Kinetic Instability in the Growth of CaF_2 on Si(111)

R. M. Tromp and M. C. Reuter
IBM Research Division, T. J. Watson Research Center, P.O. Box 218 Yorktown Heights, New York 10598

(Received 11 April 1994)

Even when thermodynamic driving forces favor a thin film to grow with a particular growth mode, this preferred growth mode may be kinetically inaccessible. While this is not uncommon at low temperature (short diffusion length), we show that in the Si(111)/CaF_2 system, during the early stage of growth, the preferred growth mode may be inacessible at temperatures as high as 660 °C, where the surface diffusion length (several microns) exceeds the terrace spacing. Once the preferred growth mode is initiated the surface morphology becomes unstable, leading to a fast and striking change in layer occupancies.

PACS numbers: 68.35.Bs, 61.14.Hg, 68.55.Bd

The growth modes of a thin film on a substrate are usually distinguished in accordance with Bauer's criteria. The film may wet the substrate and grow in a layerlike fashion (Frank–Van der Merwe growth), it may not wet the substrate and grow in islands (Volmer-Weber growth), or it may initially wet the substrate, and subsequently undergo islanding due to misfit strain (Stranski-Krastanov growth). The distinction between these well-known growth modes is made on the basis of thermodynamic arguments.

However, growth of thin films generally proceeds under conditions far away from thermodynamic equilibrium, and attempts to understand the details of the evolving surface morphology must take the kinetics of the growth process into account explicitly. In the simple case of Ag growing on a Ag(111) surface it was found that a multilayer growth mode can be changed into a layer-by-layer growth mode by adsorption of a small amount of Sb [1]. It was shown that this is due to a change in growth kinetics [2]. In particular, growth of the first monolayer is initiated by nucleation of 2D islands on the terraces of the substrate. With continued growth these 2D islands grow in size. When the radius of these islands is smaller than a well-defined *critical* radius [2], these islands are all one atomic layer high. However, at the critical radius there is a sharp increase in the rate of nucleation of 2D islands on top of the existing 2D islands, for the following reason. When the 2D island is small, the average residence time of an adatom on top of the island is small, with the island perimeter acting as a sink. With increasing island diameter the average residence time of an adatom landing on the island increases, and therefore the concentration of adatoms, C_a on the 2D island increases. Since the nucleation rate of a stable N-atom cluster is proportional to $(C_a)^N$ it depends in a strongly nonlinear fashion on the radius of the 2D island. Below the critical radius nucleation of a second-layer island is extremely unlikely, above the critical radius it is extremely likely. The transition between these two regimes is quite sharp. In this Letter we show that in the initial stages of CaF_2 growth on Si(111) a *sudden* transition occurs from a kinetically controlled to a thermodynamically controlled surface morphology. The striking abruptness of this transition is explained by considering both the effects of the Si/CaF_2 interface energy, and the kinetics of second layer nucleation. In addition, we demonstrate that thermodynamic equilibrium may be inaccessible even on length scales much shorter than the surface diffusion length. This surprising result highlights the importance of considering not only the thermodynamic driving forces, but also the details of the growth kinetics.

The growth of CaF_2 on Si(111) has been studied extensively [3–8]. At high temperature (above ~700 °C), an interfacial layer is formed between the Si substrate and the epitaxial CaF_2 overlayer, with only one F atom per Ca atom [5]. A single atomic layer of Ca atoms forms a covalent bond with the (1×1) Si surface, reminiscent of the structure of $CaSi_2$. This Ca layer is terminated by a single layer of F atoms, and forms a stable interfacial layer for subsequent growth of CaF_2. Since the molecular beam from which the film is grown consists of CaF_2 molecules, one monolayer (ML) of F is desorbed during growth of this interfacial layer. In addition, the Si(111)-(7×7) reconstruction is removed when the interfacial layer forms. At growth temperatures significantly below 700 °C photoemission experiments show that there is excess F at the interface, and not only Si-Ca but also Si-F bonds are found [3, 4]. In medium energy ion scattering (MEIS) experiments at these lower temperatures it was observed that the interfacial structure appears to be irreproducible from experiment to experiment, and that the (7×7) reconstruction is not fully removed [5]. Thus it appears that the thermodynamically stable, low energy interfacial structure consists of a CaF_1 layer between the substrate and the epitaxial CaF_2 overlayer. We will refer to this as the interfacial CaF layer. At lower temperature this structure does not form, resulting in a less perfect interface with higher interfacial energy. We will see in the following that the perfection of the interface and the

0031-9007/94/73(1)/110(4)$06.00

associated interfacial energy has a dramatic influence on the growth mode of the CaF_2 overlayer.

We have performed *in situ* studies of the growth of CaF_2 on Si(111) using a low energy electron microscope developed and constructed in our laboratory [9]. A 15 keV electron beam is focused in the backfocal plane of cathode objective lens. The lens is at ground potential, the sample potential is close to that of the field emission tip in the electron gun. Thus, the coherent and collimated incident beam is decelerated and strikes the sample with an energy in the range of 0–100 eV. On a cyrstalline sample the reflected and reaccelerated electrons form a focused low energy electron diffraction (LEED) pattern in the objective lens backfocal plane. A real space, magnified image of the sample is formed at larger spacing. By selection of the (0,0) beam (or any other diffracted beam) bright field (dark field) images can be obtained routinely at video rate and recorded on videotape. Lateral resolution is 150 Å, single height atomic steps can be observed by phase contrast.

Figure 1 shows six images obtained during growth at 660 °C. In (a) the atomic steps on the surface are clearly identified. The image was taken at a point where the first layer of CaF_2 (white) almost completely covers the Si(111) substrate (dark). In (b) only small uncovered patches remain near the step edges. When the terraces become fully covered a striking instability is seen in the growth mode (c). At the bottom of the image we see how on two adjacent terraces, in three different locations, the surface undergoes a sudden change, from a smooth and uniform light contrast, to a dense network of still brighter areas. On the videotape from which these still images were taken it is seen that the boundary between the smooth areas and the networklike areas moves at a rate of 1–2 $\mu m\ sec^{-1}$. With continued growth adjacent terraces also undergo this transition (d), (e), but the rate at which the boundaries move becomes slower. In (f) the boundary moves quite slowly, so that we can discern more clearly what is happening. During the transition the first CaF_2 layer is seen to retract, exposing the (dark) substrate, while at the same time bright areas form (the bright network), which are *two* layers high. The boundaries between the one- and two-layer high areas can be clearly seen in (f). The contrast between those two areas arises from a change in the LEED *I-V* curves with each additional layer. To accurately determine the coverage at which the transition occurs, we prepared one sample on which growth was stopped when the transition was first seen [similar to Fig. 1(c)]. This sample was removed from the microscope, and analyzed (after transport through air) with MEIS. The Ca coverage was measured to be 1.1 (± 0.1) monolayer, indicating that the transition occurs at 1 monolayer. These observations can be summarized as follows. Initially, CaF_2 forms a single-layer film on the Si substrate, until the atomic terraces have been filled. When the 1 layer coverage is exceeded, nucleation of the second layer sets off an instability in which a two-layer structure is preferred over a one-layer structure. Evidently, CaF_2 would rather bond to CaF_2 than to Si. In other words, the CaF_2-Si interfacial energy is higher (less favorable) than the CaF_2 cohesive energy. Why then does CaF_2 not grow in a two-layer growth mode from the beginning?

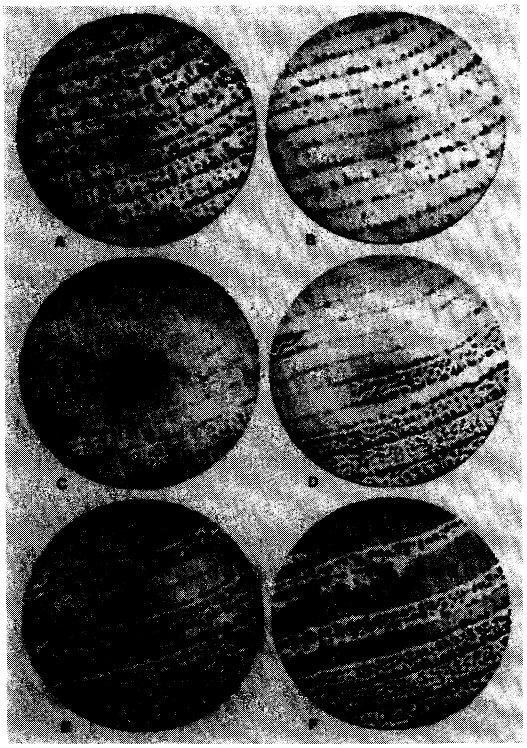

FIG. 1. CaF_2 growth at 660 °C. (a) A single-layer CaF_2 film (light) covers most of the Si(111) substrate (dark). (b) Dark patches are left only near the step edges. (c) A sudden transition to a two-layer CaF_2 structure (bright white) is occurring near the bottom of the image. (d) and (e) show how the transition progresses on more and more terraces. In (f) the boundary between single and double layer can be clearly seen (arrow). Field of view 4 μm.

We address this question by studying this transition at different temperatures. In Fig. 2 we show the surface just a few seconds before the transition occurs at a growth temperature of 600 (a), 640 (b), 660 (c), and as the transition occurs, at 660 °C (d). In (a) and (b) the substrate is not fully covered when the transition occurs, unlike (c), (d) and Fig. 1. In all other respects the transition is very similar. With the pivotal role of a critical dimension for second-layer nucleation in mind (as discussed above for Ag/Ag growth), we can understand what is happening. Suppose a small one-layer CaF_2 island is formed somewhere on the Si substrate. Additional CaF_2 molecules landing on that island can do two things: jump off the edge, or nucleate a second-layer island on top. Since the island edge acts as a sink, the

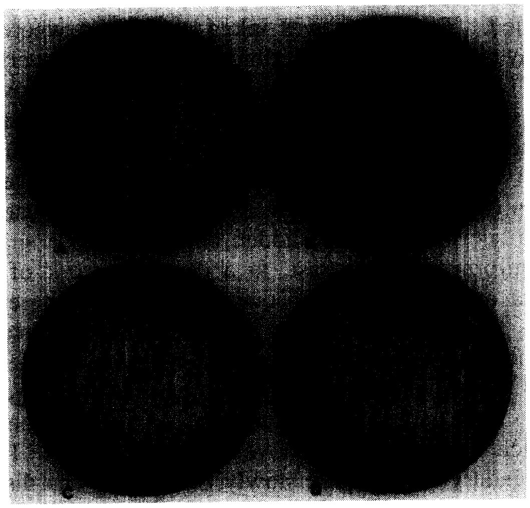

FIG. 2. The surface morphology a few seconds before the transition occurs at 600 °C (a), 640 °C (b), and 660 °C (c), and just after the transition has started at 660 °C (d). At the lower temperatures the transition sets in before the terraces are completely covered, with an islanded CaF_2 morphology. The island size increases at 640 °C, while at 660 °C the CaF_2 layer grows by step flow, until the transition suddenly changes the layer occupancies. Field of view 4 μm.

island must exceed a certain critical size before the second layer can nucleate. At low temperature this critical size is rather small, so that the transition can occur before the terrace is completely covered. In fact, we see that the transition travels along the terrace, much the same way as at higher temperature [2(d)], indicating that the transition occurs when the little islands in (a) start to run into each other, suddenly reducing the island interior-to-edge ratio. At 640 °C (b) the same thing happens, but the critical length scale is larger. With increasing temperature this critical length scale continues to increase, until it is larger than the terrace width, in Fig. 2(c). In that case, the second layer *cannot* nucleate as long as the first layer is not completely filled (i.e., as long as there are still first-layer edges left). In other words, the layer grows by step flow. As soon as the first layer is completely filled the second layer *must* nucleate somewhere, and when that happens the chemical potential suddenly drops: CaF_2-CaF_2 bonding is preferred over CaF_2-Si bonding. Newly arriving CaF_2, as well as first-layer CaF_2 accumulates in the second layer. Figure 3 shows two images at 660 °C, as the transition first sets in near the center (a) and a few seconds later (b). The field of view (8 μm) is twice as large as in Figs. 1 and 2. In Fig. 3(b) the terraces some distance away from the converted center terrace continue to fill in, as can be seen from the disappearance of the little dark areas at the step edges. But within a band of ~3 μm along the converted terrace, this filling-in occurs more slowly. The converted terrace, with a two-layer high CaF_2 network, has a lower chemical potential than the neighboring terraces, and captures CaF_2 molecules diffusing over the surface. Thus, CaF_2 molecules can travel over quite large distances, much larger than the terrace spacing. As in Fig. 1, eventually almost all of the terraces on this sample underwent the transition from one to two layers in similar fashion.

At 660 °C the thermodynamically preferred growth proceeds by the initial formation of two layers of CaF_2. However, formation of the second layer is kinetically inhibited because the critical dimension for nucleation of the second layer is larger than the step spacing. Once the second layer forms, the chemical potential suddenly drops, setting off the growth mode instability described above. If the Si-CaF_2 interfacial energy is lower, does this transition still occur? We have performed several experiments to address this question. If we take a surface grown at 660 °C, just after the transition has occurred, and heat it to 770 °C , we find that the transition reverses itself. CaF_2 spreads out over the terraces, wetting the Si substrate to complete coverage. When the temperature is subsequently lowered this structure is stable, both in static conditions and during additional growth at 660 °C. Alternatively, we may grow CaF_2 at 770 °C until the substrate is almost completely covered with a single layer film, and then lower it to 660 °C for continued growth. In this case the transition does not occur either. The reason is simple. At temperatures above 700 °C a structurally uniform and stable CaF interfacial film formed, with a low interface energy. Below 700 °C this stable structure does not form. When the film grown at 600 °C is heated to 770 °C we also find major rearrangement of Si and motion of the Si edges, due to removal of the Si(111)-(7 × 7) reconstruction. Above 700 °C this happens *during* CaF_2 adsorption.

We find that the initial stages of interface formation between Si(111) and CaF_2 are controlled by two factors. One is the interfacial energy between substrate and overlayer, which is strongly temperature dependent, with an irreversible transition to a low energy structure at ~700 °C. The second is the kinetics of second-layer nucleation, which is dominated by the critical length

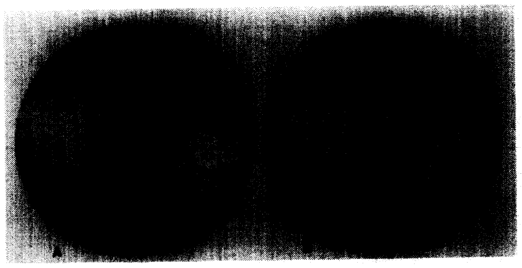

FIG. 3. (a) The surface as the transition first occurs at 660 °C. Most terraces still show small uncovered substrate regions near the stepedges. A few seconds later most terraces are fully covered (b), except for terraces within ~1.5 μm from the central converted terrace which captures incoming CaF_2 molecules over the distance, indicating a ~1.5 μm diffusion length of the CaF_2 molecules. Filed of view 8 μm.

scale for this process as previously discussed for growth of Ag on Ag. The apparent paradox that thermodynamic equilibrium cannot be attained on a length scale smaller than the length over which CaF_2 molecules can diffuse is caused by the kinetic barrier to second-layer nucleation. The interplay between thermodynamics and kinetics may give rise to complex and nonintuitive behavior, with either one playing a dominant role at different times of the growth process.

We gratefully acknowledge stimulating discussions with Jerry Tersoff, and we thank Matt Copel for the MEIS coverage measurements.

[1] H. A. van der Vegt, H. M. van Pinxteren, M. Lohmeier, E. Vlieg, and J. M. C. Thornton, Phys. Rev. Lett. **68**, 3335 (1992).

[2] J. Tersoff, A. W. Denier van der Gon, and R. M. Tromp, Phys. Rev. Lett. **72**, 266 (1994).

[3] F. J. Himpsel, U. O. Karlsson, J. F. Morar, D. Reiger, and J. A. Yarmoff, Phys. Rev. Lett. **56**, 1497 (1986).

[4] M. A. Olmstead, R. I. G. Uhrberg, R. D. Bringans, and R. Z. Bachrach, Phys. Rev. B **35**, 7526 (1987).

[5] R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **61**, 1756 (1988).

[6] G. C. L. Wong, D. Loretto, E. Rotenberg, M. A. Olmstead, and C. A. Lucas, Phys. Rev. B **48**, 5716 (1993).

[7] J. D. Denlinger, E. Rotenbergm, U. Hessinger M. Leskovar, and M. A. Olmstead, Appl. Phys. Lett. **62**, 2057 (1993).

[8] T. Nakayama, M. Katayama, G. Selva, and M. Aono, Phys. Rev. Lett. **72**, 1718 (1994).

[9] R. M. Tromp and M. C. Reuter, Ultramicroscopy **36**, 99 (1991).

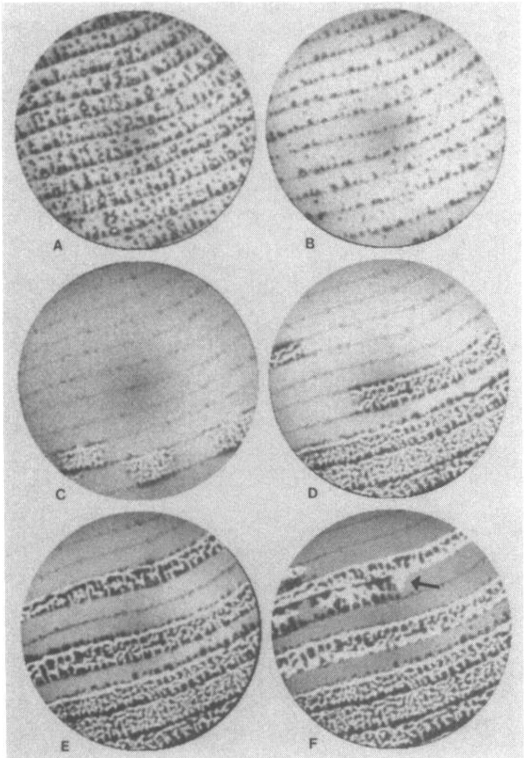

FIG. 1. CaF_2 growth at 660 °C. (a) A single-layer CaF_2 film (light) covers most of the Si(111) substrate (dark). (b) Dark patches are left only near the step edges. (c) A sudden transition to a two-layer CaF_2 structure (bright white) is occurring near the bottom of the image. (d) and (e) show how the transition progresses on more and more terraces. In (f) the boundary between single and double layer can be clearly seen (arrow). Field of view 4 μm.

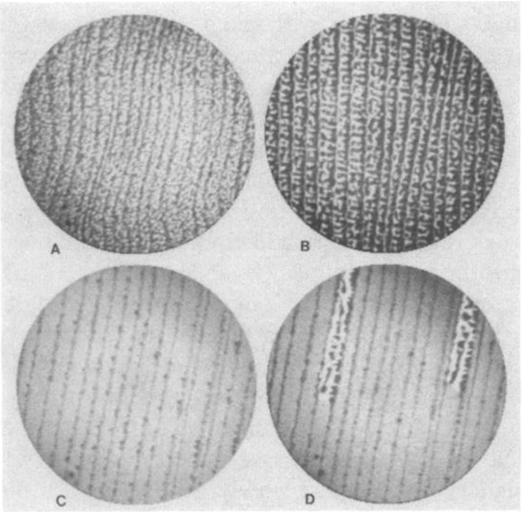

FIG. 2. The surface morphology a few seconds before the transition occurs at 600 °C (a), 640 °C (b), and 660 °C (c), and just after the transition has started at 660 °C (d). At the lower temperatures the transition sets in before the terraces are completely covered, with an islanded CaF_2 morphology. The island size increases at 640 °C, while at 660 °C the CaF_2 layer grows by step flow, until the transition suddenly changes the layer occupancies. Field of view 4 μm.

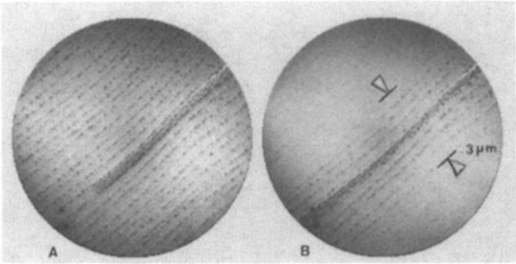

FIG. 3. (a) The surface as the transition first occurs at 660 °C. Most terraces still show small uncovered substrate regions near the stepedges. A few seconds later most terraces are fully covered (b), except for terraces within ~1.5 μm from the central converted terrace which captures incoming CaF_2 molecules over the distance, indicating a ~1.5 μm diffusion length of the CaF_2 molecules. Filed of view 8 μm.