Attractive Migration and Coalescence: A Significant Process in the Coarsening of $TiSi_2$ Islands on the Si(111) Surface

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The dynamics and coarsening of $TiSi_2$ islands on Si(111) surfaces are studied in real time with photoelectron emission microscopy. A significant fraction of events are observed in which nearby islands move attractively toward each other and subsequently coalesce. It is proposed that attractive island migration is due to the growth-decay flow of the island edges driven by a nonuniform surface concentration around the islands. The local surface concentration is induced by the neighboring islands. This coarsening mechanism should significantly affect the evolution of the island distribution.

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The evolution and subsequent coarsening of island structures on a surface are of crucial importance for controlling the fabrication of novel nanometer-scale structures and for the fundamental understanding of thin film growth processes. In an evolving surface, initially nucleated islands grow through the interactions between the islands [1]. Particularly, in postdeposition conditions where no additional material is being deposited, Ostwald ripening (OR) is considered the primary coarsening mechanism for island growth [1,2]. In OR, immobile larger islands grow at the expense of smaller islands through atom exchange between the islands. The driving force for OR is the adatom concentration difference between islands of different size [2,3]. On the other hand, recent scanning tunneling microscopy studies of homoepitaxial metal islands on metal surfaces have shown another coarsening mechanism [4–6]. Large two-dimensional (2D) Ag islands on Ag(100) displayed unexpected diffusive mobility. Island diffusion and subsequent coalescence rather than OR could dominate island coarsening. Island diffusion has been attributed to either movement of individual atoms along the island's perimeter [4] or to the evaporation and condensation events of the repeated exchange of atoms with the 2D-gas phase on the surface [5,6]. The atomic motions at the edges cause the island's center of mass to move randomly along the surface allowing island collision and coalescence. In contrast, we have observed distinctive island migration and coalescence for $TiSi_2$ epitaxial islands on Si surfaces: the coalescence of islands was not due to random island motion but due to directed island migration toward each other.

In this Letter, we report experimental results of $TiSi_2$ solid-island diffusion and coalescence on Si(111) surfaces. Our studies involve *in situ* Ti deposition and annealing, and *real-time* photoelectron emission microscopy (PEEM) [7] measurements of the island dynamics at high temperatures [8]. The experiments were performed in an UV-PEEM system (Elmitech) with a base pressure $< 2 \times 10^{-10}$ Torr. This system allows heating of the substrates to $> 1200\,^{\circ}$C, and the chamber is equipped with a Ti-filament deposition source. The UV-light source of the PEEM is either the tunable spontaneous emission of a UV free electron laser (UV-FEL) [7] with a photon energy range of 4.0 to 6.0 eV or a 100 W Hg discharge lamp with an upper cutoff energy near 5.0 eV. Sections of Si(111) wafers (*n* type, *P* doped, resistivity 0.8–1.2 Ω cm, 9×9 mm^2) were employed as substrates. The wafers were cleaned by UV-ozone exposure followed by an HF based spin etch, and then by *in situ* annealing at 900 °C for 10 min. About two monolayers (ML) of Ti were deposited at a rate of 1 ML/min on clean Si surfaces at room temperature. In this study all images were stored digitally, and 16 successive images were integrated corresponding to an integrated signal of 16/30 sec.

Figure 1 shows a sequence of PEEM images of $TiSi_2$ islands on a Si(111) surface during annealing at 1150 °C. The $TiSi_2$ islands are identified as bright spots in the images while the exposed underlying Si surface appears as the darker regions. This PEEM image contrast originates from the photo-threshold difference between $TiSi_2$ ($\sim$4.6 eV) and Si($>$5.0 eV). The dark lines extending towards the upper left side of the images are primarily shadows due to the $<10^{\circ}$ angle of the incident UV-FEL light. The progression of images shows the evolution process of the islands. In (a)–(c), two sets of nearby islands of similar diameter ($\sim$400 nm) migrate toward each other, collide, and subsequently coalesce into larger islands. In (d)–(f), the two coalesced islands move attractively again and then coalesce.

The attractive migration and coalescence of $TiSi_2$ islands is obviously distinguished from ripening and random migration and coalescence of islands. In addition to attractive migration, we have also observed the disappearance of islands without a collision. This process was attributed to OR. To explore the overall coarsening mechanism of the $TiSi_2$ islands, we analyzed the detailed behavior of the individual islands in an ensemble of

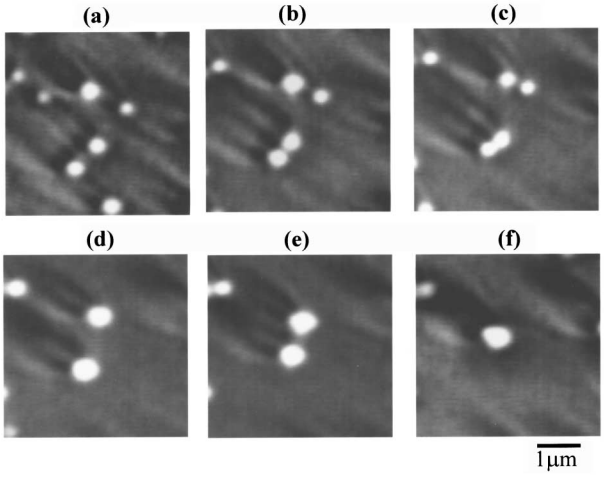

FIG. 1. PEEM images of 2 ML Ti deposition on Si(111) followed by annealing at 1150 °C. The images were obtained at the annealing temperature for (a) 10 min, (b) 14 min, (c) 17 min, (d) 21 min, (e) 23 min, and (f) 25 min, respectively. The incident light was the spontaneous emission of FEL with a photon energy of 4.9 eV.

islands. We examined the evolution of 97 islands for 10 min in PEEM images observed in a 20 μm field of view. We found that the size and surface density of the islands evolved by both ripening and the attractive migration and coalescence process. The initial average island diameter was 270 nm and after 10 min it had increased to 340 nm. Of the 37 islands that disappeared, 22 islands disappeared by ripening while 15 disappeared by attractive migration and coalescence. During ripening, the size of the neighbor islands increased or sometimes remained constant. Although the ripening was the more dominant coarsening process for our conditions, both coarsening processes contribute to the growth of larger islands.

In addition, we measured the separation distance between the islands to explore the correlation of the coarsening events to the spatial configuration of the islands. Attractive island coalescence occurred for pairs of islands with separation distances of less than $\sim 4.5r$(the separation distance was normalized by the island radius, $r_1 + r_2 = \sim 2r$).

Consider the following possible mechanisms for the attractive migration and coalescence of the $TiSi_2$ islands: First, surface migration of the islands can take place due to microscopic atom motion or due to the collective motion driven by external forces. At an atomic level the random motion of the atoms around the periphery of the island causes a random shift of island's center of mass, which may lead to diffusive motion of the islands [4]. Also, if atoms at one side of the island are more rapidly released to the surface in concert with increased condensation of atoms on the other side, the island can exhibit diffusive motion [5,6]. However, unless the atomic motion is affected by external conditions, both of these mechanisms would exhibit random island motion which would not apply for the attractive motion observed in our experiments. Second, consider the motion induced by a strain field. We note that $TiSi_2$ islands may be epitaxial with the Si substrate [9–13]. There is a lattice mismatch between the islands and the substrate, which leads to a strain field. It was suggested that this strain interaction could lead to a repulsive interaction between islands [14]. In contrast, we have only observed an attraction interaction between islands. Third, a model suggested by Voorhees and Schaefer can account for attractive island motion of 2D islands on a surface in a ripening system [15]. The numerical simulation has shown that the interisland diffusive interactions can induce significant motion of the center of mass of the islands. The origin of this motion is the shift of the center of mass that results from the growth of a larger island at the expense of a smaller island. According to the model, attractive migration can only occur for two nearby islands of different size. However, eventually the smaller island disappears without collision with the larger island. Thus, this diffusive interaction could explain the island migration but does not describe the specific island coalescence process observed in our experiment.

To explain the attractive migration and coalescence of $TiSi_2$ islands, it is necessary to consider an additional process aside from the diffusive interaction between the islands. We consider a model suggested by Tanaka to explain the attractive motions of droplets in a fluid mixture [16]. For a pair of neighboring droplets, the overlap of the concentration fields around the droplets would induce an attractive hydrodynamic force between the droplets [16,17]. This force would lead to the direct attractive motion and collision of the droplets.

Instead of the hydrodynamic forces, we propose that the mechanism responsible for attractive island migration of *solid* $TiSi_2$ islands is the growth-decay flow of the island edges due to a nonuniform concentration of drifting adatoms around the island. At high temperatures Ti atoms are emitted from the island edges and undergo surface diffusion [1]. The Ti arriving at the islands can react with surface silicon around islands [13] or Si supplied through the Si-silicide interface. A dynamic equilibrium will be established between the islands and the diffusing surface atoms, and the net flux of atoms diffusing at the edges of an island will depend on the environment of the island.

For simplicity we consider a hemisphere island of radius r on the surface. The equilibrium adatom concentration C_r of an island of radius r is given by the Gibbs-Thomson relation [18].

$$C_r = C_\infty \exp(2\gamma\Omega/rkT), \tag{1}$$

where k is the Boltzmann constant, T the absolute temperature, C_∞ the equilibrium adatom concentration

around a planar edge (i.e., $r \rightarrow \infty$), γ the surface energy per unit area of the island, and Ω the atomic volume. The atomic concentration within an island is expected to be constant. In the diffusion limited case, the island can release adatoms to or receive adatoms from the surface (in the environment of the island). At finite temperature, the adatom flux, J_r at the island edges can be determined by $J_r = -D\nabla C(r)$, and the total flux J is obtained by integrating around the island edge, so that

$$J = -2\pi r D \nabla C = \alpha D(C_r - C_o), \tag{2}$$

where α is a constant, D is the diffusion constant for the adatoms, and C_o is the equilibrium adatom concentration of the surrounding boundary far from the island. The driving force for adatom transport is the concentration difference between the island and the surrounding boundary [3]. Thus, for a given island of radius r, the island edges can grow or shrink depending on C_o.

Now consider two islands isolated from all other islands [Fig. 2(a)]. To reduce the possibility of direct ripening between the islands, we assume that both islands have equal size. If the separation distance between the islands, l, is too distant to interact with each other ($l > 4.5r$), each island will grow or shrink depending on C_o. However, if the separation distance is reduced ($l < 4.5r$), the adatom concentration profile will vary around the edges of each island [16]. We assume that C_o is lower than C_r, and we develop a picture similar to that described by McLean [19], except that emission and attachment energies are ignored. The adatom concentration of the area between the islands (C_r^{in}) will be enhanced over C_r of an isolated island because the diffusion fluxes of the two islands overlap more strongly at this region than at the other regions [16,17]. As a result, a nonuniform concentration develops around each island, and the inner facing edges have a higher probability of capturing adatoms evaporated from each island than the outer facing edges. For conditions near equilibrium, the islands will release adatoms to the surface from the outer facing edges at a rate given by (C_r^{out}-C_o) while the inner facing edges will grow at a rate given by (C_r^{in}–C_r). In other words, the facing edges of the islands grow through the absorption of Ti flux between the islands while the outer boundaries shrink via Ti out-diffusion. The spontaneous growth-decay flow of the island edges leads to movement of the island's center of mass towards each other and subsequent coalescence.

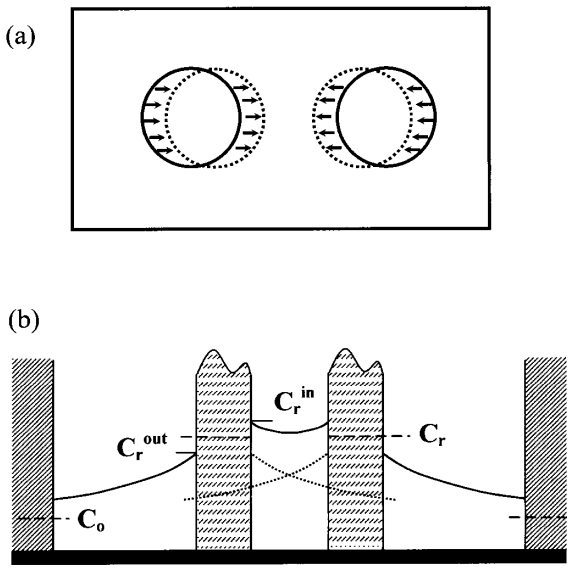

FIG. 2. (a) Schematic top view of attractive migration and coalescence of two islands. The arrows indicate the direction of growth or decay flow of the island edges. (b) Concentration profile of the islands and surrounding. The concentration C_o of the outer boundary far from the two islands (> two times separation distance) is assumed to be lower than C_r of the islands. The magnitude of the concentration is $C_r^{\text{in}} > C_r > C_r^{\text{out}} > C_o$.

According to our model, the local growth and decay of the edges should cause a shape distortion of the coalescing islands [15,16], since the curvature along the island edges is strongly related to the adatom concentration through the Gibbs-Thomson Eq. (1). The growing edges should develop higher curvature (sharper) due to a dynamic equilibrium with a higher concentration of adatoms while the decaying edges will develop lower curvature (flatter) due to a lower concentration. As shown in Fig. 3, the facing edges of the two moving islands do exhibit an increased curvature. Physically, the adatom in- and out-diffusion over the total edge length of each island determines the island growth (or decay) rate. To maintain the shape and size during migration, the decay rate of the outer edges of the island must be nearly balanced by the growth rate of the facing edge. This appears to be the case for our system.

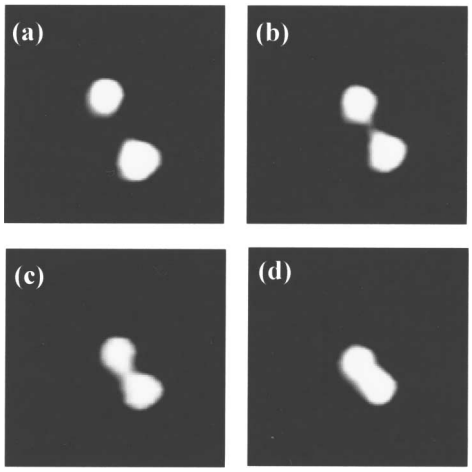

FIG. 3. A pair of islands move attractively. These images were obtained at 1150 °C for (a) 0 min, (b) 4 min, (c) 6 min, and (d) 8 min, respectively. Images are 2 μm × 2 μm.

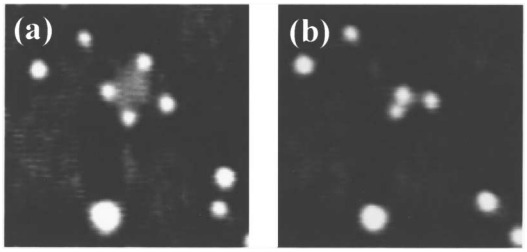

FIG. 4. A group of four islands moves toward the center of mass and coalesces. The bright emission from the inside area of the group indicates a higher concentration of Ti adatoms. These images were obtained at 1150 °C for (a) 15 min, and (b) 20 min, respectively. One island of the group of three in (b) is the result of coalescence during motion. Image = $4 \times 4\ \mu m^2$.

In some cases that are not obscured by the shadowing artifacts, there is direct experimental evidence that a nonuniform concentration around the island leads to the attractive coalescence. Figure 4 displays the dynamics of a group of islands. As time progresses, each island migrates toward the center of mass of the group and eventually coalesces into a larger island. In the PEEM images (Fig. 4), it is evident that the emission intensity from the substrate region surrounded by the group of islands is brighter than the outer region of the group. The brighter intensity from the region may reflect a higher concentration of Ti adatoms than the outer regions.

The nonuniform concentration around the island edges led to island migration toward the region of higher concentration. In contrast, a uniform concentration of adatoms around the islands would prohibit the attractive migration and coalescence. To explore this possibility, we monitored the behavior of pairs of islands while the surface was exposed to a continuous, low flux of Ti with the surface at 1150 °C. In this case island diffusion and coalescence was not observed. Instead, each island grew slightly larger and remained circular and in the same relative position to other islands. Thus, we suggest that the continuous deposition enhances the adatom concentration on the surface such that the island interactions are screened.

In summary, we have used real time PEEM to observe the surface dynamics of $TiSi_2$ islands on Si at high temperature. By monitoring the relative position of individual islands, we found that islands grew through both Ostwald ripening and attractive migration and coalescence. We proposed that the attractive migration of the islands is the growth-decay flow of the island edges due to the nonuniform concentration around the islands. In the late stage ripening observed here, both effects contributed to the coarsening with nearly equal weight. The attractive island migration and coalescence growth is a new and different pathway for island coarsening.

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