RHEED intensity oscillations observed during the growth of CaF_2 on Si(111)

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Analyses of reflection high-energy electron diffraction (RHEED) intensity changes observed during initial stages of heteroepitaxial growth of calcium fluoride (CaF_2) on Si(111) are presented. Layers obtained by deposition of CaF_2 on a hot (550 °C) substrate demonstrate a high-quality crystallographic structure. The state of the surfaces of growing layers is studied with the *in situ* combination of RHEED azimuthal plots and rocking curve. The intensity of the reflected beam is calculated by solving the one-dimensional Schrödinger equation. [S0163-1829(98)01020-0]

I. INTRODUCTION

Epitaxial fluoride materials can be used as the gate dielectric in field-effect transistors, in silicon-on-insulator structures, or in the tunneling junctions. Calcium fluoride is an insulator with a band gap of ~ 12 eV that grows in the fluorite structure with a lattice constant nearly equal to that of silicon (mismatch of 0.6% at room temperature). Because of the small lattice mismatch between CaF_2 and Si, calcium fluoride has been one of the most widely studied fluorides. Epitaxial growth of CaF_2 on Si has been actively studied for several years, and high-quality films have been grown on Si.[1–4] Typically, the molecular-beam epitaxy (MBE) technique is used and CaF_2 was grown epitaxially on Si(111) at 400–700 °C. The Si-CaF_2 interface also raises important problems about the interaction between a polar insulator with ionic bonding and a homopolar semiconductor with covalent bonding. The chemical, electronic, and structural properties of the Si-CaF_2 interface have been meticulously studied by Tromp and co-workers [medium-energy ion scattering, high-resolution transmission electron microscopy (HRTEM), low-energy electron microscopy, and transmission electron microscopy (TEM)].[5,6] Denlinger *et al.* (x-ray photoelectron spectroscopy and x-ray photoelectron diffraction),[7] Lucas, Loretto, and Wong [HRTEM, reflection high-energy diffraction (RHEED), and TEM],[8] and Sumiya, Miura, and Tanaka (ultrahigh vacuum–scanning tunneling microscope).[9,10] It has been concluded that CaF_2 dissociates to give CaF at the interface and various ordered Si-CaF structures have been observed at submonolayer coverages.

In this paper we present measurements of the intensity of the specularly reflected RHEED beam during MBE growth of CaF_2 on Si(111), which show clear oscillations, RHEED azimuthal plots[11] (the specular beam intensities are measured while rotating a sample around the axis perpendicular to the surface), and rocking curve (the intensity of one of the diffracted beams is measured for different glancing angles of the incident beam).

RHEED is an important *in situ* analysis technique, which is capable of giving quantitative information about the growth process and its control. Oscillations of specular-beam intensity were observed during MBE by Harris, Joyce, and Dobson.[12] Cohen *et al.*[13] explained the oscillations by means of the kinematic diffraction theory. Peng and Whelan[14] developed a practical computing procedure in the one-beam case and obtained RHEED oscillations with a phase shift. A one-dimensional potential $U(z)$ is found by averaging a three-dimensional potential $V(\mathbf{r})$ in planes parallel to the surface of the film. It is important that the potential $U(z)$ may be considered as the zeroth term of a Fourier series $\Sigma_{\mathbf{g}} V_{\mathbf{g}}(z)\exp(i\mathbf{g}\rho)$ (where ρ is the parallel component of $\mathbf{r}$ and $\mathbf{g}$ are the reciprocal lattice vectors normal to the surface) determined for the potential $V(\mathbf{r})$. This one-dimensional model of the scattering potential has been successfully used to interpret experimental RHEED oscillations. Mitura and Daniluk[15] reproduced frequency-doubling phenomena in RHEED oscillations observed during the growth of lead-indium alloy by dynamical calculation. Horio and Ichimiya[16] used the one-beam model for interpretation of experimental oscillations measured while depositing Ge atoms on a Ge(111) surface. Dudarev, Vvedensky, and Whelan demonstrated concepts of how to take into account incoherent scattering by statistical fluctuations of the atomic-site occupation with calculations of the specular-beam intensity.[17] Recently, Daniluk and co-workers used the one-beam model for interpretation of experimental oscillations measured while depositing Ge atoms on a Si(111) surface.[18,19] Very recently Daniluk *et al.* reproduced RHEED oscillations observed during reactive deposition epitaxy growth of YSi_{2-x} on the Si(111) surface.[20]

The epitaxial growth of CaF_2 is simulated by using a birth-death model as proposed by Cohen *et al.*,[13] and RHEED intensities are calculated within the framework of the general matrix formulation of Peng and Whelan[14] under the one-beam condition.[16,18] Under the one-beam condition, in which the azimuth of the incident beam direction varied around [112], the three-dimensional crystal lattice of Si(111) and CaF_2(111) growing layers can be regarded as a one-dimensional array of lattice planes parallel to the surface. In this condition, the crystal potential can be treated as a one-dimensional potential in the surface normal direction. This model has been used in order to analyze the diffraction measurements and to understand the dynamic processes of CaF_2 epitaxy.

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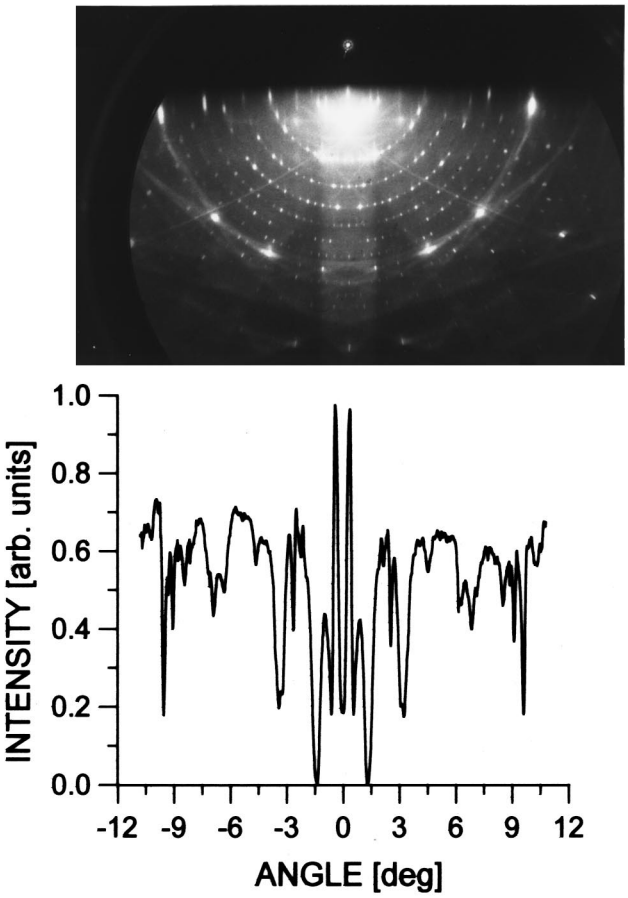

FIG. 1. Upper part: RHEED pattern of Si(111)-(7×7), room temperature. Electron energy is 18 keV, azimuth is [112], glancing angle is 2°. Lower part: azimuthal plot of Si(111)-(7×7). The value of the azimuthal angle 0° corresponds to the azimuth [11$\bar{2}$], glancing angle is 2°. About 50 points per degree were collected during the measurements of azimuthal plots.

II. EXPERIMENTAL TECHNIQUES

The CaF_2 layers were grown on low resistivity (3–6 Ω cm) *p*-type Si(111). Si substrate ($22\times5\times0.3\ mm^3$) were degreased in acetone, then dipped in a dilute HF solution (HF:methyl alcohol=1:10) immediately before putting into the chamber. A clean, well-ordered Si(111)-(7×7) surface was prepared by flashing Si wafers (in our system, 10 A, dc ~5 sec) in a vacuum $(2-3)\times10^{-10}$ hPa. Cleanness was confirmed by the existence of a very sharp (7×7) RHEED pattern. Figure 1 presents an experimental RHEED azimuthal plot and the RHEED pattern of the Si(111)-(7×7). Experiments start when the chamber base pressure reaches 1.0×10^{-9} hPa. Overlayers of calcium fluoride were deposited onto the clean Si(111) using evaporation by electronic bombardment of a Ta (tantalum) crucible for calcium fluoride. The thickness of the film was measured with an oscillating quartz-crystal frequency monitor. The calcium fluoride deposition rate was 0.1 Å/s. During RHEED measurements the energy of the incident electron beam was 18 keV. The divergence of the incident beam (i.e., the full width at the half maximum) could be estimated to be less than 0.1°. Absolute values of the glancing angle could be determined with a precision of about ±0.2°. Relative variations of the azimuth angle could be determined with a precision of about ±0.02°. We observed RHEED intensity oscillations for ultrathin films of CaF_2 during the growth on Si(111) in the [112] direction for the glancing angle equal to 2°. The value of the glancing angle corresponds to the 333 Bragg reflection for Si(111)-(7×7). Diffraction conditions (the 333 Bragg reflection and azimuthal angle varied around [112]) were especially chosen to reduce influence of surface structure.[18–20] This azimuthal direction corresponds to the one-beam condition. The state of the surfaces of growing layers is being researched with RHEED azimuthal plots and rocking curve. RHEED azimuthal plots were collected with the application of a stepped motor to change the azimuthal angle and a photodiode to detect the speculary reflected beam intensity. Signals from the photodiode were transmitted to a microcomputer. Additionally, a special detection system (charge-coupled-device-based, controlled with the microcomputer) enabled the overall RHEED patterns to be recorded.[11]

A typical result of the RHEED specular-beam-intensity oscillations measured during the growth of CaF_2 films on Si(111)-(7×7) surfaces at 550 °C for the glancing angle equal to 2° is shown in Fig. 4(a) (Sec. IV). The measurements of RHEED oscillations during the growth of CaF_2 were carried out in a broad range of temperature 200–700 °C, but we observed RHEED intensity oscillations only in a small temperature range, 550–600 °C. In this paper we deal with layers ~60 Å thick of CaF_2 deposited onto a Si(111).

III. THE DIFFUSIVE GROWTH

Cohen *et al.*[13] proposed several models of epitaxy; for our calculations we used the diffusive growth model of epitaxy. The process of the diffusive growth is described by the following set of coupled differential equations.[13,21]

$$\frac{d\theta_n}{dt}=\frac{\theta_{n-1}-\theta_n}{\tau}+k_n(\theta_{n+1}-\theta_{n+2})(\theta_{n-1}-\theta_n)-k_{n-1}(\theta_n-\theta_{n+1})(\theta_{n-2}-\theta_{n-1}). \quad (1)$$

In these equations θ_n is the coverage of the nth surface monolayers, τ is the deposition time of one monolayer, and k_n is the parameter that determines the coverage profile of the growing film surface (Fig. 2). Large values of k_n give rise to an effective mass transport from higher layers to lower layers. We assumed that growth started at $t=0$ sec and that τ was equal to 1 sec. The detailed explanation for Eq. (1) is presented in Refs. 13 and 21. The coverage evolution profiles for the diffusive growth model during the growth are shown in Fig. 2. In Fig. 2, the parameter $k_n=25$ (for all n) is used. Effectively about three surface monolayers are involved during the growth. The growth front is interrupted after deposition of 63 monolayers.

IV. RESULTS AND DISCUSSIONS

To carry out one-dimensional dynamical calculations we used the method of Peng and Whelan.[14] To determine the real part of the potential we used atomic coefficients of Ca, F, and Si atoms tabulated by Jiang and Li.[22] The imaginary part of the potential was assumed to be equal to 20% of the real part.[15,18–20] The introduction of the imaginary part of the

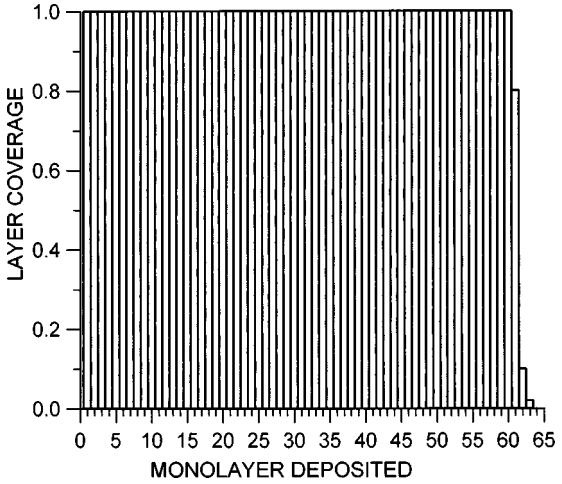

FIG. 2. The coverage profiles of the model of diffusive growth, for value of the parameter $k_n = 25$ (for all n).

potential is the realization of a simplified treatment of inelastic events (core electrons and phonons) that may happen while scattering fast electrons by the crystal. To determine a contribution of a partially full monolayer to the potential of a whole layer, we used the following formula:[15,18–20]

$$U(\theta,z) = \theta U(1,z), \tag{2}$$

where $U(1,z)$ means the potential after fulfilling the monolayer, and $U(\theta,z)$ means the potential of the growing monolayer. In all calculations we took the value of 18 keV for the electron energy and the value of 2.0° for the glancing angle.

Crystalline CaF_2 and Si have similar fcc (face-centered cubic) lattices, with a three-atom basis in the fluoride structure CaF_2, and a two-atom basis in the diamond structure Si. Let us turn now to a discussion of the structure of the Si(111)-CaF_2 interface, i.e., the Si-F-Ca-F structure (silicon-fluorine-calcium-fluorine) and the Si-Ca-F structure (silicon-calcium-fluorine). In the further part of our work we will employ these two models as model 1 and model 2, respectively. Figure 3 presents calculated crystalline potentials for growing CaF_2 layers on the Si(111), where part (a) presents model 1 and part (b) presents model 2 of the structure of the Si(111)-CaF_2 interface.

The results of one-beam calculations are shown in Figs. 4(b) and 4(c), together with the experimental results [Fig. 4(a)]. In the results presented below the following normalization was applied. For each set of experimental data; intensities were transformed according to the normalization formula[11,20] $I' = (I - I_{\min})/(I_{\max} - I_{\min})$, where I' and I are the intensities after and before the transformation, $I_{\min}$ and $I_{\max}$ are the intensity minimum and maximum in the set considered (before the transformation). The same procedure was applied in relation to the results of the calculations.

Figure 4(a) presents experimental RHEED oscillations during CaF_2 growth on a clean Si(111) surface. The irregular oscillations are clearly visible. We can see two distinct peaks here. The first one is relatively low and narrow (~ 2.5 Å). The width of this peak suggests that in the initial phase of epitaxy of CaF_2 on Si(111) a double Ca-F layer has been formed. The other peak is wide (~ 11 Å), which is the consequence of formation of three CaF_2 triple layers. Subsequently to this, the RHEED intensity rises and then remains constant at approximately the same level.

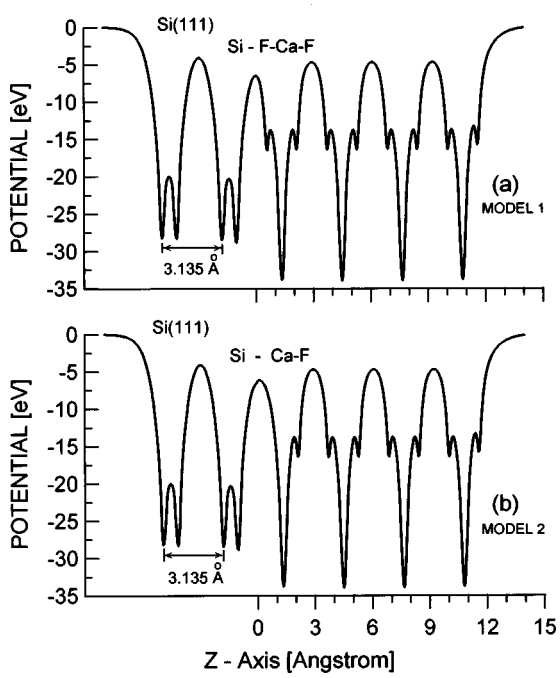

FIG. 3. One-dimensional (z direction) potentials of CaF_2(111)/Si(111). The following models were used in the calculations of Si(111)-CaF_2 interface: (a) Si-F-Ca-F, (b) Si-Ca-F.

Figure 4(b) presents the calculated oscillations of the RHEED intensity during the growth of CaF_2 layers on

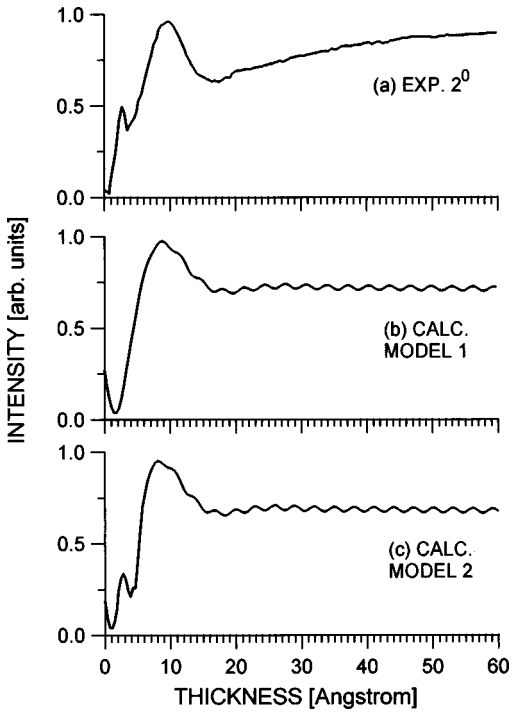

FIG. 4. RHEED intensity oscillations during the growth of CaF_2 on Si(111): (a) experiments, (b) calculated, $k = 25$, model 1 of the structure of the Si-CaF_2 interface, (c) calculated, $k = 25$, model 2 of the structure of the Si-CaF_2 interface. The values of the glancing angle are shown in the figure.

TABLE I. Summary of the parameters in the structural model 2 of the Si-CaF_2 interface, i.e., the Si-Ca-F structure (silicon-calcium-fluorine).

Si(111) lattice parameter	$c_{Si}=3.135$ Å
Interface spacing (middle of Si bilayer to Ca layer)	$d_{Si\text{-}Ca}=2.351$ Å
Ca layer to F layer spacing	$d_{Ca}-d_F=0.783$ Å
CaF_2(111) lattice parameter	$c_{CaF_2}=3.174$ Å

Si(111), when model 1 and Si-CaF_2 interface were used. Here, a characteristic oscillation mode is approximately the same as the one observed experimentally. What we can see is, however, the lack of the first, low peak and the fact that the other peak is wide (~14 Å), and has some internal structure, i.e., it is composed of a set of smaller peaks.

Figure 4(c) presents the calculated oscillations of the RHEED intensity when model 2 and Si-CaF_2 interface were used. What we can see here is the considerable agreement with the experiment. The calculated oscillations have the same character as the oscillations observed in Fig. 4(a). The first, smaller peak has been reproduced very well; the other, wider one (~11 Å) has also been observed. Subsequent to this, weak RHEED oscillations remain on a stable level with a period that is equal to one CaF_2 triple layer.

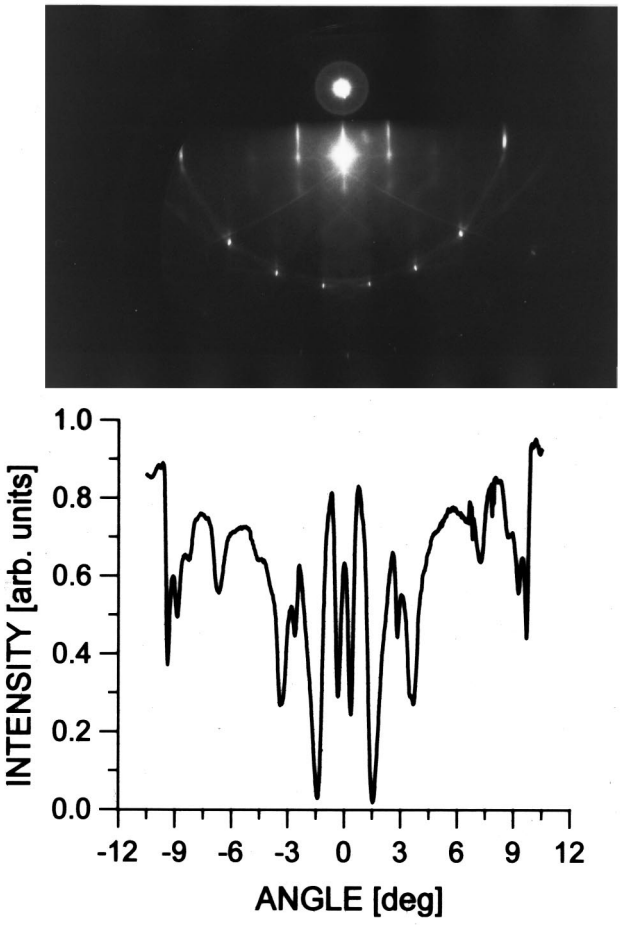

FIG. 5. Upper part: RHEED pattern of CaF_2 (60 Å thick) on Si(111)-(7×7), substrate temperature is 550 °C. Electron energy is 18 keV, azimuth is [112], glancing angle is 2°. Lower part: azimuthal plot of CaF_2 (60 Å thick) on Si(111)-(7×7). The value of the azimuthal angle 0° corresponds to the azimuth [112], glancing angle is 2°. About 50 points per degree were collected during the measurements of azimuthal plots.

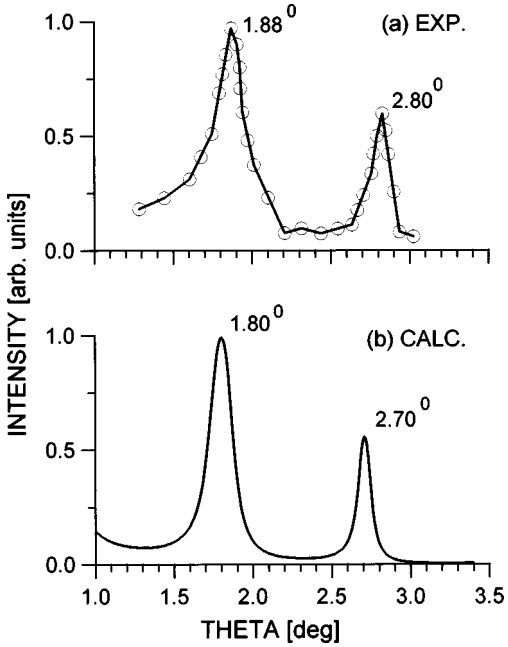

FIG. 6. Rocking curves of CaF_2 (60 Å thick) on Si(111)-(7×7): (a) experiments, electron energy is 18 keV, azimuth is [112], about 17 points per degree were collected during the measurements of rocking curve, (b) calculated. The values of the angles corresponding to the rocking curve maxima are shown in the figure.

A comparison of oscillations that have been experimentally observed during initial stages of heteroepitaxial growth of calcium fluoride on Si(111) with oscillations that have been calculated on the basis of two models of the structure of Si-CaF_2 interface shows that the greatest agreement with the experiment has been arrived at for model 2 [Fig. 3(b)] of the structure, i.e., Si-Ca-F (silicon-calcium-fluorine). It does comply with earlier papers[3–10] in which the authors considered the structure of the Si-CaF_2 interface. Table I presents the calculated parameters of the structure of the Si-CaF_2 interface. Theoretical reproduction of the changes in the RHEED intensity, which have been observed during the growth of CaF_2 layers on Si with the diffusion growth model where the growth is achieved by three incomplete monolayers, also confirms earlier conclusions that the growth of CaF_2 in high temperatures is the growth of the Volmer-Weber type.

The formation of CaF_2 layers with the MBE technique on a clean Si(111)-(7×7) surface has yielded very good results. Clear RHEED oscillations have been observed. The quality of these layers is very good, which is confirmed by the RHEED azimuthal plots and the RHEED pattern of the CaF_2 surface. Figure 5 presents an experimental RHEED azimuthal plot for the calcium fluoride layers (60 Å thick) that has been formed with the MBE technique, and corresponding RHEED pattern. On RHEED patterns only sharp spots on Laue rings are visible. For samples prepared with the use of MBE, RHEED patterns observed at the screen are much sharper and azimuthal plots include much more detail. Moreover, the quality of the surface has been verified thanks to

classic rocking curve measurements. Figure 6(a) shows an experimentally measured rocking curve for CaF_2 layers (60 Å thick). The values of the angles correspond to the rocking curve maxima for the 333 and 444 Bragg reflections, respectively. Figure 6(b) shows a dynamically calculated one-beam rocking curve for CaF_2 layers (60 Å thick) when model 2 and Si-CaF_2 interface were used, i.e., the Si-Ca-F structure. We can see that the measured positions of Bragg reflections and the calculated ones tally very well. The difference between them does not exceed 0.1°, which remains within the limits of experimental error. Assuming that results of one-beam calculations reproduce actual experimental situations, we can conclude that for a fixed, real surface we can find Bragg reflections experimentally with a precision of about $\pm 0.1°$.

V. CONCLUSIONS

The results presented in this work are significant because of two reasons. First, changes in the RHEED intensity during the growth of ultrathin CaF_2 films on a clean Si(111) surface at high temperatures have been measured; in other words, the dynamics of the growth of these layers has been investigated. Second, when dynamically modeling the RHEED oscillations that were observed for CaF_2 with two models of Si-CaF_2 interface, the greatest agreement was achieved for the Si-Ca-F structure of the interface. It has been therefore confirmed that, for deposition at high temperatures, the CaF_2 molecule dissociates to give Ca-F at the interface, and that Ca atoms react directly with Si atoms to form Si-Ca bonds.[3–10]

The measured rocking curve for CaF_2 layers confirms that it is feasible to produce CaF_2 layers of a very high quality, and the quality of their surface can be investigated by means of classic RHEED techniques.

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