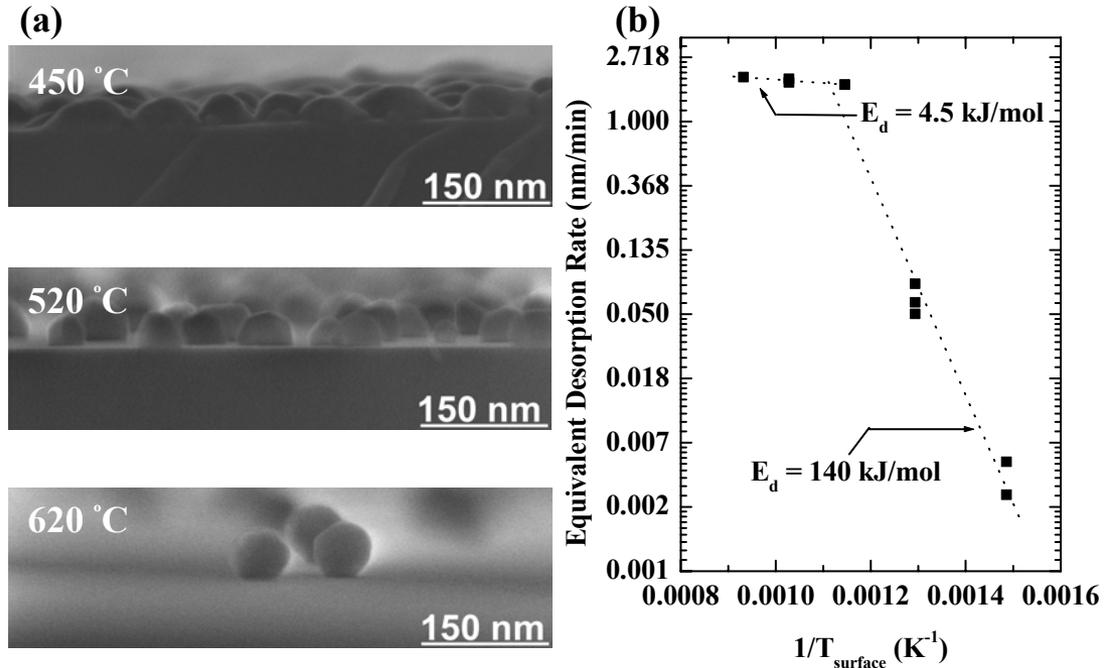


Quantitative Understanding of Selectivity During Ge Growth on Si over SiO₂

Sang M. Han, University of New Mexico, DMR-0094145

We have previously demonstrated that high-quality Ge can be grown on Si by the “touchdown” of Ge seeds through a thin layer of SiO₂ during Ge molecular beam exposure.[†] - This outcome opened a new venue to grow lattice-mismatched semiconductors on Si, potentially enabling the integration of optoelectronic, radio-frequency, and photovoltaic devices with Si-based integrated circuits. - The success of the touchdown technique squarely relies on selective growth of Ge on Si rather than on SiO₂. This selectivity is commonly explained by the chemical reaction between Ge and SiO₂, producing volatile SiO and GeO. Contrary to this conventional belief, our latest experimental observations demonstrate that no appreciable chemical reaction occurs between Ge adspecies with clean SiO₂ surface and that the strength of interaction between Ge and SiO₂ is much weaker than that of Ge and Si. At the growth temperature, the activation energy for Ge desorption is estimated to be 4.5 kJ/mol, indicating that the Ge-SiO₂ interaction can be described as a Van der Waals interaction.



(a) High-resolution scanning electron microscopy image of Ge islands on SiO₂ at different substrate temperatures. The Ge desorption rate is calculated from accurately calibrated Ge beam flux and experimentally measured amount of adsorbed Ge. (b) The plot of desorption rate vs. 1/T yields the activation energy (E_d) for Ge desorption. E_d is approximately 4.5 kJ/mol near growth temperatures.

[†] Two journal articles have been published in *Appl. Phys. Lett.*, and a patent prosecution is underway on this topic.

Our latest experimental evidence shows that the SiO_2 film thickness remains constant after a prolonged exposure to Ge molecular beam at growth temperatures. This observation is contrary to the conventional belief that the reaction between Ge and SiO_2 producing volatile SiO and GeO is responsible for the selective growth of Ge on Si rather than on SiO_2 .

In order to understand the selectivity quantitatively, we (1) calibrated the Ge beam flux against the effusion cell temperature, (2) estimated the rate of Ge adsorption based on the volume of Ge islands formed on SiO_2 (see Fig. (a)), and (3) calculated the rate of desorption by subtracting the rate of adsorption from the flux. For the initial stage of growth, we have thus determined the Ge desorption rate as a function of substrate temperature. The plot of desorption rate in natural log scale vs. inverse substrate temperature ($1/T_{\text{surface}}$) provides the desorption activation energy (E_d) of 4.5 kJ/mol in the temperature range of 600 to 800°C. E_d is about 40 times lower than any possible chemical bond energy in the Ge-Si-O system. The magnitude of E_d is consistent with a simple mode of charge-induced Van der Waals (VdW) force. Based on this preliminary observation, we conclude that the interaction between Ge adspecies and SiO_2 is of purely physical nature. We also speculate that this low desorption activation energy is responsible for the selective growth of Ge on Si rather than on SiO_2 .

Atomic Level Understanding of Ge Island Formation on SiGe Wetting Layer

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Understanding the selectivity mechanism on an atomic level requires knowledge of the main transport species on the growth surface and their surface activities. - It is our vision that this atomic-level understanding of selectivity will enable selective growth of other lattice-mismatched semiconductors on Si. - Using scanning tunneling microscopy (STM), we have discovered that adatom pairs, instead of ad-dimers, are the predominant species that exist on the growth surface characterized as SiGe wetting layer. Figure 1 on the right shows two different modes of STM operation: filled state [Fig. 1 (a)-(b)] where the substrate is negatively biased with respect to the STM tip and empty state [Fig. 1 (c)-(d)] where the substrate is positively biased with respect to the STM tip. These images ($100\text{\AA}\times 50\text{\AA}$) reveal that adatom pairs are invisible in filled state images, while showing up in empty state images. The images also show that the adatom pairs assume a chevron-like chain structure. We experimentally captured, by empty-state imaging, the transition of these adatom pairs, turning into a compact island (Fig. 2). These islands eventually lead to the formation of Ge “huts” and “domes,” often dubbed as quantum dots.

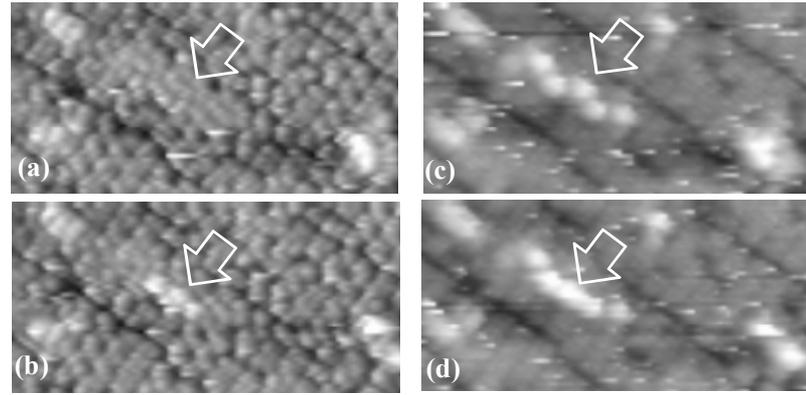


Fig. 1: (a)-(b) Filled state images of adatom pairs before and after forming a line structure. (c)-(d) Empty state images of adatom pairs before and after forming a line structure.

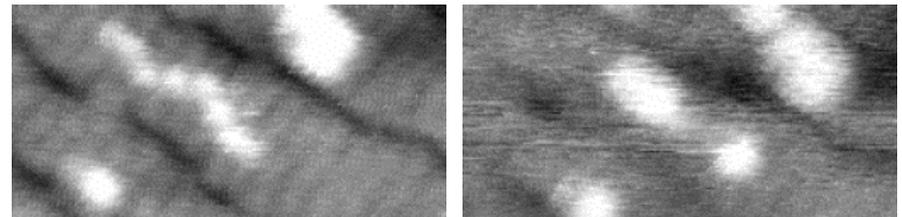


Fig. 2: Scanning tunneling microscopy images capture chevron-like Ge adatom pairs transforming into an island. Rather than Ge addimers or monomers, the adatom pairs appear to be the main precursor to form Ge islands on SiGe wetting layer. Our current approximation on the activation barrier of this transformation is approximately 1 eV.

The 1st step in establishing an atomic-level, mechanistic understanding of selectivity is to identify the main transport species on growth surfaces. We have recently identified that adatom pairs (or c-dimers) are likely the main transport species on 2x1 SiGe wetting layer, using scanning tunneling microscopy. These adatom pairs heavily populate the SiGe alloyed surface in contrast to the traditional addimers. Fig. 1 shows filled (Fig. 1(a)-(b)) and empty (Fig. 1(c)-(d)) state images of a typical SiGe wetting layer, on which a sub-monolayer of Ge adspecies are adsorbed. The adatom pairs generally appear in a chevron structure and only in empty state images. The white arrow in Fig. 1(a) points to a “ghost” image of adatom pairs, whereas the chevron structure is clearly shown in Fig. 1(c). The only exception is that when the pointed adatom pair migrates along the underlying dimer row at elevated temperatures (>100 °C) and forms a straight chain (Fig. 1(d)). Then, the electronic structure of the adatom pair appears to undergo a dramatic change, showing up in the filled state image (Fig. 1(b)).

With the main transport species identified, we have been characterizing their surface activities qualitatively and quantitatively on 2x1 SiGe wetting layer and on partially oxidized Si surface. In Fig. 2, two empty state images are seen (a) before and (b) after transition from the metastable chevron structure to the more traditional compact island. A series of temperature-dependent experiments are currently underway to quantitatively determine the activation energy for this event. Additional experimental goals for the near future are:

- Elucidate the chemical identity of adatom pairs (i.e., Si-Si, Ge-Ge, or Si-Ge) by recognizing possible asymmetry in their surface activities.

- Establish the population dependence of adatom pairs as a function of Ge-Si lattice strain and thus as a function of Ge concentration in the SiGe wetting layer.

- Observe the transition of adatom pairs to stable dilute dimer row islands as a function of surface temperature and measure the transition activation barrier using atom-tracking scanning tunneling microscopy (AT-STM).

- Extract the energetics of formation, dissolution, and diffusion of adatom pairs, using AT-STM.

- Observe the formation of adatom pairs at cryogenic temperatures.

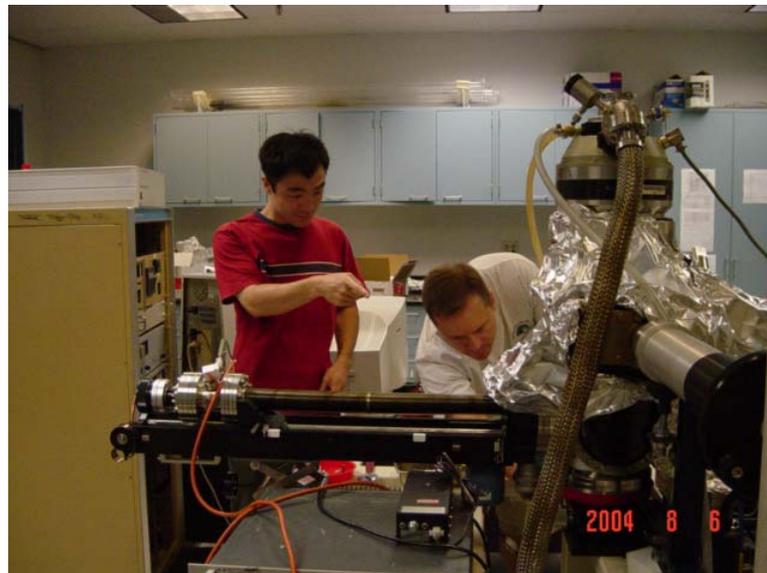
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Research Education:

The NSF support has provided for four graduate students (Qiming Li, Madhava Kosuri, Kyle J. Solis, and Henry Gerung) and three former undergraduate students (Angela Zivkovich, Kyle J. Solis, and Darin Leonhardt). Angela is currently pursuing a PhD in chemical engineering at UC Santa Barbara. She was one of the finalists of Rhodes Scholarship from New Mexico in 2003, and she received a 2004 NSF Graduate Fellowship. Kyle joined Prof. Han's research group in Fall 2003 to pursue a PhD in chemical engineering. In Summer 2004, Joshua Krauss from University of Wisconsin – Madison participated in Prof. Han's research through NSF Research Experience for Undergraduates (DMR-0354157). Josh's latest work under Qiming's supervision led to quantitative understanding of Ge selectivity on Si over SiO₂.

Outreach:



Prof. Han promotes undergraduate research. Joshua Krauss (right), an undergraduate student from University of Wisconsin - Madison, is learning the molecular beam epitaxy technique from a 4th year graduate student Qiming Li (left).