CaF$_2$-Si(111) as a model ionic-covalent system: Transition from chemisorption to epitaxy

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(Received 20 May 1993)

The demands of chemisorption and epitaxy are quite different for electronically dissimilar systems. The transition between these two regimes in CaF$_2$-Si(111) is studied with transmission-electron microscopy and photoemission. Changes in the electronic structure of the evolving growth surface are expressed in the composite growth mode, a Stranski-Krastanow pathway to layer-by-layer growth, which begins with CaF$_2$ coherent island formation on a Si-CaF layer. After this transition, layer-by-layer CaF$_2$ homoepitaxy is possible even at room temperature, and the critical thickness can be extended.

On the basis of thermodynamic considerations, a given heteroepitaxial system can adopt one of three growth modes: purely layer-by-layer (Frank-van der Merwe), purely islanding (Volmer-Weber), and layer-by-layer followed by islanding (Stranski-Krastanow). The choice is governed by the relative magnitudes of $\sigma_f$, the interface free energy, $\sigma_s$ and $\sigma_{ss}$, the surface free energies of the epilayer and of the substrate, and any strain energy arising from lattice mismatch. For systems with negligible lattice mismatch, layer-by-layer growth is predicted if $(\sigma_f + \sigma_s) < \sigma_{ss}$ and islanded growth if $(\sigma_f + \sigma_s) > \sigma_{ss}$. However, for systems with small $\sigma_s$ and non-negligible lattice mismatch, initial growth is lamellar, but subsequent layers may lower the total energy by forming islands, either with strain-relieving misfit dislocations beneath them, or with elastic deformation around them.

The above scheme works quite well for electronically similar systems. For heteroepitaxy between electronically dissimilar materials, however, where interface reactions can alter surface and interface energies, this picture must be modified. In this work, we investigate CaF$_2$-Si as a prototypical ionic-covalent heteroepitaxial system. CaF$_2$ is an ionic insulator; Si is a covalent semiconductor. Both CaF$_2$ and Si have fcc-type lattices with nearly the same lattice parameter at room temperature. Previously, it has been assumed that CaF$_2$ grows in a layer-by-layer mode on Si since $\sigma_{CaF_2} < \sigma_{Si}$. However, CaF$_2$ chemisorption onto a Si(111) surface is fundamentally different from subsequent CaF$_2$-CaF$_2$ homoepitaxy. As the electronic structure of the epitaxial CaF$_2$ develops during CaF$_2$-Si growth, the effective growth surface changes from a covalent one to an ionic one, and the heats of formation and surface diffusion kinetics can drastically change.

In this paper, we show that the transition from chemisorption to epitaxy governs the growth modes of CaF$_2$-Si. At previously defined optimum substrate temperatures near $T_s \sim 700 \, ^\circ C$, the transition from initial chemisorption to final epitaxy can be schematized in a sequence of three stages: Initial CaF$_2$ chemisorption on Si(111), a surface with a high dangling-bond density, produces a reacted, nonstoichiometric Si-CaF surface layer, with the interface Ca in threefold ($T4/H3$) sites, which is particularly efficient at tying off dangling bonds. We find that CaF$_2$ does not wet this reacted Si-CaF layer and further growth begins as islands on the reacted layer. Such nonwetting behavior was also observed using x-ray photoelectron diffraction. Under appropriate kinetic conditions, however, the islands are coherent: These strained coherent islands, a few molecular layers thick, appear to nucleate at steps and can completely cover the reacted layer to form a flat, epitaxial layer of CaF$_2$. The final stage is essentially CaF$_2$ homoepitaxy, which is layer-by-layer, and can proceed even at room temperature. This process can be described as a Stranski-Krastanow pathway to layer-by-layer growth. Perturba-
tions of the kinetic parameters during this process can drive this observed composite growth mode to a simple Stranski-Krastanow mode. Moreover, isothermal growth of thick CaF$_2$ films at high temperatures (∼700 °C) results in strain-induced defects. We found that by maintaining CaF$_2$ homoepitaxy near room temperature, where the lattice mismatch is reduced, the critical thickness for strain driven relaxations can increase from ∼12 F-Ca-F triple layers (TL’s) to more than 55 TL’s. Finally, by changing the temperature of initial ionic-covalent chemisorption, we show that atomically flat CaF$_2$-Si heterostructures with different interface structures can be grown.

Samples were prepared in an ISA/Riber molecular-beam-epitaxy system equipped with Knudsen cells for CaF$_2$ and Si deposition, an in situ reflection high-energy electron diffraction (RHEED) system, and x-ray photoemission spectroscopy (XPS) using a Camcera MAC-2 analyzer and Al Kα excitation. Transmission-electron microscopy (TEM) and x-ray crystal truncation rod scattering (CTR) were performed on samples capped with a thin (50–100 Å) layer of amorphous Si. TEM measurements were made using a JEOL 2000C microscope operating at 200 keV. A 12-kW Rigaku rotating-anode source coupled to a 4-circle Huber diffractometer operating in a triple-crystal mode$^{13}$ was used for the CTR measurements. Shiraki etched$^{14}$ Si substrates, oriented to within 0.5° of (111), were outgassed thoroughly, and then heated to 880 °C to remove the protective oxide. Sharp (7×7) RHEED patterns were obtained below a thermocouple reading of ∼800 °C in our system. The pressure during CaF$_2$ growth was typically ∼1×10$^{-10}$ torr. Unless otherwise stated, all CaF$_2$ growth was done at a cell temperature of 1150 °C, corresponding to CaF$_2$ deposition rate of ∼30 Å per minute during the initial stages of growth. Further details are described elsewhere.$^{10}$

Figure 1 shows a series of transmission-electron micrographs and the corresponding spin-orbit deconvolved Ca 2p$_{3/2}$ core-level photoemission spectra taken from the same samples before amorphous-Si capping. These samples were all grown at $T_i$ = 720 °C, and have nominal coverages of less than 5 TL’s. At submonolayer coverages, RHEED measurements during growth indicate the successive formation of ordered reconstructions, (3×1), (4×1), and finally (1×1), which persists at all higher coverages. Figure 1(a) corresponds to a sample soon after the onset of the (1×1), while Figs. 1(b) and 1(c) correspond to progressively thicker coverages. TEM micrographs are all bright-field, two-beam images taken using Si (220) reflections set slightly positive of the Bragg angle, with the incident beam direction close to (111). Under these conditions changes in image contrast are dominated by strain in the Si(220) planes. Figures 1(a) and 1(b) show homogeneous regions bordered by white lines on one side and dark on the other. We interpret the regions as strained coherent CaF$_2$ islands. Clearly the island coverage increases from 1(a) to 1(b). In Fig. 1(c) the islands have almost completely filled the surface, and the isolated regions with black and white edges are now holes in the film. Linear features showing faint contrast are visible within some of the islands in each of the three images, but are most discernable in Fig. 1(c). These features correspond to line defects at Si bilayer steps. These images suggest that CaF$_2$ grows as coherent islands which are confined to terraces between steps; the nucleation may be at step edges, as suggested by TEM images from islanded films (see below). The widths of most islands are comparable to the known terrace widths of the wafers. Moreover, the observed island growth is parallel to step edges and new islands are nucleated at larger coverages.

We now compare the above TEM results with photoemission spectra taken from the same samples. The Ca 2p photoemission shows two components separated by ∼2.8 eV; the low binding-energy component has been attributed to Ca bonded to Si in the Si-CaF interface layer, while the other to Ca in bulk CaF$_2$ in succeeding layers.$^{8,9}$ Least-squares fits shown in Fig. 1 employ two experimentally derived line shapes for interface and bulk Ca signals. In particular, the interface line shape required special attention because of a slight metalliclike broadening as well as a satellite loss feature at 4.5 eV higher binding energy relative to the main interface line.$^{15}$ The interface-bulk photoemission intensity ratios were compared for the samples shown in the plan-view TEM micrographs in Figs. 1(a)–1(c). In Fig. 1(a), the coherent

![FIG. 1. Bright-field, two-beam, TEM micrographs and corresponding spin-orbit deconvolved Ca 2p$_{3/2}$ core-level XPS data taken from CaF$_2$ films grown at 720 °C on Si(111): (a) Si-CaF layer + 24±5% coherent island coverage, deposition time of 12 s; (b) Si-CaF layer + 45±10% coverage, 16 s; (c) Si-CaF layer + 88±5% coverage, 32 s. Diffraction vectors are marked as arrows and the scale is the same for all three figures. Binding energy is measured from the interface Ca 2p$_{3/2}$.](image-url)
islands cover only ~24% of the surface, while the intensities from bulk and interface photoemission are roughly equal. On Fig. 1(b), where the coherent island coverage is ~45%, one can see that the interface-bulk photoemission ratio is not consistent with single TL thick coherent islands, which would give a ratio between 1/1 and 2/1. Using fractional coherent island coverages estimated from the TEM images and a CaF$_2$ exponential attenuation length appropriate to our geometry, 10 the coherent island thicknesses are ~2.7 TL’s (~24% coverage), 3.9 TL’s (~45%), and 4.8 TL’s (~88%) for Figs. 1(a)–1(c), respectively, with an estimated error of ~1 TL. A coherent island thickness of 4 ± 1 TL’s for the film in Fig. 1(c) has also been measured using CTR scattering. 17

Figure 2 compares Ca 2p$_{3/2}$ photoemission results for 4–5 TL films grown under different conditions; a flat film grown at conditions described above [Fig. 2(a)], and one grown at 770°C [Fig. 2(b)], resulting in thick CaF$_2$ islands that do not uniformly cover the surface. These islands have relaxed back to their bulk lattice constant, as evidenced from the corresponding TEM image [Fig. 2(d)], where such islands are visible as areas exhibiting moiré contrast. Although the islands only cover a fraction of the surface, the interface photoemission intensity for the islanded film is comparable to that for a flat film. This suggests the initial formation of a complete layer of reacted Si-CaF which effectively functions as a new substrate, on which all subsequent islanding or layer-by-layer growth occurs. Furthermore, the island widths in Fig. 2(d) are less than the anticipated terrace widths. This indicates that the islands nucleate at step edges and grow across terraces. Islanding behavior is also seen in CaF$_2$ films grown at 720°C if the deposition rate is reduced by lowering the temperature of the effusion cell to 1050°C.

The islanding behavior observed is consistent with a smaller heat of adsorption for CaF$_2$–Si-CaF than for CaF$_2$–CaF$_2$. This difference may be attributed to changes of the surface Madelung potential due to the altered Ca ionicity at the interface layer. 8 This is consistent with the observed thermal desorption behavior, which indicates a larger evaporation rate of CaF$_2$ from the reacted Si-CaF layer than that from CaF$_2$ (111). For coverages comparable to that in Fig. 1(a), less than 100 s is required for the (1×1) RHEED pattern to evolve into a (4×1) at a desorption temperature of $T = 720°C$. However, the amount of CaF$_2$ evaporated from a 8-TL-thick film was negligible after a 2.5-h anneal at the same temperature. In fact, the reacted Si-CaF layer can form at temperatures even higher than the Si(111)-1×1→7×7 transition, and as long as $T_1$ is decreased for subsequent layers, two-dimensional (2D) growth can still result. Due to the large disparity in the adhesion of CaF$_2$ on the reacted Si-CaF layer and that on CaF$_2$, growth of the first CaF$_2$ layer on the reacted layer defines a rate-limiting step during lateral island growth, and additional layers can nucleate on this CaF$_2$ layer before the Si-CaF layer is completely covered.

Step and terrace morphology play a pivotal role in CaF$_2$–Si growth. Since Si atoms at step edges are highly reactive, with two rehybridized dangling bonds each, 18 the local structure of the reacted Si-CaF layer can be different at steps, and may provide nucleation sites for the observed coherent islands. Moreover, the large step and kink binding energies in ionic systems 19 will tend to confine such islands to grow along step edges. From the TEM images in Figs. 1(a) and 1(b), it is the island density rather than the island size that increases with coverage. This suggests that the time scale for lateral island growth is shorter than that for their nucleation. Although CaF$_2$ does not wet the 2D substrate defined by the Si-CaF composite surface, its wetting of the 1D “substrate” defined by the steps and/or island edges 20 provides a competing process. If the kinetics favor step flow growth of the coherent islands, then the islands uniformly cover the reacted layer, allowing the system to switch to layer-by-layer CaF$_2$ homoepitaxy. If the kinetics are shifted away from growth on the Si-CaF layer, at low deposition rates or high $T_1$, then the dominant growth process will be CaF$_2$ on CaF$_2$ islands, leading to incomplete coverage and catastrophic increases in island heights. In this case, no transition to layer-by-layer CaF$_2$ homoepitaxy can occur. The role of substrate temperature and deposition rate has also been studied using photoelectron diffraction. 12 It is possible to alter the CaF$_2$–Si interface structure by chemisorbing the initial layers at $T_1 < 550°C$ (Ref. 9) instead of the usual $T_1 < 700°C$. The Ca 2p shift decreases from 2.8 eV at $T_1 = 720°C$ to 1.9 eV at $T_1 = 300°C$ [see Fig. 2(b)]. The binding-energy difference is manifested in a shift of the bulk components relative to the interface component rather than vice versa. 3 Ca vacancies in the interface layer may provide an explanation for this difference. The existence of such vacancies is suggested by XPS data. 12

The lattice mismatch between Si and CaF$_2$ varies from 0.6% at room temperature to 2.4% at 720°C. The critical thickness for pseudomorphic films grown isothermally at 720°C is 12 TL’s. By depositing 6–7 triple layers of
CaF$_2$ at 720°C as a “template” for subsequent room-
temperature growth, the critical thickness can be
significantly increased. Figure 3(a) is a dark-field TEM
micrograph of a sample grown with this “template”
method. The bright lines are an array of line defects,
which occur at steps and are a consequence of the type-
A – type-B orientational difference between Si and the
CaF$_2$ overlayer. Figure 3(b) shows a CTR measured
from another sample grown using the “template” method.
A least-squares fit to the rod intensity gives $d = 2.78 \text{ Å}$,
$a_T = 3.170 \text{ Å}$, $N = 30$, where $d$ is the interface separation
between the CaF$_2$ epilayer and Si substrate, $a_T$ is
the tetragonally distorted CaF$_2$ (111) perpendicular lattice
parameter, and $N$ is the number of CaF$_2$ triple layers.
Using this method, pseudomorphic growth has been
achieved up to ~55 TL’s. It has been previously report-
ed that ionic homoeptaxy on net neutral surfaces can
occur at room temperature. However, a Madelung
potential calculation suggests that the diffusion barrier on
the CaF$_2$ (111) surface is ~1 eV, so the persistence of
layer-by-layer growth at low temperatures seems un-
expected. It is possible that the latent heats of condensa-
tion provide the deposited CaF$_2$ molecules with the
necessary mobility.

In conclusion, the transition from chemisorption to ep-
itaxy can have fundamental implications for the heteroepi-
taxial growth of electronically dissimilar materi-
als. By manipulating this transition, the growth mode,
the interface structure, and the critical thickness of
CaF$_2$-Si(111) can be changed. Moreover, the existence of
layer-by-layer growth in general cannot be deduced from
a simple surface energy comparison of the bulk epilayer

We are grateful to Phil Cullen for his technical sup-
port. G.C.L.W., E.R., and M.A.O. would like to thank J.
D. Denlinger and K. Haynes for helpful discussions.
D.L. acknowledges the National Center for Electron Micro-
scopy for the use of the JEOL-200CX TEM. This
work was supported by the Director, Office of Basic Energy
Sciences, Materials Sciences Division of the U.S.
Department of Energy under Contract No. ACO3-
76SF00098.

1For a review, see the two volumes of Strained-Layer Super-
lattices, edited by T. M. Pearsall (Academic, San Diego, CA,

2D. J. Eaglesham and M. Cerullo, Phys. Rev. Lett. 64, 1943

3C. W. Snyder, B. G. Orr, D. Kessler, and L. M. Sander,

4R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. 61, 1756
(1988).


6Ph. Avouris and R. Wolkow, Appl. Phys. Lett. 55, 1074

7J. Zegenhagen and J. R. Patel, Phys. Rev. B 41, 5315

8See, for example, D. Rieger, F. J. Himpsel, U. O. Karlsson,
B 34, 7295 (1986).

See, for example, M. A. Olmstead, R. I. Uhrberg, R. D.

10C. A. Lucas and D. Loretto, Appl. Phys. Lett. 60, 2071

11Previous studies usually mention a range of temperatures
conducive to CaF$_2$ growth on Si, usually ~50°C wide and
centered near 700°C. We found that the width of this tempera-
ture window can vary from ~200°C to 0°C (where the
growth window has completely disappeared) by varying the
growth rate, the vicinal angle, and the pressure. For
example, we were not able to grow on samples with ~4° miscut, where
step height variations or facetting can occur. This makes
comparsion between different experiments problematic. The
topology of the results presented here, however, should still
be valid.

12J. D. Denlinger, E. Hessinger, M. Leskovar, and


14A. Ishizaka and Y. Shiraki, J. Elechrochem. Soc. 133, 666
(1986).

15E. Rotenberg, J. D. Denlinger, Uwe Hessinger, M. Leskovar,
and Marjorie A. Olmstead (unpublished)

16The attenuation length was derived by comparing the inter-
face and bulk intensities for larger CaF$_2$ thicknesses, where
the growth is layer-by-layer.

17CTR scattering is based on interference effects arising from
surface and interface terminations in crystalline materials.
See, for example, I. K. Robinson, R. T. Tung, and
R. Feidenhans'1, Phys. Rev. B 38, 3632 (1988), and references
therein.

18M. Schluter, K. M. Ho, and M. L. Cohen, Phys. Rev. B 14,
558 (1976).

19See, for example, M. H. Yang and C. P. Flynn, Phys. Rev.


21This is analogous to the work on (Ni, Co)$_2$S$_2$: see, for example,
R. T. Tung and F. Schrey, Appl. Phys. Lett. 54, 852
(1989).

22See, for example, W. F. Egelhoff, Jr. and I. Jacob, Phys. Rev.

23C. A. Lucas, G. C. L. Wong, C. S. Dower, F. J. Lamelas, and
FIG. 1. Bright-field, two-beam, TEM micrographs and corresponding spin-orbit deconvolved Ca $2p_{3/2}$ core-level XPS data taken from CaF$_2$ films grown at 720°C on Si(111): (a) Si-CaF layer + 24±5% coherent island coverage, deposition time of 12 s; (b) Si-CaF layer + 45±10% coverage, 16 s; (c) Si-CaF layer + 88±5% coverage, 32 s. Diffraction vectors are marked as arrows and the scale is the same for all three figures. Binding energy is measured from the interface Ca $2p_{3/2}$. 
FIG. 2. Ca $2p_{3/2}$ photoemission from (a) a flat 4–5 TL CaF$_2$ film (thickness obtained with a CTR measurement), deposition time of 33 s, (b) an islanded sample with the same deposition time, (c) a flat 4–5 TL film grown at 300°C, deposition of 32 s. (d) Bright-field TEM micrograph of sample in (b).
FIG. 3. (a) A weak-beam, dark-field image taken from a CaF$_2$-Si(111) film grown using the “template” method. The beam direction is close to [111]. The CaF$_2$ was deposited for 70 s at 720°C followed by 210 s at 70°C. (b) A CTR from a film grown using the “template” method, measured through the [111] Bragg reflection, giving a CaF$_2$ film thickness of 30 TL’s. The CaF$_2$ was deposited for 80 s at 720°C followed by 420 s at 70°C.