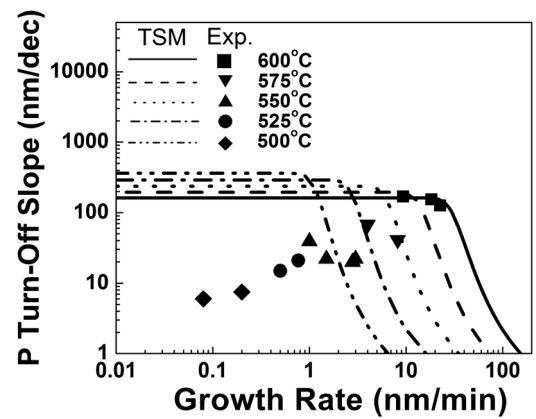


FIG. 4. Experimental data (points) of phosphorus turn-off slope vs. growth rate and the fitting curves (based on TSM).

from the TSM in equilibrium. This discrepancy cannot be resolved by simply adjusting the fitting parameters.

In the CVD process, hydrogen is used as a carrier gas and it is well established that hydrogen could cover the surface by forming Si–H or Ge–H bonds.<sup>20</sup> At high temperatures, most of those bonds break easily and hydrogen desorbs, so the surface coverage of hydrogen is nearly zero. At low temperatures, however, the thermal energy is too low to break the Si–H or Ge–H bonds efficiently, so hydrogen will cover most of the surface layer. Our data show that the phosphorus turn-off slope is nearly constant with growth rate at a fixed temperature, suggesting that it is in the regime of thermal equilibrium, with the segregation depending on  $\Delta E_{surf}$ . At the heart of our model, we assume phenomenologically that the presence of surface hydrogen changes the relative energy of P atoms in the surface and sub-surface layers such that the segregation energy  $\Delta E_{surf}$  is reduced. Thus, at lower temperatures, the segregation will be suppressed due to higher hydrogen coverage on the surface. Because of two types of surface sites (with or without H), in principle, we could model the problem with two segregation energies and a fraction of phosphorus segregation to each site. However, the two energies would probably depend on the local numbers of Si or Ge atoms, leading to too many parameters. Prior works by MBE and TPD used an effective segregation energy<sup>16,17</sup> to investigate the H effect on Ge segregation in Si (100), which we follow in this study. Thus, we treat  $\Delta E_{surf}$  as a single effective parameter which varies with hydrogen coverage as the temperature changes.

With the motivation of H-coverage affecting phosphorus segregation, a fit between the experimental data and the model is obtained by using  $\Delta E_{surf}$  as a fitting parameter (Fig. 5(a)).  $\Delta E_{surf}$  is plotted vs. temperature in Fig. 5(b). At a H pressure of 6 Torr (Fig. 5(a)), the reduced segregation at lower temperatures originates from a smaller segregation energy  $\Delta E_{surf}$ . The decrease of  $\Delta E_{surf}$  with decreasing temperature will reduce the ratio of phosphorus populations in the surface vs sub-surface layers ( $n_2/n_1$ ), resulting in a reduction of the segregation. On the other hand,  $\Delta E_{surf}$  increases with temperature because of less H coverage at higher temperatures. The reduced segregation energy of P in  $\text{Si}_{0.7}\text{Ge}_{0.3}$  with more H coverage surface follows the trend of Ge segregation in Si.<sup>16,17,21</sup> To confirm that the main effect of

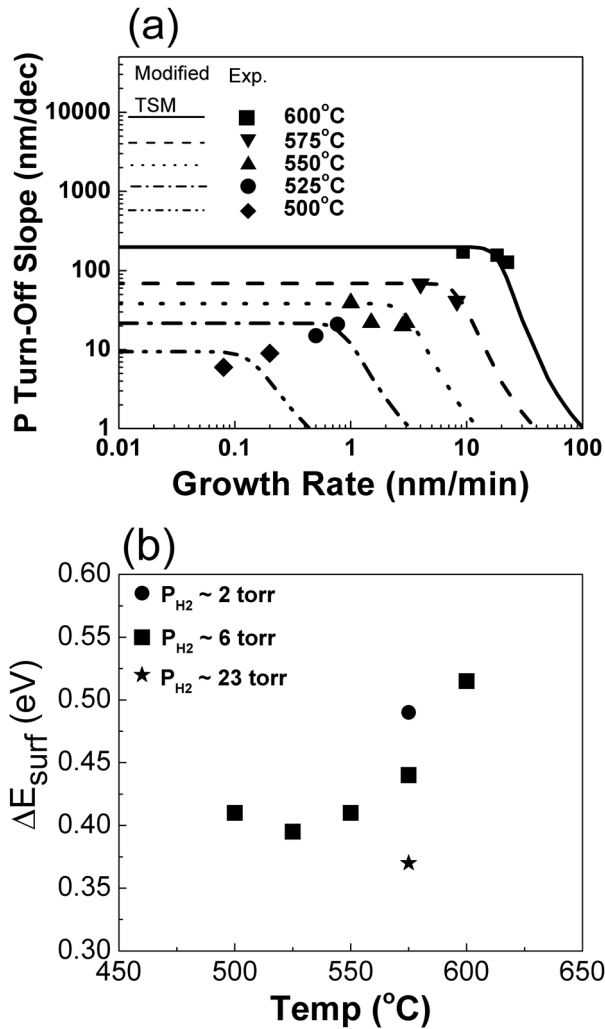


FIG. 5. (a) Experimental data (points) and modified TSM curves of P turn-off slopes vs. growth rate by considering the effect of surface hydrogen (at 6 Torr) on the segregation energy, (b) segregation energy ( $\Delta E_{surf}$ ) vs. temperature for hydrogen pressures of 2, 6, and 23 Torr.

segregation reduction comes from a change of H coverage rather than a change of attempt frequency or other effects with temperature, we adjusted hydrogen pressure to vary its surface coverage<sup>22</sup> at 575 °C (Fig. 5(b)). As expected, with higher hydrogen pressure (23 Torr), the segregation is suppressed, leading to a lower effective segregation energy. The opposite trend is shown with a lower hydrogen pressure of 2 Torr. The segregation energy obtained in this work ranges between 0.37 and 0.52 eV, which is lower than those published for P in Si of 0.67–0.86 eV<sup>10,12</sup> without H coverage. The difference could be explained by the presence of surface hydrogen on  $\text{Si}_{0.7}\text{Ge}_{0.3}$  surface in this work and the effect of Ge.

The surface segregation of phosphorus and the resulting high doping level at the surface limits the gating of modulation-doped Si/SiGe 2DEGs. By reducing the growth temperature of the SiGe cap layer to give a sharp turn-off slope of 13 nm/dec and the surface doping level below  $1 \times 10^{16} \text{ cm}^{-3}$ , we achieved effective gating with extremely low gate leakage current at 4 K.<sup>23</sup> This enabled an extremely low electron density of  $8.3 \times 10^{10} \text{ cm}^{-2}$  with mobility of  $63\,000 \text{ cm}^2/\text{V s}$  at 4 K.<sup>24</sup>

In conclusion, we studied the surface segregation of phosphorus in  $\text{Si}_{0.7}\text{Ge}_{0.3}$  films grown by RTCVD. The segregation in relaxed layers is stronger than in strained layers. Furthermore, the segregation in relaxed layers is reduced as the temperature is decreased due to the higher surface coverage of hydrogen. We proposed a phenomenological model to explain the effect of surface hydrogen on phosphorus segregation, where surface hydrogen changed the bonding structure of host atoms in the surface layer and reduced the segregation energy  $\Delta E_{surf}$  as the growth temperature is decreased. Thus, the segregation is suppressed at lower temperatures. An extremely sharp phosphorus turn-off slope of 6 nm/dec in relaxed  $\text{Si}_{0.7}\text{Ge}_{0.3}$  layers grown at 500 °C was also reported.

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