Growth mechanism and clustering phenomena: The Ge-on-Si system

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The clustering behavior of Ge thin films deposited on Si has been investigated by ion scattering and electron microscopy. Post-deposit-annealed Ge is shown to cluster according to an Ostwald ripening mechanism. The cluster-volume growth is linear in time, and the cluster-size distribution is in agreement with the theoretical prediction. Cluster formation during low deposition rates is also studied. This permits an estimate of the limit for the application of the Ostwald-ripening approach to the nonzero deposition-rate regime.

INTRODUCTION

The growth of heterostructures and epitaxial superlattices is motivated by new device configurations and "band-gap engineering." Within the Si-Ge-Sn family, pseudomorphic epitaxy must be highly strained due to the large lattice-constant mismatch among the constituents.[1] A limitation for the formation of all strained-layer superlattices is clustering occurring above a critical thickness of the overlayer.

In this paper we focus on the dynamics of clustering in the Ge/Si system, including a comparison between "post-deposition" and "during-deposition" growth. We show that the late stage of clustering is well described by a ripening mechanism which predicts the time dependence of the growth rate and the cluster size distribution.

EXPERIMENT

Samples were prepared in an ultrahigh vacuum system containing Si and Ge sources and equipped with standard surface analytical tools including a Van de Graaff accelerator for ion scattering analysis.[2] Measurements were carried out on sputter-annealed Si(111) and Si(100) substrates. Starting surfaces were atomically clean, as indicated by Auger spectroscopy, and displayed sharp Si(111)-7×7 and Si(100)-2×1 low-energy-electron-diffraction (LEED) patterns. Ge deposition was carried out at rates of 1×10^{14} cm^{-2} min^{-1} with the Knudsen cell at 1300 K. Samples were held at room temperature during deposition for post-deposit annealing investigations and at 815 K for cluster growth during deposition. In addition, a room-temperature deposited sample was covered with Si prior to annealing to compare the influence of a capping layer on the clustering process. The Si overlayer was grown from an *in situ* electron beam evaporator with a deposition rate of about 1×10^{15} cm^{-2} min^{-1}. Quantitative determination of Ge coverages and cluster heights was made by standard Rutherford backscattering techniques (RBS).[2] In addition, *ex situ* reflection electron microscopy (REM) and transmission electron microscopy (TEM) were used in order to characterize the cluster shapes and size distribution.

For the electron microscopy investigations, the Si was first cut into 2.5×2.5 mm^2 pieces, which were mechanically polished to 250 μm from the substrate side while protecting the Ge film side with wax. These pieces were finally etched chemically in a solution containing 3 parts acetic acid, 5 parts nitric acid, and 3 parts hydrofluoric acid. TEM was done using a Philips 420 electron microscope operated at 120 kV.

RESULTS AND DISCUSSION

As shown in earlier studies of the Ge/Si system, the growth mode matches the Stranski-Krastanov (SK) model, i.e., cluster growth after the formation of a uniform layer. The uniform layer thickness is between 3 and 4 monolayers (ML) according to different authors.[3–6] Using both ion scattering and Auger spectroscopy, SK growth was confirmed in the present work. Post-deposition annealing of a 2-ML Ge on Si(100) sample showed no clustering up to 900 K, that is, a uniform (SK) layer is formed and does not cluster even at high temperatures.

We first investigated the growth of the Ge clusters in the post-deposit phase for layer thicknesses in excess of the SK thickness, i.e., about 7-ML deposition at room temperature. Figure 1 shows a plot of the cube of the cluster height (h_c) vs time for Ge/Si(100) at different temperatures. The linear dependence allows the extraction of growth rates which are combined in an Arrhenius plot in the inset of the figure. The activation energy Q of the cluster growth is $Q=1.0\pm0.1$ eV. This value is in the range of values obtained for other systems.[7,8] The time dependence is strongly suggestive of Ostwald ripening as the basic driving force of cluster growth.[7] However, an important difference from earlier measurements is the large zero offset at all but the highest temperature. This may be an indication of a different ripening process in the early stages as discussed by Lifshitz *et al.*[9]

In recent papers we have investigated the cluster-growth mechanism for Sn on Si (Ref. 10) and Ga on Si.[7] By a combination of ion scattering and electron microscopy we showed that the cluster growth at elevated temperatures can be described as Ostwald ripening. This

idea was also used to describe cluster formation in the GaAs/Si system,[8,11] a practical system of current interest.

The successful description of the film morphology via the ripening mechanism raises two additional questions. (1) Can this description be extended to clustering during deposition? Note that the ideal description of ripening involves mass conservation, i.e., no further material is added during cluster growth.[8] (2) A second question concerns the applicability of clustering for faceted clusters as often observed in epitaxial systems. The previous work on Ga and Sn involved nonfaceted clusters.

To address the first question we compared post-deposition cluster growth and growth during deposition. This comparison consists of the following measurement. (1) In the first case we determine the cluster size as a function of time at elevated temperature after low-temperature deposition. This kind of measurement was described above and the results are given in Fig. 1. Note that these measurements conform to the mass conservation condition. (2) The comparison measurement determines cluster size formed during growth with the substrate at the same elevated temperature. Such a measurement is shown in Fig. 1 (open circles) for deposition of Ge at 815 K. The total deposition time in both cases was 45 min and the point is plotted at 24 min. The uncertainty in the SK layer thickness implies that clustering does not start until 18–24 min into the deposition. The size of the cluster is in reasonable agreement with the post-deposition data illustrating the applicability of the approach.

We investigated the post-deposition- and during-deposition-grown cluster structures in more detail by microscopic techniques. Figure 2 shows two REM pictures of Ge clusters on Si(111). The top structure (a) represents a 9.0-ML deposition at room temperature with 10-min post-deposition annealing at 925 K. The bottom structure (b) shows clusters formed during deposition of 13.8 ML (40-min deposition time) with the substrate at 815 K. Both samples display the same cluster shape. We used REM to confirm that the cluster shape is conserved during the cluster ripening for cluster sizes from 200 to over 1000 Å.

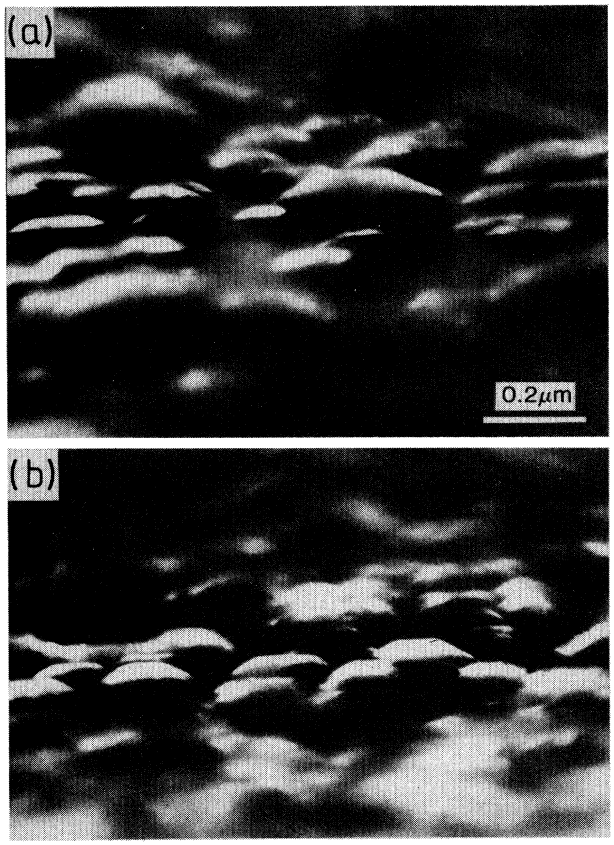

FIG. 2. Reflection electron micrographs of Ge clusters on Si(111): (a) after deposition of 9-ML Ge at room temperature and post-deposit annealing for 10 min to 925 K; (b) after deposition of 13.8 ML during 40 min at 815 K sample temperature. This second procedure allows cluster growth during the deposition.

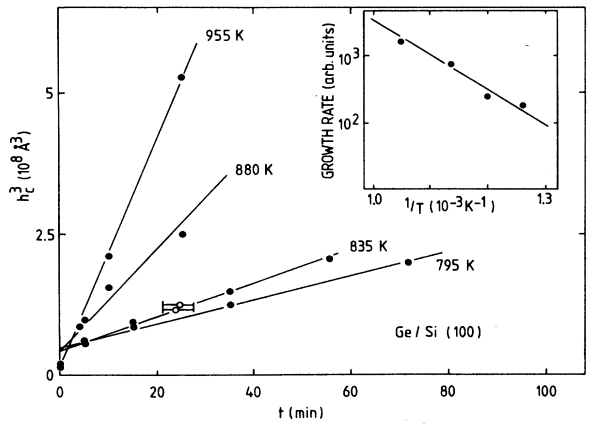

FIG. 1. Cluster growth process for Ge/Si(100) displayed as the cube of the cluster height vs time for different temperatures (●). The initial coverages were in the range of 6.8–7.4-ML Ge. The inset shows the corresponding Arrhenius plot to these data. For comparison, two points (○) for the growth "during deposition" at 815 K is added.

The corresponding top view of the clusters (Fig. 3) was examined by TEM (same samples as in Fig. 2). The characteristic structure of the Moiré fringes is identical in both cases. The outer region, where the fringes are widely spaced, is more elastically strained (fewer misfit dislocations) than the inner region, where the fringes are closely spaced. This is consistent with the geometry of the Ge clusters: the flat-top region is thicker and the sloped-edge region is thinner. We also note that the boundary between these two Moiré-fringe ranges is well defined, consistent with the flat-top geometry.

From such planar TEM micrographs, we compiled cluster size distributions for several post-deposition-grown structures [Fig. 4(a)] and cluster structures formed during deposition [Fig. 4(b)]. The theoretical cluster distribution is given by[9,12]

$$h(\rho)=\begin{cases}\left[\dfrac{3}{3+\rho}\right]^{7/3}\left[\dfrac{\frac{3}{2}}{\frac{3}{2}-\rho}\right]^{11/3}\exp\left[\dfrac{-\rho}{\frac{3}{2}-\rho}\right] & \text{for } \rho<\frac{3}{2} \\ 0 \quad \text{for } \rho\geq\frac{3}{2}\end{cases} \tag{1}$$

with $\rho=r/r_c(t)$ and r_c is the critical radius, i.e., the radius of those clusters which neither decompose nor grow at the given time. r_c is determined from the curves in Fig. 1. We find reasonable agreement with the theoretical curves. However, the broadening in Fig. 4(a) is in agreement with former results for Sn on amorphous C (Ref. 13) and Au on NaCl (Ref. 14) as reported by Chakraverty.[15]

The advantage of compiling cluster size distributions is that changes in the transport mechanism for clustering change both the power law of the cluster height versus time curve and the cluster size distributions. Therefore, this analysis is an additional confirmation of the validity of an Ostwald-ripening process in combination with a specific mass transport mechanism.

The successful applicability of the Ostwald-ripening description for samples grown during deposition at elevated temperature [Fig. 4(b)] can be understood as follows: The Ostwald-ripening model is exactly valid only for zero deposition rates. However, there is an upper limit to the deposition rate where it approximately applies. This limit can be estimated from a comparison of the free concentration between the growing clusters in the ripening model and the modification of this concentration by the additional deposition. As long as the free concentration is greater than the supersaturation, the Ostwald-ripening model will describe the cluster growth. To quantify this limit, a value for the free concentration in the Ostwald regime is needed. A rough theoretical estimate shows that the free concentration for Ge on Si could be of the order of 0.1–0.3 ML.[16] The supersaturation σ is given by the impinging flux not incorporated into clusters. Thus

$$\sigma=\mathbf{R}\tau\ , \tag{2}$$

where τ is the time necessary to diffuse to a cluster; $\tau=l^2/D$ with l the mean spacing between clusters ($\sim 10^4$ Å) and D is the diffusion coefficient of Ge from Fig. 1 (D at 650 °C is 4×10^{-11} cm^2/sec). Imposing the limit σ less than 0.2 ML implies R less than 5×10^{13} cm^{-2} min^{-1}. This limit is close to the experimental parameter used in this study and supports the idea of Ostwald ripening even during growth.

As a final observation we note that the continuous cluster growth in this system can be suppressed by capping the structure prior to the annealing step. We did not observe cluster growth above our detection limit for a Si(111)/(12-ML Ge)/(50-ML Si) structure at 1000 K for 300 min. The same structure without a Si cap clearly displays clusters for less than 5-min annealing. The supression factor of the cluster-growth rate can be estimated to be at least 2 orders of magnitude. This result is in agreement with the conclusions of a similar study by Marée *et al.*[5] In Ostwald ripening the driving force for clustering depends on the formation of an equilibrium between a free concentration of adatoms and the clusters, hence the strong change due to capping is not surprising.

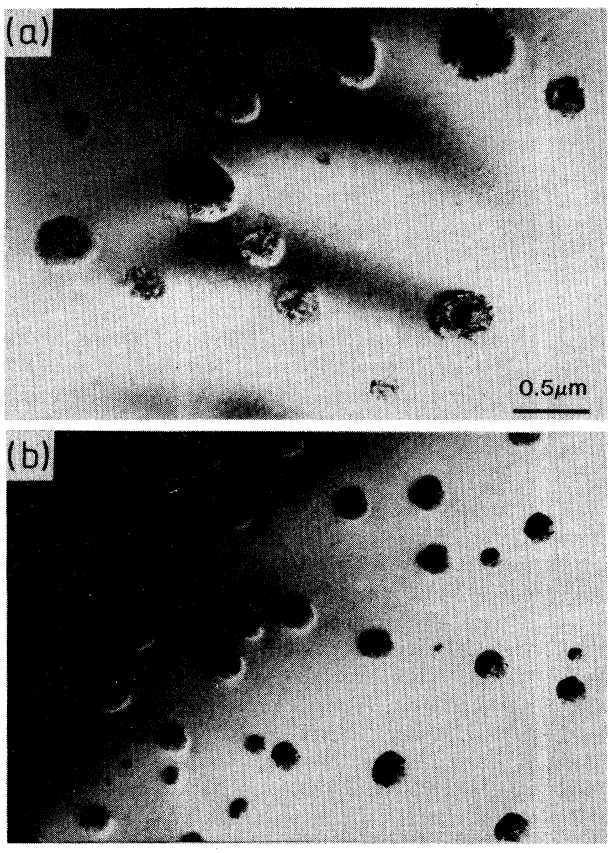

FIG. 3. Transmission electron micrographs of the same samples as in Fig. 2. Note the Moiré fringes display lower density towards the center of the cluster.

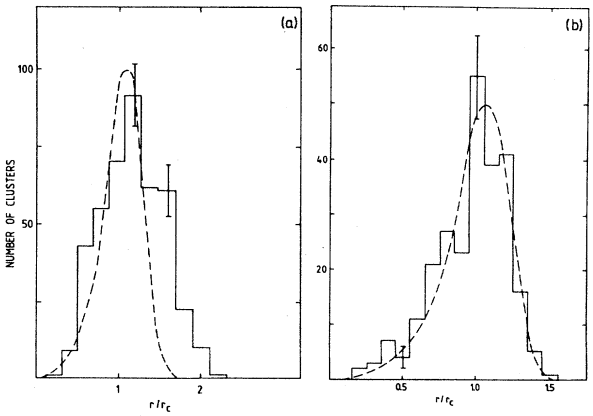

FIG. 4. Cluster-size probability vs cluster radius (a) for 12.9-ML Ge/Si(100) deposited at room temperature, then annealed for 70 min to 835 K, and (b) for the same sample as in Figs. 2(b) and 3(b). In both cases a theoretical curve based on the Ostwald ripening mechanism (dashed curve) is shown.

CONCLUSIONS

We have used Rutherford backscattering and TEM techniques to investigate clustering in the Ge/Si system. For post-deposition annealing we find the cluster-volume growth rate to be linear with time in agreement with an Ostwald-ripening mechanism.

In addition, we showed that the cluster size distribution grown using a low impinging Ge flux matches the theoretical curve for the ripening mechanism. This result is in agreement with a rough estimate of a limit for the application of the Ostwald-ripening model to the "during-deposition" regime.

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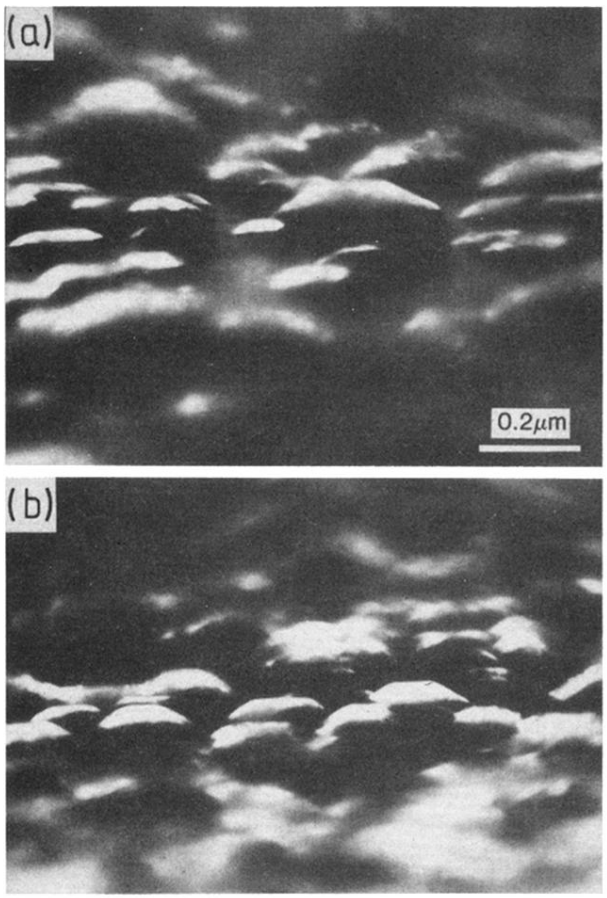

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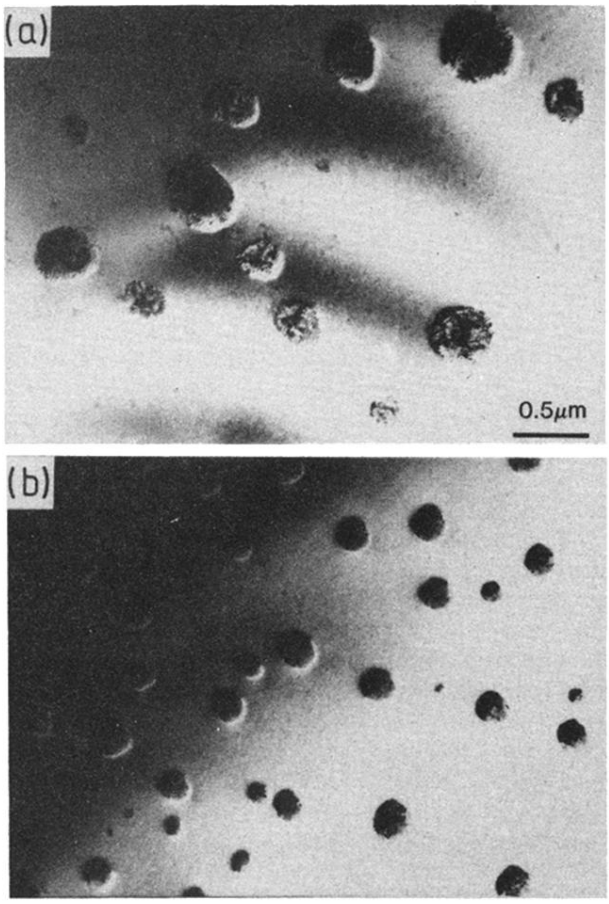

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