The Role of Temperature on Morphological Properties of Gallium Nanowires: A Kinetic Monte Carlo Study

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ABSTRACT

We have investigated the effects of temperature on surface morphology during deposition of Ga on Si(100) at room-temperature (RT) under Ultra-High Vacuum (UHV) conditions , using kinetic Monte Carlo (kMC) simulations. Specifically, we are interested on the impact of temperature on key quantifiable quantities such as the ratio of homogeneous to heterogeneously nucleated islands , R, as well as the mean island size. In this study, the relevant energetic and kinetic parameters were first calculated using Density Functional Theory (DFT) which were then used as input to the simulation model. Our simulations unequivocally show that as temperature increases the population of homogeneously nucleated islands grows at the expense of their heterogeneous counterparts. This suggests that the thermally driven increase in adatom surface mobility may have some asymmetric effect on the respective rates of homogeneous and heterogeneous nucleation. Interestingly, the observed shift in the balance between the two types of islands with increasing temperature were accompanied by a corresponding decrease in the mean island size. The latter observation is somewhat surprising *vis-a-vis* prediction from conventional mean-field nucleation theory that longer (or bigger) islands should dominate at higher temperatures as a result of more efficient surface equilibration.

*Keywords:*Density Functional Theory, Kinetic Monte Carlo, Self-assembly

INTRODUCTION

Since the early nineties, studies concerning the growth of novel nanostructures known as nanowires have evolved from a mere curiosity to a major scientific undertaking that we know of today. Arguably, the impetus to these pioneering studies was the wide availability and rapidly increasing resolution of scanning tunneling microscope (STM) and similar imaging instruments providing researchers a detailed glimpse of their structure and surface characteristics. On the theoretical front, parallel advances in computational techniques such as first-principles calculations, as well as more coarse-grained approaches such as kinetic Monte Carlo (kMC) simulations, made it possible to probe lingering questions that have long baffled experimentalists concerning these nanostructures.

One realization of nanowires is via room-temperature (RT) deposition under ultrahigh vacuum (UHV) conditions of select group III and group IV atoms on low-index Si surfaces, specifically the Si(100) and Si(111). Early STM studies (Itoh, *et al.,* 1993; Baski *et al*., 1991) reveal, among others, that the lateral dimension of these wires approaches one, i.e., they are in fact 1-D atomic wires. (In this study, the terms “nanowires”,

"atomic wires", "1-D wires", "1-D islands", or simply "islands" will be used interchangeably.) Additionally, an effective repulsion between two neighboring nanowires ensures that their minimum lateral separation is two lattice constants.

The interest on nanowires reflects the relentless drive to reach the limit of miniaturization in integrated circuits (IC), an important component in the rapidly expanding microelectronics industry. As a practical matter, manipulation of IC components built on top of Si-based substrates demands utmost precision and control, which in turn cannot be achieved without a good understanding of the underlying microscopic surface processes. It is in this regard that computer modeling techniques such as molecular dynamics or kMC simulations have become essential, as they have been successfully used to study systems as diverse as quantum dots to polymers (Kratzer, *et al.,* 2002; J. Huang, *et al.,* 2005).

In the present study, of interest are the 1-D islands formed by Ga atoms on Si(100) surface during deposition under UHV conditions. Specifically, these islands could be either homogeneously nucleated, such as the case when two diffusing Ga atoms meet, or heterogeneously nucleated, such as when these adatoms are pinned by defects and other impurities. It should be stressed that although defects on Si(100) typically include missing Si monomers, dimers, or even trimers, these types show little reactivity with diffusing adatoms (Albao, *et al.,* 2005; Albao, *et al.,* 2010). Instead, a distinct class of defects known as C-defects, believed to be trapped water molecules, have been known to pin these adatoms more effectively, acting as nucleation centers (Javorsky, *et al.*, 2008).

From a practical standpoint, heterogeneously nucleated islands are preferred over homogeneously nucleated ones because the former's nucleation centers can be predicted based on the knowledge of the defect distribution. Since these nanowires typically grow on one side of a defect, leaving the other side unreactive to diffusing adatoms (Kocan, *et al.,* 2008), one can in principle control not only the direction of growth, but also their mean island size.

In this work, "heterogeneous island" and "homogenous island" will be used interchangeably with "heterogeneously nucleated island" and "homogeneously nucleated island" for brevity.

METHODOLOGY

The Si(100) surface was modeled as a N × N square lattice of adsorption sites, with each site corresponds to the physical binding site situated between the trenches of Si dimer rows. Initially, the surface was seeded with C-defects, with the choice of the defect-density consistent with experimentally known values, i.e. 10^{-3} defect/site (Javorsky, *et al.*, 2008). Furthermore, the atomic wire's growth pattern follows the so-called parallel dimer model (Nogami, 1997) in which it grows along a direction orthogonal to that of the Si dimer rows. In the model, the growth direction was conveniently chosen to be the horizontal direction. Next, rate constants pertaining to the relevant microscopic processes were calculated using the Arrhenius relation, $h = \nu \exp(-E_{act}/k_BT)$, which is generally appropriate for thermally activated surface processes. In the above, Eact is the activation energy, ν is the prefactor, typically of the order of 10^{13} s^{-1} and ultimately related to the vibrational frequency for atoms or molecules trapped in potential wells, while T is the substrate temperature. Below we list the key elementary processes included in our growth model and deemed operative during the course of the initial adsorption and subsequent growth of the atomic wires: :

(1) **Adsorption.** Potential sites available for adsorption are selected randomly and tested for availability. Sites already occupied by a Ga adatom, as well as those laterally adjacent to an atomic wire or another adatom are excluded. In addition, such sites should not be labeled as defect sites. The rate of deposition is typically of the order 10-4 ML/s and reflects typical experimental flux rate.

(2) **Detachment.** Terminal datoms - atoms found at the end of an island and not chained to a defect- as well as newly deposited adatoms, can detach and reattach at end sites.

(3) **Adatom diffusion and nucleation.** An adatom diffuses freely on the surface until it (i) meets another adatom (homogeneous nucleation), (ii) hop onto a site adjacent to a defect (heterogeneous nucleation), and (iii) reaches a site next to a terminal adatom, in which case it gets incorporated into the existing island (aggregation). Both nucleation mechanisms described herein are reversible, that is, a newly formed island can decay, mimicking the inherent atomic wire instabilities as was observed (Albao, et al, 2010; Kocan, et al, 2007).

Having described the fundamental features of the simulation model, we now comment briefly on the Bortz-Kalos-Lebowitz (BKL) algorithm employed in the simulations (Bortz, 1975). Very briefly, in the BKL algorithm one compiles a comprehensive catalogue of all the microscopic elementary processes on the surface including a list of species capable of executing them. These lists are dynamic – they are updated every kMC step. Unlike the Metropolis algorithm where processes are executed with certain probability that depends on whether the impending move would bring the system closer to equilibrium or not, the BKL algorithm is inherently reject-free and is thus deemed more efficient. The latter algorithm ensures that at each iteration, the system advances in configurational space and thus no move is ever wasted.

Finally, we make a brief comment on the relatively narrow temperature range (300-500 K) in which such simulation data are collected. Prior experiments suggest that at temperatures higher than 500 K, 1-D islands may begin to coexist with 2-D islands (Adams, et al, 1997). As our model does not explicitly incorporate adsorbate lateral interactions, it is not our aim to simulate 2D-island growth. Thus, we confine this study to the temperature regime where the technologically interesting 1D-islands dominate.

RESULTS AND DISCUSSIONS

Figure 1 presents snapshots of typical surface morphologies of Ga/Si(100) system for all the three temperatures considered in this study. In addition, Table 1 shows the homogeneous to heterogeneous island ratio R for each temperature.

As can be seen in Figure 1, both homogeneous and heterogeneous islands are present on the surface at all temperatures. A more detailed analysis of the plots reveals that as the temperature rises, so does the number of homogeneous islands, while the number of heterogeneous islands remains roughly unchanged. This trend is evident in Table 1 where the homogeneous to heterogeneous island ratio, R, is provided for all three temperatures. It is worth noting that R significantly climbed from 0.76 at 300 K to 12.58 at 500 K, signifying that homogeneous nucleation is favored at higher temperatures. On hindsight, this observation does not seem surprising since heterogeneous nucleation rate is controlled by the number of C-defects which remains constant even as the temperature increases. We note however, that at the relatively low coverage of 0.1 ML (where 1 monolayer (ML) is defined as 1 Ga adatom per site) some of these C-defects remain unpaired with adatoms even at temperatures as high as 500 K, signifying that heterogeneous nucleation is somewhat inhibited. The source of the apparent suppression in heterogeneous nucleation becomes clear when one realizes that diffusion is confined mainly along the horizontal direction or parallel to the orientation of the islands. Also, it should be pointed out that C-defect density is extremely low, of the order of 10-4 defect/site, ensuring that heterogeneous nucleation is a rare event. In contrast, a similar suppression in homogeneous nucleation was not observed. Since the flux rate, and thus the adatom density, is independent of temperature it is reasonable to ask why there is a higher incidence of homogeneous nucleation at higher temperatures, causing R to jump 17-fold from its simulated value at 300 K to its final value at 500 K. In the simulations, we monitored incidence of collisions and observed that the frequency of such collisions increases in proportion with the number of islands. With this observation a clearer picture emerges. At higher temperatures, a surfeit in thermal energy translates into enhanced adatom mobility, therefore increasing the incidence of collisions and homogeneous nucleation. In contrast, C-defects, whose concentration provides the natural limit to the density of heterogeneous island and is very small to begin with, do not increase with temperature. Additionally, a highly anisotropic diffusion ensures that the incidence of adatoms being pinned by C-defects (leading to heterogeneous nucleation) is minimal even at higher temperatures.

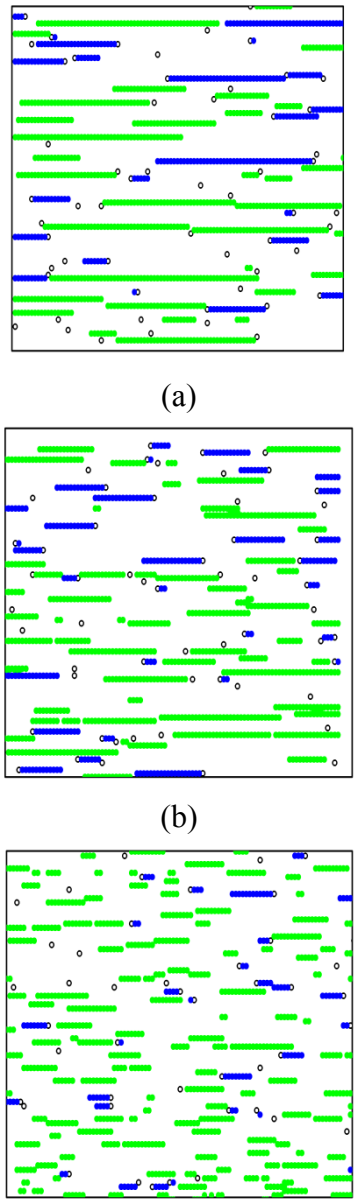

Figure 1. Simulated surface morphology of deposited Ga on Si(100) at (a) 300 K, (b) 400 K, and (c) 500 K temperature values. Green lines denote homogeneous islands while the blue ones indicate their heterogeneous counterparts. Unfilled black circles denote C-defects where heterogeneous nucleation starts. All lattices are 100x100 in size.

A quick look at Figure 2, on the other hand, conveys a slightly different picture. The plot reveals that aggregation, or growth, in general is suppressed in favor of nucleation, as signified by the marked decrease in mean island size with increasing temperature. In conventional homogeneous and heterogeneous systems, mean-field nucleation theory predicts exactly the opposite, i.e, islands tend to be longer at higher temperatures, indicative that aggregation becomes the dominant mechanism in that regime. It should be mentioned that similar anomalous behavior has been observed for Ga/Si(100) by Albao and co-workers (Albao, et. al., 2005) in a related study that does not explicitly take into account the presence of C-defects. In that kMC paper, the authors found a monotonically decreasing form for the scaled island size distribution rather than the expected monomodal shape. Extensive analysis revealed that, just like in the present study, restricted aggregation - the fact that growth was confined to two ends of the atomic wires - was responsible for the system's rather unconventional behavior. Thus we can only conclude that with or without C-defects (and heterogeneous nucleation) – scaled island size distribution on Ga/Si(100) is monotonically decreasing rather than monomodal in shape .

Table 1. Homogeneous to heterogeneous island ratio, R, for different temperatures.

Temperature (K)	*R*
300	0.76
400	2.71
500	12.58

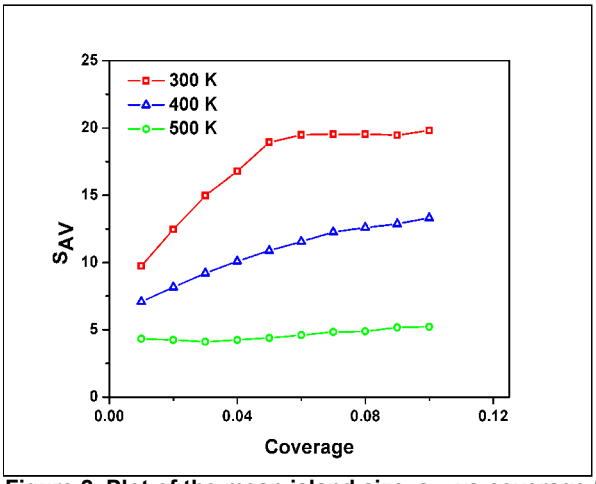

Figure 2. Plot of the mean island size, s_{AV} vs coverage for various temperatures.

CONCLUSION

It was shown in this work that temperature impacts the balance between homogeneous and heterogeneous islands. On the one hand, increased adatom mobility at higher temperatures translates into frequent adatom-adatom collisions, which in turn greatly boosts homogenous nucleation. On the

other hand, the corresponding increase in heterogeneous nucleation with increasing temperature was not observed due to the extremely low C-defect density which remains roughly constant throughout the narrow temperature (300 – 500 K). Furthermore, the highly anisotropic nature of adatom diffusion on Ga/Si(100) (i.e., along the direction parallel to the island's orientation) restricts contact between a C-defect and an adatom, a necessary step toward heterogeneous nucleation. In addition, contrary to prediction of nucleation theory for conventional homogeneous systems, the mean island size decreases with temperature, a result mirrored in previous studies where the effect of C-defect was not explicitly taken into account. Therefore, the present work confirms that the presence of C-defects has no impact on this unconventional trend.

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