Direct Identification of Critical Clusters in Chemical Vapor Deposition

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The kinetics of heteroepitaxial island nucleation on the Si(111) surface during ultrahigh vacuum chemical vapor deposition with the precursor GeH_4 was studied by scanning tunneling microscopy. The results can be described within the framework of rate-equation based nucleation theory, modified by an additional energetic barrier for the attachment of adatoms at steps. This barrier results from the passivation of steps by dissociation products from the GeH_4 precursor. A critical nucleus size of 9 atoms is derived. Scanning tunneling microscopy images provide direct evidence for the existence of stable clusters consisting of 10 atoms and allow the unequivocal identification of their structure.

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The nucleation of islands is one of the fundamental processes in epitaxial layer formation, and precise knowledge of the processes that take place at the initial stages is essential in controlling the growth of thin films. Considerable progress has been made in understanding nucleation processes on surfaces under conditions usually found for molecular beam epitaxy (MBE) [1–3]. Growth of ultrathin layers is, however, often carried out from a molecular precursor, via chemical vapor deposition (CVD). Under these conditions the understanding of island nucleation at the atomic level is much more complicated and, in particular, hampered by the presence of coadsorbates (e.g., hydrogenated species) during the growth process, which may affect surface diffusion, island nucleation, and further island growth [4–8].

We have chosen the deposition of Ge on Si(111) from the precursor GeH_4 as an example here. Since Ge can be deposited via MBE or CVD, this system is ideally suited to compare the nucleation characteristics of layers grown via the two methods. Here we address the nucleation behavior of this CVD system, using the concept of a critical cluster for theoretical description. This concept, and the minimum size of a stable island obtained by attachment of one more atom to the critical cluster, is widely accepted for the description of kinetically controlled epitaxial growth processes [1]. The critical cluster size i^* is defined in such a way as that clusters consisting of more than i^* atoms are stable. Clusters with i^* or less atoms, which are formed, e.g., by density fluctuations, either dissociate or become stable islands by further incorporation of atoms. It is important to note, however, that except for the simplest case of $i^* = 1$, critical clusters and the resulting smallest stable islands have never been observed directly. Here we present an analysis of the island density in a complex CVD system, based upon extended rate equations theory [5], from which we obtain the critical island size ($i^* = 9$) and prove this result by direct observation of the smallest islands, consisting of $i^* + 1$ atoms, by high resolution scanning tunneling microscopy.

Data on the density of epitaxial islands nucleated under well-defined conditions can be evaluated within the framework of classical nucleation theory, based on rate equations as introduced by Venables and co-workers [1,9,10]. Prerequisites for the validity of that model, at least in its original version, are complete condensation of monomers, isotropic diffusion, and formation of two-dimensional islands without Ostwald ripening or coalescence. According to that model, the saturation density of homogeneously nucleated islands N_S is given by $N_S \propto R_g^{i^*/(i^*+2)} = R_g^{\eta}$ and $N_S \propto e^{\beta(E^*+i^*E_d)/(i^*+2)}$, where $\beta = 1/k_BT$, k_B is the Boltzmann constant, T is the surface temperature, and i^* is the critical cluster size. E^* represents the difference in free energy between the critical cluster and its individual adatoms. E_d is the diffusion barrier for monomers on the surface. From the former of these two relations, the critical cluster size i^* can be obtained by measuring N_S as a function of the growth rate, at constant surface temperature. From the latter relation the term $(E^* + i^*E_d)$ can be determined by measuring N_S at constant growth rate as a function of T. With the knowledge of i^* now either E^* or E_d can be calculated if the other of these two energies is known.

Using this model a value between 5 and 7 was determined for the critical cluster size i^* for Si homoepitaxy on Si(111)-(7 × 7) under MBE conditions at 680–770 K and deposition rates between 0.005 and 1.25 bilayers min^{-1} [4,11]. A critical cluster consisting of 6 adatoms was proposed, which contains three additional Si-Si bonds compared to 6 isolated adatoms. In this case E^* has a value of 5.1 eV (1.7 eV per Si-Si bond [12]). Furthermore, from measuring N_S as a function of T, an energy barrier of 0.75 eV was determined for the diffusion of Si adatoms on that surface [13,14].

However, it was not possible to properly interpret analogous measurements of the island density for Si nucleation on Si(111) grown under CVD conditions from the precursors Si_2H_6 [4] or SiH_4 [6] within the framework of classical nucleation theory. In those studies $N_S \propto R_g^{2.9}$ and $N_S \propto R_g^{1.25}$ were obtained for silane and disilane, respectively. The exponents 2.9 and 1.25 cannot be explained within the simple nucleation theory, where the exponent $\eta = i^*/(i^* + 2)$ has physically meaningful values only between

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$1/3 \leq \eta \leq 1$ ($1 \leq i^* \leq \infty$). It has been argued that the effective diffusion barrier E_d, the cluster formation energy E^*, or the size i^* of the critical cluster may depend on the steady-state hydrogen coverage, which in turn depends on the surface temperature and the pressure of the gaseous precursor, which determines the growth rate in the high temperature regime [4,6].

Another modification of the standard rate-equation description, which explicitly takes into account the presence of coadsorbates [5], introduces an additional barrier E_B for the incorporation of diffusing adatoms into existing islands. There are indeed several experimental evidences for the existence of such a barrier when H and/or Cl atoms are present as coadsorbates [15,16].

In the limit of fast adatom diffusion on the terraces and slow attachment to the island edges, that model [5] yields the following expression for the island density N_S: $N_S \propto e^{2\beta[E^*+i^*(E_d+E_B)]/(i^*+3)} R_g^{2i^*/(i^*+3)}$. Under these conditions, the exponent η is defined as $\eta = 2i^*/(i^* + 3)$, and the relation above now yields physically reasonable values for i^* for $1/2 \leq \eta \leq 2$. A value of $\eta = 1.25$, which was obtained earlier for CVD homoepitaxy of Si on Si(111) from the precursor Si_2H_6 for pressures between 7×10^{-6} and 1×10^{-4} mbar and temperatures between 770 and 810 K [4], hence indicates a critical cluster size of $i^* = 5$, which is virtually the same as for MBE growth evaluated by classical nucleation theory. These previous studies, however, have one point in common: The critical clusters and the smallest stable islands, respectively, have never been observed directly in such systems. In the present study we succeeded not only to derive the critical cluster size i^* for Ge deposition on Si(111)-(7×7) on the basis of Kandel's modified nucleation theory, but also to directly identify the critical cluster by high resolution STM images and this way to connect theory and experiment.

The experiments were performed in an ultrahigh vacuum (UHV) system equipped with a home-built STM, x-ray photoelectron spectroscopy (XPS), and facilities for annealing the sample [17]. The STM images were acquired at room temperature (300 K) in the constant current mode using tungsten tips. The samples were cut from p-doped Si(111) wafers with a resistivity between 1 and 20 Ω cm and cleaned using standard procedures [17]. GeH_4 had a purity of 99.999%. The tunnel voltage U_T is always the voltage applied at the sample with respect to the tip. The coverages and growth rates were directly determined from the STM images by measuring the area of the grown islands.

To investigate the nucleation behavior of heteroepitaxial Ge islands on Si(111)-(7×7) under CVD conditions we measured the density N_S of homogeneously nucleated islands, i.e., on large terraces away from steps, as a function of the precursor pressure and the surface temperature. We will first discuss the nucleation characteristics at a constant temperature for GeH_4 pressures between 3.5×10^{-6} and 3.5×10^{-5} mbar. For these experiments we have chosen a temperature of 730 K, which is high enough to prevent complete passivation of the surface by hydrogen released by dissociation of GeH_4 under our experimental conditions [18]. A temperature of 730 K is also low enough to yield a sufficiently large number of homogeneously nucleated islands. The resulting STM images obtained after deposition of 0.2 bilayers (BL) of Ge under these conditions are shown in Fig. 1. Most of the islands are triangular with their tips pointing towards the $[11\bar{2}]$ directions of the substrate. This indicates that the islands have largely grown without stacking fault with respect to the substrate. Only few islands are found, which are rotated by 60° with respect to the majority of the islands and which have grown with a stacking fault; examples are encircled in Figs. 1(b) and 1(c). The formation of epitaxial islands on Si(111) during CVD has been reported and discussed in the literature earlier [17]. The density of homogeneously nucleated islands was determined by counting at least 100 islands far away from steps or domain boundaries of the substrate for each precursor pressure.

A plot shows that the logarithm of the island density depends linearly on the logarithm of the growth rate (Fig. 2), i.e., the island density depends on the growth rate via a power law. For the slope of the line and hence the exponent in the power law we obtain $\eta = 1.51$, which is above the range of physical meaningful values for η within standard nucleation theory.

Applying Kandel's ansatz of a modified rate-equation description, which accounts for coadsorbed species by introducing an additional barrier E_B for the condensation of adatoms at steps of stable islands, leads to a modified expression for the island density N_S, where the exponent η is

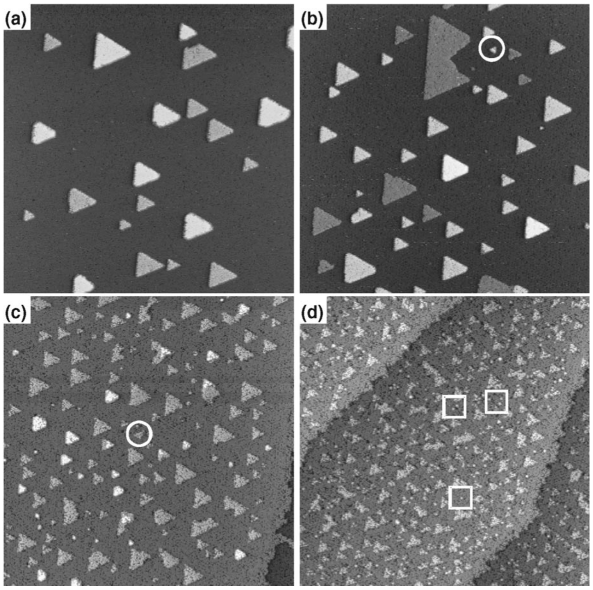

FIG. 1. Island densities after deposition of 0.2 BL Ge from GeH_4 on Si(111)-(7×7) at 730 K for GeH_4 partial pressures of (a) 3.5×10^{-6} mbar, (b) 5×10^{-6} mbar, (c) 1.5×10^{-5} mbar, and (d) 3.5×10^{-5} mbar. Tunnel voltage $U_T = +2.0$ V. Image sizes 250 nm × 250 nm.

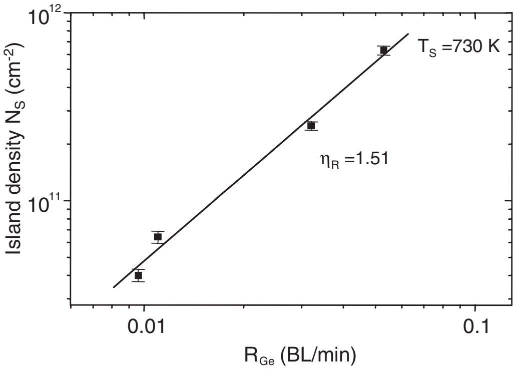

FIG. 2. Island density as a function of the growth rate in Ge deposition from GeH_4 at a growth temperature of 730 K and for a Ge coverage of 0.2 BL. The line is a linear fit and points towards $\eta = 1.51$.

now given by $\eta = 2i^*/(i^* + 3)$ [5]. The experimental value of $\eta = 1.51$ results in a critical cluster size of 9 atoms. Hence, islands consisting of at least 10 atoms should be stable. This value is identical to that obtained for MBE growth of Ge on Si(111) [19]. For Si a critical cluster size of 5–7 atoms was obtained, which is reasonable because the Ge-Ge binding energy is smaller than that for Si-Si, which may lead to a larger minimum stable cluster size for Ge. In addition, the lattice mismatch between Si and Ge, which leads to pronounced effects in later growth stages [20], will increase the total energy of the clusters so that more bonds may be necessary for stabilization, again tending towards a rather large minimum stable cluster size.

We can construct a straightforward model for the critical cluster for Ge-CVD on Si(111) [Fig. 3(a)]. For this model we assume that the (7×7) reconstruction of clean Si(111) is released and transforms into a (1×1) structure, as observed for growth of larger next-layer islands, which is schematically shown in Fig. 3. The cluster consists of two layers. The Ge atoms of the first layer (atoms 1–6) are located in threefold hollow (T_4) sites of the Si substrate. On top of the first Ge layer there are three more Ge atoms on T_4 sites (atoms 7–9). This is the critical cluster with $i^* = 9$. Adding one more Ge atom (atom 10) at the top center of this clusters, and bonding it to atoms 7, 8, and 9, additionally stabilizes this cluster. Apparently, it is sufficiently stable to survive the time until attachment of the next Si adatom without decomposition and this way becomes a stable island.

A closer look at the STM images indeed reveals the presence of specific clusters on the surface besides the common triangular islands. Some of them are marked by squares in Fig. 1(d). To characterize these small clusters in more detail, additional experiments were made under conditions which maximize the number of these islands. Exposing the clean surface to 3940 L GeH_4 at 670 K, followed by additional annealing at the same temperature for 10 minutes, yields a large number of these clusters [Fig. 3(b)], which are now the most frequent surface species and have a height between 2.5 and 3.5 Å. Epitaxial triangular islands with additional adatoms on top (white dots) are also present [17], and two of them are outlined by triangles. The inset in Fig. 3(b) resolves one of the clusters in detail. These clusters have a single maximum at the center, surrounded by three more maxima, which have a lower height than the central maximum. These secondary maxima form the tips of an equilateral triangle which point towards $[11\bar{2}]$ directions, the same directions as the two marked triangular islands.

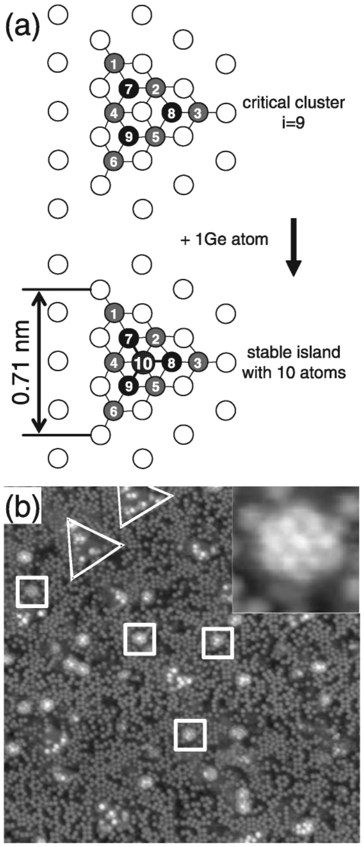

FIG. 3. (a) Model for the transition of the critical cluster ($i^* = 9$) to the smallest stable island. (b) Si(111)-(7×7) surface after exposure to 3940 L GeH_4 at 670 K, followed by tempering at the same temperature for 10 min. Image size 60 nm × 60 nm, $U_T = +1.0$ V. Some of the clusters discussed in the text are marked with squares. The inset (1.9 nm × 1.9 nm) shows a cluster in detail.

The clusters correspond exactly to the model for the smallest stable clusters (10 atoms), respectively, [Fig. 3(a)]. The triangular arrangement of the secondary maxima corresponds to atoms 7, 8, and 9 of the model. The central maximum is atom number 10, which converts the critical nucleus with $i^* = 9$ atoms to the smallest stable island with $i^* + 1 = 10$ atoms. Hence, we have indeed identified the critical cluster in this heteroepitaxial CVD system.

To determine the additional energy barrier E_B that has to be overcome during the attachment of adatoms to island edges, we measured the island density at a coverage of 0.2 BL Ge as a function of the deposition temperature at a

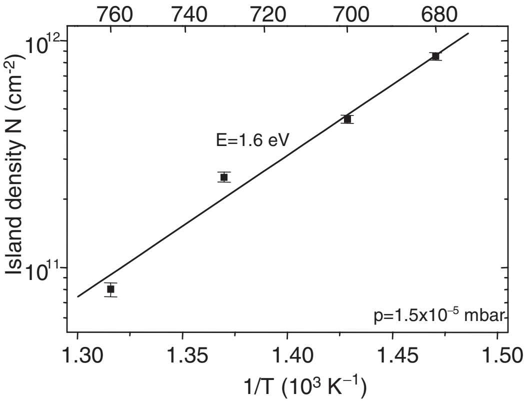

FIG. 4. Island density as a function of the growth temperature in Ge deposition from GeH_4 at a partial pressure of 1.5×10^{-5} mbar. The slope of the resulting linear fit yields an activation energy of $E_{\mathrm{eff}} = 1.6$ eV.

GeH_4 pressure of 1.5×10^{-5} mbar and temperatures between 680 and 760 K. The results are displayed in Fig. 4 in an Arrhenius plot of the (logarithmic) island density vs the inverse temperature. The data can be fitted with a straight line, from its slope we calculate an effective energy barrier of $E_{\mathrm{eff}} = 1.6 \pm 0.1$ eV. Following Kandel's modified theory of island nucleation, the additional barrier for adatom attachment, E^*, is related to E_{eff} by $E_{\mathrm{eff}} = 2[E^* + i^*(E_d + E_B)]/(i^* + 3)$.

The energy gain E^*, which results from the agglomeration of individual Ge adatoms in the critical cluster, can be estimated from literature data. Arranging atoms 1–6 first according to our model [Fig. 3(a)] does not contribute significantly to E^*, since new bonds are not created as compared to six individual atoms. However, new bonds are introduced by adding atoms 7–9 to the first layer of the cluster. These atoms contribute to E^* by their bonds with atoms 1–6. Hence, E^* is given by the energy necessary to remove the three atoms 7–9 from the cluster. Earlier measurements [21–23] showed that the energy barrier for removing one Ge atom from an island is around 1.0 eV. Hence, from the relation given above for E_{eff} and $i^* = 1$ a value of 0.73 eV can be calculated for $(E_d + E_B)$. The barrier for diffusion of a Ge adatom on Si(111), E_d, has been determined earlier as $E_d = 0.59$ eV [24]. With these data we obtain a value of (0.14 ± 0.06) eV for the additional barrier E_B.

This value for E_B appears to be rather small. One must keep in mind, however, that the diffusion barrier of 0.59 eV was determined for Ge atoms on Si. Under CVD conditions, i.e., in the presence of adsorbed hydrogen and with GeH_x as the diffusing species, the diffusion barrier is probably different. GeH_x species are likely to have a lower diffusion barrier on Si than Ge atoms, as suggested earlier [25]. A lower value for E_D would increase the barrier for adatom attachment correspondingly. Therefore, the value of $E_B = 0.14$ eV has to be considered as a lower limit.

The kinetics of island nucleation under CVD conditions have been studied for Ge deposition on Si(111)-(7 × 7) from the precursor GeH_4. The data can be understood within the framework of a nucleation theory which specifically takes into account an additional barrier for adatom attachment to steps, which is the result of step passivation by coadsorbates. The resulting critical cluster size derived for this system under present deposition conditions is 9. The smallest stable clusters have been directly observed in the experiment: their size of 10 atoms is in perfect agreement with the results obtained from the growth kinetics.

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