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

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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).[1] The choice is governed by the relative magnitudes of σ_i, the interface free energy, σ_e and σ_s, 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 $(\sigma_e + \sigma_i) < \sigma_s$ and islanded growth if $(\sigma_e + \sigma_i) > \sigma_s$. However, for systems with small σ_i and non-negligible lattice mismatch, initial growth is laminar, 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.[2,3]

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.[4–10] 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$_2$ chemisorp-

tion 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 $T_s \sim 700\,°C$,[11] 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,[4,8,9] 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.[12] 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 ($\sim 700\,°$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 Cameca MAC-2 analyzer and Al $K\alpha$ 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 2000CX 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 $\sim 800\,°$C in our system. The pressure during CaF$_2$ growth was typically $\sim 1 \times 10^{-10}$ 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 $T_s = 720\,°$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 $\langle 220 \rangle$ 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 im-

ages, 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
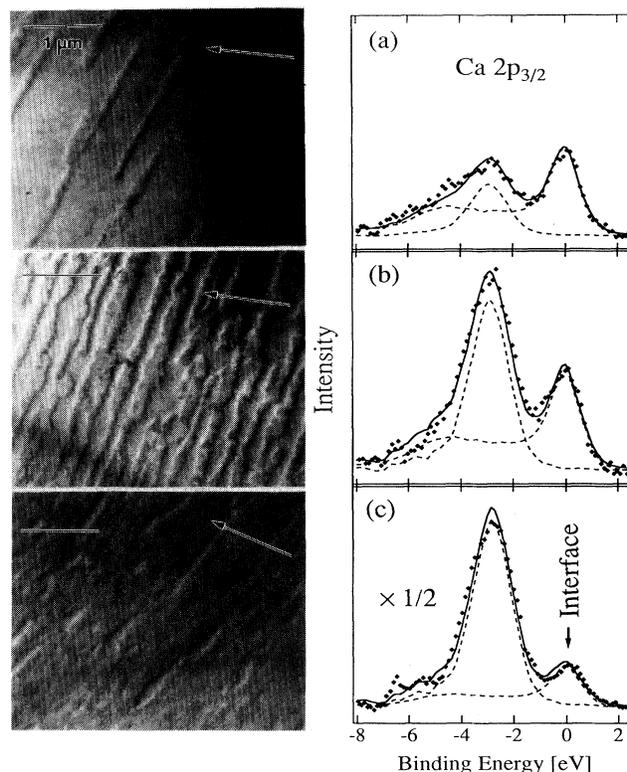

FIG. 1. Bright-field, two-beam, TEM micrographs and corresponding spin-orbit deconvolved Ca $2p_{3/2}$ core-level XPS data taken from CaF$_2$ films grown at 720 °C on Si(111): (a) Si-CaF layer$+24\pm5$ % coherent island coverage, deposition time of 12 s; (b) Si-CaF layer $+45\pm10\%$ coverage, 16 s; (c) Si-CaF layer $+88\pm5\%$ 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 $2p_{3/2}$.

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,[16] 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_s 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_s, 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 $T_s<550$ °C (Ref. 9) instead of the usual $T_s\sim700$ °C. The Ca $2p$ shift decreases from 2.8 eV at $T_s=720$ °C to 1.9 eV at $T_s=300$ °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.[9] 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
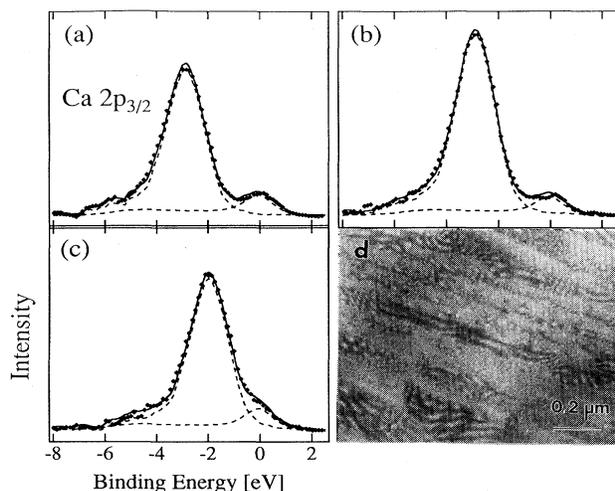

FIG. 2. Ca $2p_{3/2}$ photoemission from (a) a flat 4–5 TL CaF_2 film (thickness obtained with a CTR measurement), deposition time of 33 s, (b) an islanded sample with the same deposition time, (c) a flat 4–5 TL film grown at 300 °C, deposition of 32 s. (d) Bright-field TEM micrograph of sample in (b).

CaF$_2$ at 720 °C as a "template" for subsequent room-temperature growth,[21] 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 $d = 2.78$ Å, $a_T = 3.170$ 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 reported that ionic homoepitaxy on net neutral surfaces can occur at room temperature.[19] 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 unexpected. It is possible that the latent heats of condensation provide the deposited CaF$_2$ molecules with the necessary mobility.[22]

In conclusion, the transition from chemisorption to epitaxy can have fundamental implications for the heteroepitaxial growth of electronically dissimilar materials. 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
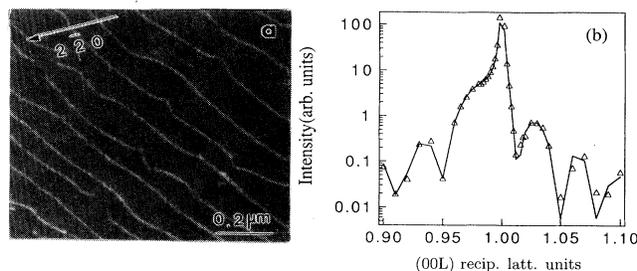

FIG. 3. (a) A weak-beam, dark-field image taken from a CaF$_2$-Si(111) film grown using the "template" method. The beam direction is close to [111]. The CaF$_2$ was deposited for 70 s at 720 °C followed by 210 s at 70 °C. (b) A CTR from a film grown using the "template" method, measured through the [111] 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.

and the bulk substrate. We believe these results have conceptual relevance for application in other heteroepitaxial systems.[23]

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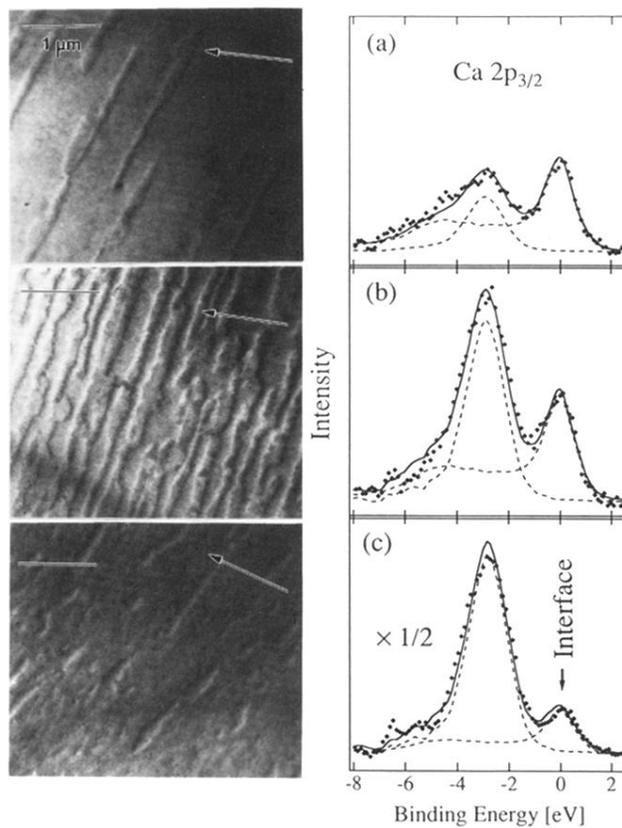
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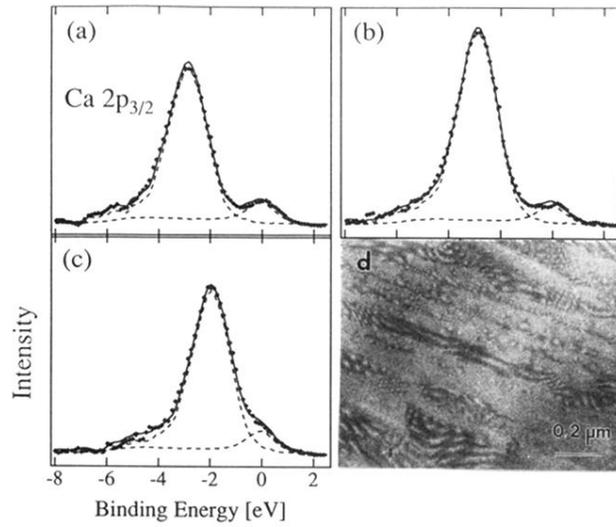
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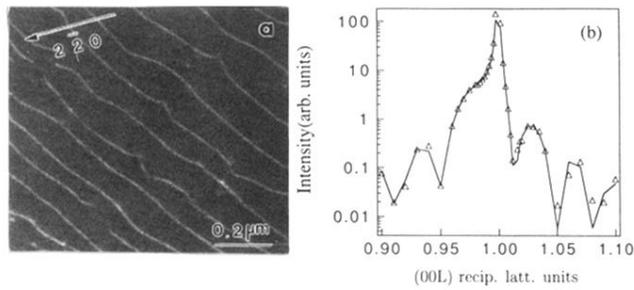
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