Two-Dimensional Structural Modulation in Epitaxial CaF_2 Overlayers on Si(111)

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(Received 25 September 1992; revised manuscript received 5 January 1994)

Using high-resolution x-ray diffraction a CaF_2 thin film epitaxially grown on Si(111) is found to exhibit an incommensurately modulated structure parallel to the interface. The overlayer consists of a triangular network of discommensurations, separating regions with two different site occupations of the interfacial Ca, $H3$ and $T4$. The 2D spatial modulation in CaF_2 is induced by the competition between the strong interfacial bonding and the bonding in the film. Remarkably, the in-plane lattice distortion generated at the interface propagates many atomic layers through the CaF_2 film.

PACS numbers: 68.35.Bs, 61.10.Lx, 68.55.Bd

In the last decade significant advances have been made in understanding the behavior of two-dimensional (2D) systems by studying the structure and properties of monolayer or submonolayer adsorbates weakly interacting with the substrate. A classic example has been the system Kr physisorbed on graphite [1,2]. Lately, attention has turned to systems where the monolayer-substrate interaction is stronger. Such systems are exemplified by Tl electrochemically adsorbed on Ag(111) [3], the reconstructed surface of Au(111) [4], and Pb [5] and Cu [6] chemisorbed on Si(111). Little is known, however, about the structural behavior of the systems with epitaxial overlayers which interact strongly with the substrate. In this paper, we report an x-ray-diffraction study of a CaF_2 thin film epitaxially grown on Si(111). We find that the thin CaF_2 film exhibits an incommensurate structure parallel to the heterointerface. The strong overlayer-substrate interaction (covalentlike bonding) at the interface induces a 2D spatial modulation of the overlayer. The interpretation of the x-ray diffraction pattern leads to a structural model involving a triangular network of discommensurations separating the overlayer regions with two different interfacial geometries. Remarkably, the in-plane lattice modulation waves, induced by the interfacial bonding, propagate many atomic layers through the CaF_2 film. This new insight into the interface and overlayer structures of the epitaxial systems may elucidate the interfacial electronic properties [7–9] as well as mechanisms that underlie thin film growth [10,11].

CaF_2 is an insulator material which can be grown epitaxially on Si(111) with excellent quality, due to the similar cubic lattice structure and close lattice match to Si (bulk lattice mismatch η_0=0.6% at room temperature). In the present study, a thin CaF_2 film was grown on Si(111) at 700 °C by means of molecular-beam epitaxy (MBE) [12], followed by rapid thermal annealing [7] to 850 °C for 30 s. The film was protected by an amorphous Si layer of a few tens of angstroms thickness before it was taken out of the MBE chamber. X-ray measurements were made *ex situ* under normal ambient conditions.

High-resolution x-ray glancing-incidence diffraction and reflectivity measurements were carried out at beam lines X22C and X22B, respectively, at the National Synchrotron Light Source. In glancing-incidence geometry, a radial resolution of 0.003 $Å^{-1}$ full width at half maximum (FWHM) and a transverse resolution of 0.001 $Å^{-1}$ FWHM were achieved using slits. We use a hexagonal coordinate system [4] to index reciprocal space. The H and K directions lie parallel to the Si(111) plane, as illustrated in Fig. 1(a). Open circles correspond to the positions of Si rods of scattering oriented normal to the surface or interface (crystal truncation rods [13]), which can be indexed by in-plane reciprocal-lattice vectors $\{\mathbf{G}\}$. Within the H-K plane the unit is $a^* = 4\pi/\sqrt{3}a = 1.889$ $Å^{-1}$, where a is the nearest-neighbor distance in

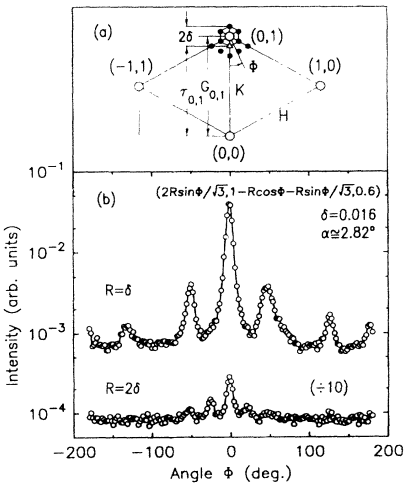

FIG. 1. (a) A schematic diffraction pattern of CaF_2/Si(111). Open circles are Si rods; the triangle and solid circles are CaF_2 rods. (b) Ring scans around (0,1) with radii of $R = \delta$ and 2δ. The angle Φ is shown in (a). α is the incident angle of x rays. Solid lines are guides to the eye.

0031-9007/94/72(15)/2430(4)$06.00

each Si(111) layer. Along the surface normal (L direction), the unit is $c^* = 2\pi/3d = 0.668$ Å^{-1}, where d is the Si(111) spacing.

A schematic diagram of the observed in-plane diffraction pattern of the CaF_2/Si(111) sample is shown in Fig. 1(a). Each Si rod is decorated with a multiplicity of rods arising from the CaF_2 overlayer. For clarity, only the CaF_2 rods around (0,1) are shown. The strongest CaF_2 rod, shown as a triangle at $(0,\tau_{0,1})$, is separated from the (0,1) rod by a wave vector $\delta = G_{0,1} - \tau_{0,1}$, incommensurate with the substrate periodicity, where δ is a direct measure of the average in-plane lattice mismatch ($\eta_{\|}$). Figure 1(b) shows two ring scans, taken in the $L = 0.6$ plane around circular paths centering at (0,1) with radii of $R = \delta$ and 2δ, respectively. The angle Φ is measured relative to the $[0,-1]$ direction. In the scan profile with $R = \delta$, the six peaks, separated by about 60°, correspond to the six rods close to (0,1) [14]. The five peaks in the scan with $R = 2\delta$, separated by about 30°, correspond to the additional satellite rods. The main CaF_2 peak is at $K < 1$, which results from the larger in-plane lattice spacing of CaF_2 as compared to that of Si. The fact that $\delta(=\eta_{\|}=0.016)$ is even larger than the bulk value $\eta_0(=0.006)$ can be attributed to the large thermal-expansion-coefficient mismatch [15] and implies that the CaF_2 overlayer is under an in-plane tensile strain of 1% ($\epsilon_{\|} = \eta_{\|} - \eta_0$).

The presence of satellite peaks cannot be understood on the basis of a homogeneously strained overlayer which would give rise to only the main overlayer peaks. The satellite rods in fact originate from the in-plane spatial modulation of the incommensurate overlayer. The hexagonal pattern of the main CaF_2 reflections implies that the strain field in the overlayer has a hexagonal symmetry. The thin film under strain can be viewed as a quasi-2D system in which the interactions within the overlayers compete collectively with the overlayer-substrate interaction. The consequence of such a competition is that the overlayer lattice is distorted from a uniformly strained structure and the atoms relax their positions under the influence of the substrate potential, resulting in a net reduction of the total strain energy. With these ideas in mind, the static structure of a modulated CaF_2 film can be discussed in analogy to the description of a pure 2D system [2,16]. We consider the overlayer to be a solid, with reciprocal-lattice vectors $\{\tau\}$, whose atoms are displaced by an interaction potential of the substrate with wave vectors $\{\mathbf{G}\}$. The corresponding diffraction pattern consists of main peaks at τ and satellite peaks at $\tau+\mathbf{G}$, a proper combination of the two sets of vectors. This assignment is in agreement with our observations [17].

To understand the structural modulation quantitatively, the system can be simplified to a one-dimensional (1D) problem by only considering the scans in one of the high-symmetry directions (say the K direction, [010]). Figures 2(a)–2(c) display three radial scans taken along

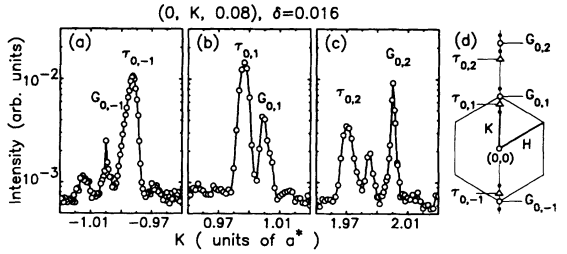

FIG. 2. Radial scans through (a) $(0,-1)$, (b) (0,1), and (c) (0,2) with $L = 0.08$. The peak separation is δ. Solid lines are drawn to guide the eye. (d) is a schematic of the H-K plane showing the positions of τ, G, and satellites (dots).

the K direction near $(0,-1)$, (0,1), and (0,2) [Fig. 2(d)] with $L = 0.08$. In addition to the main CaF_2 peaks τ and the sharp components at $K = -1$, 1, and 2, corresponding to the Si contribution G, several satellite peaks were also observed, which can be indexed by a combination of G and τ, or equivalently by $\tau+m\delta$ ($m = 0, \pm1, \ldots$) [17]. The existence of satellites and the peak intensities can be understood on the basis of 1D structural modulation of CaF_2 by Si in the $\langle\overline{1}20\rangle$ direction. Figure 3(a) shows a schematic of a 1D model of the CaF_2/Si(111) interface: Because of the strong interfacial bonding, the overlayer atom at the location nb (with respect to Si) is shifted by a displacement $y_n b$ ($b = \sqrt{3}a/2$). This 1D approximation considers only the atomic modulation in the $\langle\overline{1}20\rangle$ direction. In search of a possible modulation function, we have performed an extensive numerical analysis [17] by Fourier analyzing a variety of 1D modulated incommensurate lattices, each with 62 atoms in a superlattice ($\delta = 0.016 \approx 1/62$), to obtain the normalized intensity $I(K)=|\sum_{n=0}^{62}\exp(i2\pi K x_n)|^2$ where K is a 1D scattering vector in the [010] direction, and $x_n = n + y_n$ is the position of the nth CaF_2 unit cell with $n = 0, 1, \ldots, 62$ and y_n being a modulation function ($0 \le y_n \le 1$). We found that I(K) is rather sensitive to the atomic arrangement and the system could be best described by a double sine-Gordon (SG) soliton lattice model with

$$y_n = \frac{\pi}{5}\left\{A_1 \arctan\left[\exp\left(\frac{n-p_1}{s_1}\right)\right] + A_2 \arctan\left[\exp\left(\frac{n-p_2}{s_2}\right)\right]\right\}, \quad (1)$$

of which each term is a SG soliton (steplike) function [18] with a total lattice displacement A_i occurring over a certain region (FWHM$=2s_i$) at the position p_i in a superlattice ($i = 1, 2$).

Our numerical analysis reveals that the interfacial Ca atom has two preferential sites with respect to Si as illustrated in Fig. 3(a). This is in agreement with earlier x-ray standing wave results. For about a monolayer CaF_2 on Si(111), it was established [19] that under high temperature growth Ca atoms register preferentially at both the high-symmetry threefold hollow sites ($H3$) and

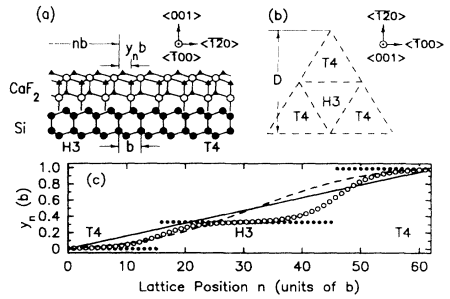

FIG. 3. (a) A 1D schematic (side view) of the CaF_2 lattice modulation by Si. $n + y_n$ gives the position of an interfacial Ca relative to Si. (b) A schematic (top view) of the domain wall pattern. Dashed lines represent discommensurations separating the two regions, $H3$ and $T4$. The dimension of the superstructure D is about 205 Å. (c) The modulation functions y_n versus the lattice position n. Model B, open circles; C, filled circles; D, dashed line; and E, solid line.

tetrahedral sites ($T4$). In our simulation, we investigated a system in which the CaF_2 unit cells locate at x_n, in the $\langle\bar{1}20\rangle$ direction, with a lattice shift y_n given by Eq. (1), in units of b. The optimum set of parameters, determined by comparing the calculated intensity ratios of the satellites to the main reflections, $I(\tau + m\delta)/I(\tau)$, with the corresponding values of the data, shown in Fig. 2 [Table I (B) and (A)], are $A_1 = \frac{1}{3}$, p_1=15.5, s_1=4.0; $A_2 = \frac{2}{3}$, p_2=47.0, and s_2=4.5. The function y_n with these parameters is plotted in Fig. 3(c) (open circles). It is evident that there are two plateaus with y_n=0 (or 1), and $\frac{1}{3}$ corresponding to $T4$ and $H3$ sites, respectively. The site transitions at p_1 and p_2 are gradual with FWHMs of $2s_1$=8 and $2s_2$=9 unit cells, respectively. The domain size ratio of $H3$ to $T4$ is roughly 1:1. Thus, the thin CaF_2 overlayer consists of two different sublattices in which Ca atoms register near $H3$ sites ($H3$ domain) and near $T4$ sites ($T4$ domain), separated by discommensurations (domain walls) where site configurations change from one to another. There exists a lateral strain modulation across the overlayer with the largest strain in the regions of domain boundaries. For comparison, three other trial functions y_n were plotted in Fig. 3(c) and the corresponding calculated intensity ratios were listed in Table I (models C–E): a lattice with commensurate domains and sharp walls (FWHM=1) at p_1=15.5 and p_2=46.5 (C: filled circles); a sinusoidal modulation with an amplitude 0.1b (D: dashed line); and a uniform incommensurate structure (E: solid line). It is clear that the calculated values of models C–E do not agree with the experimental results (A) at all.

For a 2D CaF_2 overlayer, the hexagonal symmetry of the diffraction pattern implies that there are three primary modulation wave vectors in the high-symmetry directions. In addition, the existence of scattering at $(-\delta, 1-\delta)$ and $(\delta, 1-2\delta)$, corresponding to peaks at Φ=±30° [Fig. 1(b), $R = 2\delta$], requires that modulation waves with primary wave vectors coexist in coherent regions of the overlayer. Therefore, in two dimensions, the domain walls form a triangular network in which each domain is surrounded by three domains of the other kind, as depicted in Fig. 3(b). The dimension of the superlattice, $D = 2\pi/\delta a^*$, is estimated to be about 205 Å while the correlation length ξ, deduced from the longitudinal FWHM of the main CaF_2 peak (ξ=2/FWHM), is about 220 Å, slightly larger than the unit cell of the incommensurate structure. Within each domain, the overlayer lattice is distorted in such a way that Ca atoms are pulled towards the nearby preferential sites. A detailed 2D displacement field of the overlayer atoms can, in principle, be obtained by measuring intensities of many main and satellite reflections. Its pattern may be similar to the 2D lattice distortions, characteristic of a "triple-**q**" state, in the charge-density-wave state of 2H-$TaSe_2$ [20] and in the low-temperature phase of neodymium [21].

TABLE I. Comparison of intensity ratio $I(\tau + m\delta)/I(\tau)$. A: experimental results (Fig. 2); B–E: calculated values for four models (for details, see text).

K=$\tau_{(H,K)} + m\delta$	$\tau_{(0,-1)}$			$\tau_{(0,1)}$			$\tau_{(0,2)}$		
m	-2	-1	1	-1	1	2	1	1	2
A: Exp. Data	0.06	0.11*	0.03	0.00	0.18*	0.02	0.00	0.44	0.10*
B: SG Solitons	0.07	0.11	0.04	0.04	0.11	0.07	0.00	0.90	0.20
C: Sharp Walls	0.67	0.59	0.00	0.00	0.59	0.67	1.84	19.8	11.5
D: Sine	0.00	0.26	0.18	0.16	0.25	0.00	0.67	0.74	0.00
E: Uniform	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

* Estimated intensities of broad components of the peaks.

It has been shown experimentally [7,8] and theoretically [9] that dielectric properties of a CaF_2/Si(111) interface depend sensitively on the detailed atomic bonding configurations. Previous correlation between the geometric and electronic structures of this interface, nevertheless, was based on atomic models in which only a single bonding site and no strain modulation were considered. The incommensurately modulated structure of CaF_2 suggests that Ca atoms can register at many possible sites on Si(111), corresponding to various strained bonding configurations. This new structure may help elucidate the electronic properties of the CaF_2/Si(111) interface. In addition, ordered misfit boundaries and overlayer strain gradients, observed in this system, are interesting behaviors which may be relevant to the "dislocation-related" electronic state [22] and the strain-induced 2D quantum confinement [23] in semiconductor systems.

We turn now to a description of the out-of-plane structure. In x-ray reflectivity studies, the scattering intensities were measured in the L direction at a fixed (H, K), an in-plane vector of the overlayer or substrate [4,17]. Figure 4(a) displays the nonspecular reflectivity along the main CaF_2 rod $(0, 1-\delta)$. The two intense peaks at $L = 1$ and 4 correspond to the CaF_2 Bragg reflections, which appear near the Si (0,1) rod due to the type-B CaF_2 orientation [24]. The sharp peak at $L = 5$ is the tail of the Si Bragg peak (0,1,5). The slight shift of the CaF_2 peaks away from the integers results from the perpendicular lattice mismatch: $\eta_\perp = -0.4\%$, implying that CaF_2

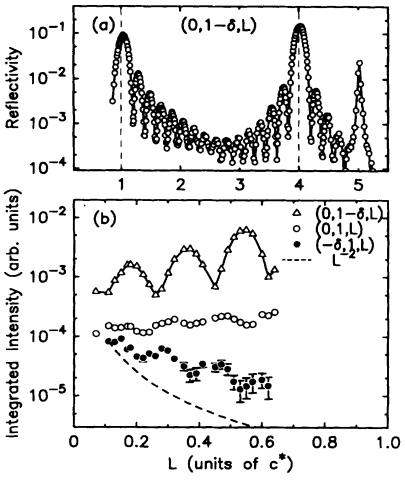

FIG. 4. Reflectivity profiles. (a) CaF_2 $(0, 1-\delta, L)$: Open circles are peak intensities. (b) Data points are integrated intensities obtained from scans through the corresponding rods. The dashed line corresponds to an L^{-2} variation. The solid line is a guide to the eye.

is under a 1% compressive strain ($\epsilon_\perp = \eta_\perp - \eta_0$) normal to the interface. The interference fringes arise from the finite thickness of CaF_2 which is estimated to be 51 Å ($\sim$ 16 CaF_2 layers), in agreement with 50 Å thickness determined by Rutherford backscattering spectroscopy.

To address the question of how many CaF_2 layers are subject to the in-plane lattice modulation, x-ray reflectivities of the main CaF_2 rod $(0, 1-\delta)$, and satellite rods (0,1) (also a Si rod) and $(-\delta, 1)$ were measured [Fig. 4(b)]. All data points are integrated intensities obtained from fits to scans through the corresponding rods. Open triangles correspond to the low-L section of the main rod [Fig. 4(a)] showing the interference fringes. Figure 4(b) shows that *all the satellite rods* also exhibit oscillations with *the same periodicity* as the main CaF_2 rod, in contrast to a smooth L^{-2} variation (dashed line) as expected for a model of a single-layer modulation. It is important to note that the satellite rods originate from the modulations in CaF_2. The common periodicity of the main and satellite rods indicates that the thickness of the modulated layer is almost the same as that of the grown CaF_2 film. Thus, the covalent Si substrate may practically be treated as a rigid solid free of distortion. It is clear that the spatial modulation waves, induced by the substrate potential at the heterointerface, are not confined in the interface region but propagate *through* the thin CaF_2 film. This surprising result suggests that the covalentlike Ca-Si bonding at the interface is stronger than the ionic Ca-F bonding in the film, which allows the interfacial interaction to compete with the collective interactions of a thin film containing many atomic layers. This behavior may be an important factor to consider in thin film growth [11,25], especially in 3D integration and in multilayered systems, because the structure and symmetry of an overgrown film may be influenced by the substrate through an intermediate layer.

In summary, we have presented the results of an x-ray scattering study of an epitaxial CaF_2 film on Si(111). The CaF_2 overlayer exhibits a 2D modulated incommensurate structure parallel to the interface and is composed of regions with interfacial Ca atoms at $H3$ and $T4$ sites, separated by a network of discommensurations. Remarkably, the in-plane modulation waves generated at the interface propagate many atomic layers through the CaF_2 film. This structural behavior can be understood on the basis of competing interactions between the atomic bonding at the interface and that in the film. Our results suggest that similar behavior may exist in other heteroepitaxial systems with small lattice mismatch, including metal-semiconductor interfaces, where the detailed atomic structures play a key role in the Schottky barrier height formation.

We would like to thank D. Gibbs, S.G.J. Mochrie, B.M. Ocko, and S.K. Sinha for useful discussions. Work performed at ANL is supported by the DOE Contract No. W-31-109-ENG-38 and at BNL by the DOE Contract No. DE-AC0276CH00016.

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