Island Nucleation in a Reactive Two-Component System

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The flux and temperature dependence of titanium silicide islands formed by reactive deposition near 500 °C indicate a critical nucleus containing 2 Ti atoms and a single activation energy of $E_d + \frac{1}{2}E_2 = 1.4 \pm 0.2$ eV, where E_d and E_2 are the surface diffusion and cluster binding energies, respectively. These values are not consistent with STM observations of Ti dimer-vacancy hopping at lower temperatures and show that silicide island nucleation involves a different, highly mobile Ti species.

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The nucleation and growth of islands on surfaces has been studied for many years and is summarized in recent review articles [1,2]. In the case of adsorbed atoms moving on an inert substrate the process is well described by conventional nucleation theory (CNT) and is essentially determined by atomistic parameters for surface diffusion and binding energies of adatoms to clusters. Values for these parameters may be determined by comparing scaling predictions with suitable experimental measurements. These values may also be determined by direct observation of atomic motion using scanning tunneling microscopy (STM), at least at low temperatures [3–5]. It is questionable however whether such STM results extend to the higher temperature (and deposition rate) involved in practical growth processes. If there are multiple processes with different activation energies, as is often the case, a crossover behavior at higher temperature is expected as different processes become dominant [6]. Thus, direct observations at lower temperature can/should be combined in complementary fashion with scaling predictions and measurements at high temperature to obtain a complete understanding of island growth.

The primary motivation for the present study is to see whether the CNT can adequately describe a reactive two-component system. Reactive in this context means that cluster binding energies may be very large, and the substrate lattice may be disrupted by the reaction process. A second motivation is to extract atomistic kinetic parameters for a silicide-forming system. These parameters are virtually unknown even though surface kinetics plays a dominant role in these much-studied systems [7,8]. Silicide island structures, in particular, have received much attention recently since they can spontaneously form into nanoscale epitaxial dots or wires, which are important both for fundamental and applied reasons [9].

We have chosen the Ti/Si(100) system, largely because STM measurements of "hopping rates" at low temperature are available for comparison [5]. We find, surprisingly, that the nucleation behavior is well described by a CNT model with a single set of reasonable diffusion and cluster binding energies over the temperature range 400–700 °C. The island nucleation process is dominated by two Ti atoms, while further island growth involves Si thermal adatoms from nearby step edges. The energy parameters from the CNT model, however, do not agree with those determined from STM observations of Ti dimer-vacancy (Ti-DV) motion at lower temperatures [5]. We conclude that the silicide nucleation involves a different Ti species that is highly mobile.

Within CNT, the density of stable nuclei n_x for 2D island growth in the complete condensation regime is given by [1]

$$n_x = \eta \left(\frac{F}{D_0} \right)^{(i/i+2)} \exp\left(-\frac{E^*}{kT} \right), \qquad (1)$$

where η is a dimensionless number near unity, F is the deposition flux, D_0 is the surface diffusion prefactor, i is the number of atoms in the critical cluster, and $E^* = (iE_d + E_i)/(i + 2)$ is a weighted sum of diffusion activation energy E_d and cluster binding energy E_i. The diffusion prefactor may be written as $D_0 = (a^2 \nu_0)/4$ where a^2 is the unit cell area and ν_0 is an attempt frequency. One may further specify a sequence of cluster binding energies vs cluster size, as in rate equation models, or multiple binding energies at specific sites, as in Monte Carlo simulations. The linked energy parameters within E^* are experimentally accessible from the slope of $\log(n_x)$ vs $1/T$. The diffusion and binding energies may be separated if the critical cluster size is known. This can be obtained from the flux dependence at a fixed temperature, or from the $1/T = 0$ intercept of $\log(n_x)$ vs $1/T$ using an estimate for D_0.

Little is known about surface diffusion and cluster/step binding energies for silicide-forming systems (transitions metals on silicon) [10–12]. Indeed, even the atomic structure of related surface reconstructions remains largely unknown, with the notable exception of Co/Si(111) [13–17]. It is known that surface diffusion of the late transition metals Co, Ni is anomalous, since mass transport occurs via bulk Si interstitials rather than surface paths [18]. Ti, in contrast, has a low solubility in Si, and is thought to diffuse via a genuine surface mechanism. Indeed, Ishiyama *et al.* [5,19] report two Ti/Si(100) surface structures, a "pedestal site" and a "Ti dimer vacancy" (Ti-DV), as well as conversion and hopping rates for these structures. From observations in the range 280–360 °C, they reported Ti-DV diffusion with $E_d = 1.8 \pm 0.1$ eV and $\nu_0 = 10^{14\pm1}$ sec^{-1}. They also reported the disappearance of pedestal sites into some "mobile invisible" state with Arrhenius parameters $E = 1.6 \pm 0.2$ eV and $\nu_0 = 10^{14\pm2}$ sec^{-1}. They also reported the disappearance of pedestal sites into some "mobile invisible" state with Arrhenius parameters $E = 1.6 \pm 0.2$ eV and $\nu_0 = 10^{14\pm2}$ sec^{-1}. Formation of each Ti-DV is accompanies by the release of two Si adatoms, which collect as Si adlayers.

Titanium was deposited onto radiantly heated P-doped Si(100) wafers (0.02 ohm cm) by sublimation from a high purity wire source. Coverage was calibrated using a crystal thickness monitor with accuracy 20%. Temperature was determined from thermocouple measurements on an identical sample stage with accuracy ±50 °C.

In Fig. 1 we show island density vs Ti flux F on a double-log scale to show the power law dependence, $n_x \sim F^{i/i+2}$, and thereby allow determination of i. These data indicate a critical nucleus size in the range $i \sim (2–5)$. It is clearly larger than 1.

In Fig. 2 we show STM images to illustrate the temperature dependence of island growth. At 300 °C, numerous bright features appear and are attributed to adsorbate island structures. They are rather variable in size and shape, however, and difficult to count reliably. Vacancies also form and tend to order into chain structures. At 400 °C, distinct round islands 2–3 nm diameter form mostly on the terraces and occasionally at the step edges. There is no apparent preference for step edges nor depletion region surrounding the steps. The vacancy structures are numerous and better ordered than at 300 °C. At 500 °C, the islands are well formed 3×8 nm rectangles, and appear both on midterrace and at step edges. Terrace vacancies are relatively rare and isolated. Pure Si adlayers form around some of the islands as labeled in the figure. These layers show the expected orientation of dimer rows, which are perpendicular to the underlying terrace. The island structures are distinct from these adlayers. We presume these are titanium silicide islands. The stoichiometry is not known. At 700 °C, the islands are more rounded, even hemispherical, ~10 nm diameter.

The temperature dependence of island density is shown in Fig. 3, with a fit to Eq. (1), excluding the point at 300 °C where the island structures are indistinct and difficult to count. The fitted values are $\log(F/D_0)^{i/i+2} = -7.4 \pm 0.5$ and $E^* = 0.70 \pm 0.1$ eV. It is useful to note the erosion of step edges during silicide island growth, as illustrated in the figure inset. The B-type step edges (perpendicular to dimer rows on the terrace above) are eroded while the A-type remains fixed. The volume of silicon missing from the step edge is roughly equal to the volume of silicide islands, assuming a stoichiometry of $\mathrm{TiSi_2}$, although we have not attempted an accurate measurement of this type.

We first determine the critical cluster size i in order to separate the weighted energies in E^*. This is best done using the $1/T = 0$ intercept of the Arrhenius plot. This gives $\log \eta(F/D_0)^{i/i+2} = -7.4 \pm 0.5$. Using the known flux ($\sim 10^{-3}$ ML/sec), and nominal values $D_0 = a^2 10^{12}$/sec and $\eta = 1$, we find $i = 2.0 \pm 0.3$. This agrees with the value determined from the Ti flux scaling and is more precise. Using the value $i = 2$, we then have $E_d + \frac{1}{2}E_2 = 2E^* = 1.4 \pm 0.2$ eV, where E_2 is the binding energy of a two-atom cluster. Evidently, island nucleation in the Ti/Si(100) system follows the CNT scaling laws reasonably well with single values for E^* and i in the temperature range 400–700 °C. It remains to identify the physical meaning of E^* and i.

We note that there are two moving species, Ti and Si. Either or both may contribute to the critical nucleus, in

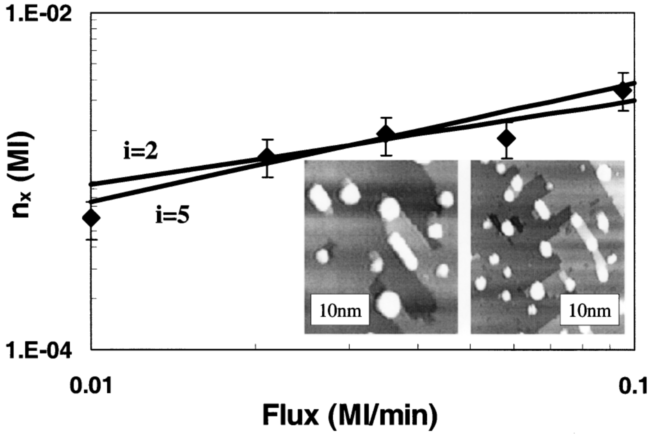

FIG. 1. Ti flux dependence of island density at 450 °C. Error bars are derived from multiple images with the same sample preparation. The lines indicate $i = 2$ and $i = 5$, which roughly bracket the data. Representative STM images (−1.5 V, 2 nA) at the highest and the lowest flux are shown as insets to the figure.

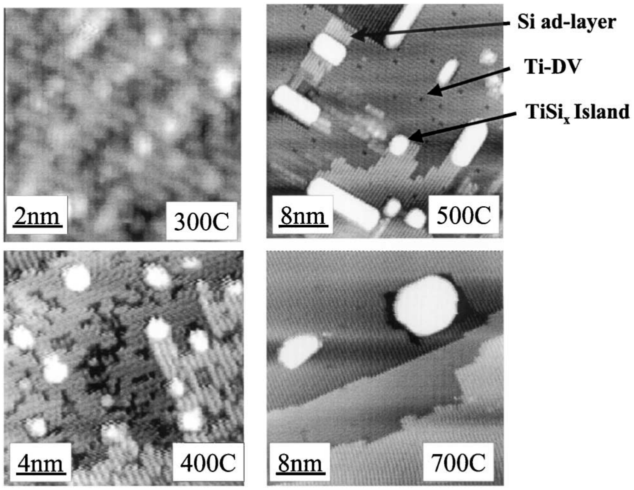

FIG. 2. STM images (−1.5 V, 2 nA) showing island structures at various temperatures, with nominal flux 0.03 Ml/min and coverage 0.1 Ml.

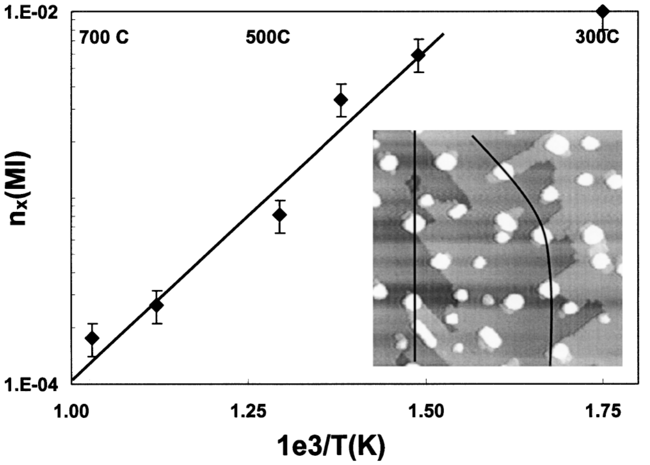

FIG. 3. Temperature dependence of stable island density, with nominal flux 0.1 Ml/min and coverage 0.1 Ml. Error bars are derived from multiple images with the same sample preparation. The line is a best fit to Eq. (1), excluding the point at 300 °C. Fit values are $\log \eta (F/D_0)^{i/i+2} = -7.4 \pm 0.5$ and $E^* = 0.70 \pm 0.05$ eV. Inset: STM image (−1.5 V, 2 nA, 100 nm^2) for growth at 450 °C. Black lines are drawn to indicate the original step position determined from the line of silicide islands that pin the step.

principle. We compare our values with relevant numbers from the literature, first for Si/Si(100) and then for Ti/Si(100). Low-energy electron microscopy observations of Ostwald ripening of Si islands on Si(100) at 700–1000 °C yield $(E_d + E_f) = 1.45 \pm 0.15$ eV [20] where E_f is the formation energy for Si dimers. STM observations of the edge detachment rate near 300 °C yield a similar value $(E_d + E_f) = 1.55 \pm 0.15$ eV [21]. Direct observations of the hopping rate along dimer rows near 200 °C yield $E_d = 1.09 \pm 0.05$ eV [22], and quenching experiments from $T > 800$ °C yield $E_f = 0.35 \pm 0.05$ eV [23]. These numbers are strikingly close to our values determined from silicide island nucleation, although we note that E_2 and E_f are not directly comparable since they refer to physically different processes. This might be taken as evidence that Si/Si motion dominates the silicide island nucleation process. Qualitative inspection of the STM images, however, shows that pure Si adlayers exist and are distinct from the silicide islands: they are clearly not related to the silicide nucleus. Furthermore, the silicide island density would not vary with Ti flux if Si alone formed the critical nucleus. *The agreement of kinetic parameters for silicide island nucleation with literature values for motion of Si/Si(100) is apparently a coincidence.* Silicon adatoms *are* required however to sustain the growth of the silicide following nucleation and most of this silicon apparently comes from nearby step edges. It is useful to note that the equilibrium population of Si adatoms released from step edges at 500 °C is $n_{\text{eq}} \sim 0.01$ Ml [23], and the diffusion equilibration time $\tau \sim L^2/D$ is approximately 1 sec for terraces of this length, using $E_d \sim 1.1$ eV for Si/Si(100) [24]. Thus the observed erosion of step edges during island growth is reasonable and results from the trapping of Si thermal adatoms by the silicide islands.

Considering now Ti motion, we note that the rate of surface diffusion of Ti-DVs obtained by direct STM observation [5] is clearly not consistent with our value for E^*. Indeed, putting the Ti-DV values into the CNT model yields a stable island density of 0.5 Ml at 300 °C, which is ~100× larger than the observed silicide island density. Furthermore, simple inspection of the STM images shows that the Ti-DVs are distinct from the silicide islands and are more numerous. It is clear that Ti-DVs do not contribute significantly to the nucleation of silicide islands.

What then comprises the critical nucleus for silicide islands? Our data show it contains two Ti atoms with energy parameters $E_d + \frac{1}{2}E_2 = 1.4 \pm 0.2$ eV. We believe that these atoms are the "fast migrating, invisible" Ti atoms hypothesized by Ishiyama *et al.* [5] as a link between the random disappearance and the reappearance far away of Ti pedestal atoms. The reported activation energy of 1.6 ± 0.2 eV for each of these processes implicitly contains diffusion, formation, and barrier energies, so is not directly comparable with our energy parameters. We cannot separate the weighted sum of diffusion and binding energies in E^*. We note, however, that the activation energy for interstitial diffusion of Ti through bulk Si (1.5 ± 0.1 eV) [25] is compatible with E^* if the two-atom cluster binding energy is small (<0.2 eV). The latter might be compared with the bulk solubility of Ti in Si (2.8 eV) [25], which corresponds to the cluster binding energy *per Ti atom* in the limit of large clusters. The critical nucleus binding energy is evidently much smaller than this.

A question remains as to the role of Si adatoms in the critical nucleus. This is not determined directly from our experiments. Si adatoms may participate directly in the nucleation stage, or they may simply be spectators that attach later as needed to sustain growth of the silicide. This might be tested directly by altering the flux of Si adatoms. In the case of reactive deposition, the Si flux comes from the step edges and is thermally activated. Roughly speaking, this temperature dependent flux would tend to flatten the Arrhenius plot for $n_x(1/T)$. A proper model for island nucleation during reactive deposition should include two distinct components with different fundamental energies and should explicitly include thermal activation of the substrate component. It would be useful to formally develop such a model. One can anticipate that a single component model might adequately describe a two-component system if only one component is rate limiting in the relevant range of growth parameters. This is apparently the case for the present system Ti/Si(100).

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