Low-temperature interface structure of CaF_2/Si(111) studied by combining x-ray standing waves with component-resolved photoemission

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X-ray photoelectrons excited by x-ray standing waves (XSW) are used to study the atomic structure of the low-formation-temperature (370°C) interface between CaF_2 and Si(111). The core-level shift of the photoemission spectra of the Ca atoms at the CaF_2/Si interface is used to distinguish interface Ca atoms from atoms in other (bulk) layers in the XSW measurements. Therefore, we obtained quantitative structure information specific to the buried CaF_2/Si interface avoiding some of the ambiguities of XSW. Even at the low growth temperatures used here, the interface is well ordered, with interface Ca atoms exclusively adsorbed on T_4 sites. The majority of the interface layer has CaF stoichiometry. The CaF_2 films consist of domains with type-*A* and type-*B* orientation.

The heteroepitaxial system calcium fluoride (CaF_2)/silicon (Si) serves as a model system for atomistic processes during the epitaxy of two very dissimilar materials such as the ionic crystal CaF_2 and the covalently bound Si.[1] The growth of CaF_2 on Si was expected to be relatively straightforward because both materials have similar structures and lattice constants (0.5% lattice mismatch at room temperature). Investigations of the growth and structure of CaF_2/Si, however, have shown that this system involves several complications. For instance, the interface chemistry leads to CaF_2 dissociation at high growth temperatures.[2] It is assumed that incomplete interface reactions at temperatures below $\sim 650\,°C$ provoke poorly ordered interface layers.[3] Therefore, CaF_2 is usually deposited at high temperatures to grow high-quality epitaxial films on Si.[4] The interface structure of CaF_2/Si(111) grown at high temperatures ($\geqslant 650\,°C$) has been investigated extensively using different experimental techniques such as x-ray photoelectron spectroscopy (XPS),[2,5] x-ray photoelectron diffraction (XPD),[6–8] x-ray diffraction,[9–11] medium energy ion scattering,[12] and x-ray standing waves (XSW).[3]

Although most studies on the interface structure of CaF_2/Si(111) are focused on films grown at high growth temperatures because of their high crystalline quality, lower growth temperatures are desirable for technological applications due to the improved homogeneity[13] and electrical properties[14] of the CaF_2 films. These applications include, e.g., nanoelectronic devices[15,16] exploiting the large (12.1 eV) CaF_2 band gap and Si-based optoelectronics.[17] Therefore, we investigated the interface structure of ultrathin CaF_2 films grown on Si(111) at 370 °C with XSW.

XSW is a powerful experimental technique to study the atomic structure of adsorbates.[18] In particular, it can be used to precisely determine the position of atomic species regularly adsorbed on a surface with respect to the substrate lattice planes within 1% of the lattice plane spacing. In studies of the structure of multilayer films or buried interface layers, however, XSW suffers from an ambiguity of the results: atoms of the same species but different adsorption sites cannot be distinguished and thus cause intermixed signals. Atoms on different sites are, however, surrounded by different environments causing shifts of their core-level photoemission spectra. As proposed before,[18] these core-level shifts can be used to obtain separate inelastic signals from atoms on different adsorption sites.[19] Here, we present an application of this technique to the quantitative structure analysis of an interface.

The standing wave field is generated by the interference between the incident and the Bragg-reflected x-ray beam. Its phase ν is varied from 0 to π by scanning the x-ray energy over the Bragg condition. This shifts the standing wave pattern by half a lattice plane distance. Photoemission of atoms in the standing wave field reflects the resulting local intensity variation by a change in its intensity, the inelastic signal Y,

$$Y \propto 1 + R + 2\sqrt{R} f_c \cos(\nu - 2\pi\Phi_c). \tag{1}$$

R denotes the x-ray reflectivity. The coherent position Φ_c and the coherent fraction f_c are given by

$$f_c e^{i\Phi_c} = \frac{1}{N} \sum_n e^{2\pi i \vec{H} \cdot \vec{r}_n}, \tag{2}$$

where $\vec{H}$ denotes the scattering vector of the corresponding Bragg reflection and $\vec{r}_n$ the position of the nth atom. Φ_c describes the position of the atoms contributing to Y while f_c provides a measure for their order. Perfectly ordered atoms on equivalent adsorption sites lead to a coherent fraction of
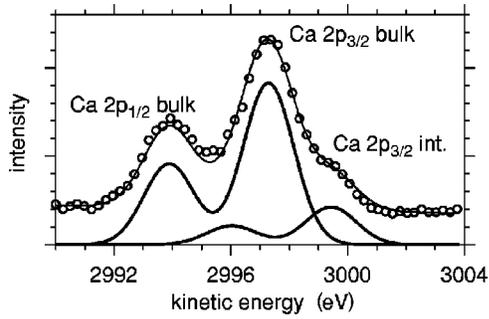
FIG. 1. XPS spectrum of the Ca $2p$ emission obtained for 1.7 TL CaF$_2$ deposited at 370 °C on Si(111) by using 3350 eV x rays. The $p_{1/2}$-$p_{3/2}$ splitting is clearly resolved. The curves are fitted using the sum of two Gaussian curves for both bulk and interface contributions.

1, while multiple nonequivalent adsorption sites or random disorder (e.g., thermal vibrations) reduce f_c.

The atomic positions obtained by XSW may not be unique for two reasons: First, there may be several adsorption sites for one atomic species. This leads to a reduced coherent fraction and an averaged position is obtained by the coherent position [see Eq. (2)]. Second, atomic positions can only be obtained modulo the spacing of the Bragg planes used for the measurement. Therefore, it is impossible to distinguish between atoms in different layers, e.g., atoms at the interface and atoms in the overgrowing layers. This restriction can be circumvented if atoms in different layers can be distinguished by their inelastic signals. In this paper, we present an application of XSW by using XPS to determine the structure of buried interfaces.

It is well known that the binding energy of Ca core-level electrons at the interface is decreased by 2.4–2.7 eV depending on the detailed atomic configuration at the interface.[8,20] This core-level shift (CLS) is attributed to different environments of atoms at the interface in comparison to bulk atoms.[20] Distinguishing interface and bulk contributions to the Ca $2p$ photoelectron signal (cf. Fig. 1) one can determine simultaneously the structure of the interface and the overgrowing film, respectively, by means of XSW. The ratio of bulk and interfacial Ca, however, cannot be determined by the intensity ratio of the correspondent XPS peaks because in the measurement geometry used here both photoelectron diffraction effects and the film morphology can influence the intensity ratio. Nevertheless, the XPS data are consistent with the results of Denlinger et al.[7]

We deposited (1.7 ± 0.4) triple-layer (TL) CaF$_2$ to ensure that the interfacial layer is completely closed and does not exhibit any reconstruction as has been reported for the sub-

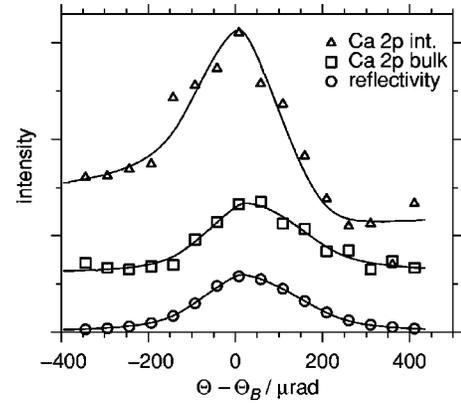FIG. 2. XSW results using the (220) Bragg reflection for 1.7 TL CaF$_2$ deposited at 370 °C on Si(111). The circles, squares, and triangles show the measured values for the x-ray reflectivity, Ca $2p$ bulk, and Ca $2p$ interface photoemission components, respectively. The curves show the fits of the data with the clear difference between the inelastic signals Y of the bulk compound and interface compound.

monolayer range at higher growth temperatures.[2,21] One triple-layer denotes one molecular CaF$_2$ layer consisting of one Ca layer embedded between two F layers (7.8×10^{14} molecules/cm^2).

The XSW measurements were carried out at the BW1 undulator beamline of the Hamburg synchrotron radiation laboratory at Deutsches Elektronensynchrotron in Hamburg, Germany. Both sample preparation and XSW measurements were done in situ without breaking the ultrahigh vacuum (UHV). Si samples were chemically cleaned before insertion into the UHV system. After annealing at ~550 °C for 12 h, the oxide was removed by increasing the temperature upto 850 °C for 10 min. CaF$_2$ was evaporated from an electron-beam-heated graphite crucible at the deposition rates of ~0.1 TL/min, controlled by quartz microbalances.

The results obtained from the XSW data (c.f. Fig. 2) for a 1.7 TL CaF$_2$ film grown at 370 °C are shown in Table I. The x-ray energy used for all measurements is 3350 eV. Coherent positions and coherent fractions are determined separately for both Ca atoms at the interface and in higher layers by using the interface and bulk contribution to the Ca $2p_{3/2}$ photoemission, respectively. XSW measurements were carried out using both (111) and (220) Bragg reflections to determine atomic positions via triangulation.

The high coherent fractions obtained for the interface Ca atoms point to a well-ordered interface. The coherent position $\Phi^{111}_{\text{Ca}_{\text{interf.}}} = 0.94$ in [111] direction is used to compute the average interface distance $d = (0.294\pm0.013)$ nm, which is

TABLE I. XSW results for 1.7 TL CaF$_2$ deposited at 370 °C on Si(111). Φ_c and f_c were obtained for two different Bragg reflections [(111) and (220)].

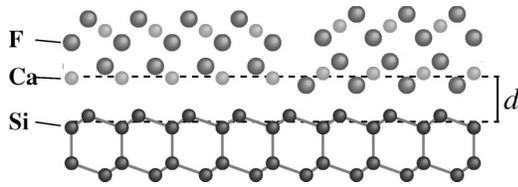| Inelastic signal	$\Phi_c^{(111)}$	$f_c^{(111)}$	$\Phi_c^{(220)}$	$f_c^{(220)}$
Ca $2p_{3/2}$ bulk	0.96 ± 0.01	0.77 ± 0.02	0.22 ± 0.04	0.13 ± 0.04
Ca $2p_{3/2}$ interf.	0.94 ± 0.01	0.82 ± 0.04	0.39 ± 0.02	0.95 ± 0.19
F $1s$	0.20 ± 0.01	0.27 ± 0.02	0.42 ± 0.02	0.16 ± 0.03

FIG. 3. Schematic model of the atomic arrangement at the CaF_2/Si(111) interface showing both type-*B* (left) and type-*A* orientation (right) with CaF and CaF_2 stoichiometry at the interface, respectively.

the spacing between the topmost Si lattice plane, i.e., the plane in the middle of the topmost Si bilayer, and the first Ca layer, assuming that the topmost Si layer is not relaxed (see Fig. 3). In connection with the (220) coherent position $\Phi_{Ca_{interf.}}^{220} = 0.40$ this shows that interface Ca atoms adsorb exclusively on T_4 sites.

In contrast to the interface, the interpretation of the XSW results for the bulk is not straightforward. In particular, the coherent fraction $f_{Ca_{bulk}}^{220}$ needs a more complex interpretation. CaF_2 can grow on Si(111) in two different orientations: type *A* and type *B* where the CaF_2 lattice is rotated by 180° around the [111] direction. Type-*A*-oriented CaF_2 films are observed only for low growth temperatures and are metastable.[1,22] The coherent position of the bulk Ca atoms in [111] direction equals approximately the coherent position of the interface Ca atoms. This is consistent with CaF_2 growing in a bulklike structure on the interface layer and is independent of the CaF_2 orientation. In contrast to the [111] direction the XSW results obtained using the (220) Bragg reflection exhibit a strong dependence on the film orientation. Neither pure type-*A* nor type-*B* orientation is consistent with the XSW data presented here. Therefore, the measured values for $\Phi_{c_{bulk}}^{220}$ and $f_{c_{bulk}}^{220}$ can be explained only by assuming a mixture of type-*A*- and type-*B*-oriented domains with (25 ± 12)% of the CaF_2 film grown in *A*-type orientation.

In the bulk CaF_2 lattice only two nonequivalent F atom positions exist with respect to the (111) lattice planes: F atoms residing 1/4 of the Ca interlayer distance below and above the Ca layers. If the number of F atoms below and above the Ca layers is equal, the coherent fraction of the F atoms vanishes, because the F interlayer spacing is almost exactly half the Si lattice plane distance. The measured coherent fraction f_F^{111} of the F atoms, however, has a finite value of 0.27. This is expected for an unbalanced occupation of the upper and lower F layer. Using f_F^{111}, the occupation ratio can be determined. The resulting coherent position mainly reflects the majority site position. From the measured Ca position, values of $\Phi_F^{111} = 0.19 \pm 0.01$ and $\Phi_F^{111} = 0.69 \pm 0.01$ are expected for a predominant occupation of the upper or lower F layer, respectively. Our data yield $\Phi_F^{111} = 0.20 \pm 0.01$ and $f_F^{111} = 0.27 \pm 0.02$, in excellent agreement with deficient F in the lower F layer. Taking into account a total deposit of (1.7 ± 0.4) TL CaF_2 and assuming no desorption of F from the upper F layer, the measured coherent fraction of F yields a value of (0.28 ± 0.16) ML for the amount of F found at the lower interface F layer. This value

represents an upper limit since the disorder contribution to reducing the coherent fraction cannot be determined separately.

During the initial growth stage, the fully coordinated CaF_2 molecules react with the Si surface, removing the (7×7) reconstruction for deposition above $\sim 200\,°C$. Here, several reactions may occur:[1] (i) adsorption of CaF_2 molecules, (ii) dissociation of CaF_2 with both Si—Ca—F and Si—F bonding, (iii) Si—F bonding with Ca evaporation, and (iv) Si—Ca—F bonding with F desorption.

The last case occurs at temperatures above $\sim 650\,°C$. Ca evaporation [case iii)] seems to be suppressed by the rather strong bonding between Si and Ca. On one hand, XPD measurements show no evidence for ordered F atoms below Ca atoms before second layer nucleation for CaF_2 films grown at 450 °C.[7] Furthermore, it is reported that the interface layer contains only $\sim 2/3$ ML Ca.[6] This behavior can be explained by case (ii) with Si—F species blocking $\sim 1/3$ of the adsorption sites. On the other hand, at 370 °C we observed a mixture between type-*A* and type-*B* orientations. The film orientation is determined by the interface structure.[22] While the Si—CaF structure leads to type-*B* orientation (high temperatures), the overgrowth of both non-dissociated Si-CaF_2 [case i)] and Si-F covered areas [case ii)] may cause type-*A* orientation. Structures of the Si-F-CaF_2 type, however, can be excluded by our XSW data, because they are inconsistent with the values of f_c^{111} for bulk Ca atoms. In conclusion, both the first case and the second case with an additional rearrangement of the Si—F areas during second layer growth may apply to the submonolayer regime. At least, for coverages sufficiently larger than 1 TL and growth temperatures below 600 °C we propose an interface consisting of both Si—CaF and Si—CaF_2 domains.

The Ca adsorption site at the interface was subject to controversial discussions in literature. Both unique T_4[10,12] as well as H_3/T_4 mixtures[3,23] were suggested for films grown at high temperatures. For the interface of CaF_2/Si films grown at 370 °C we showed that Ca atoms adsorb exclusively at T_4 sites. Even taking a relaxation of the outermost Si layer into account, the interface spacing $d = (0.294 \pm 0.013)$ nm measured by XSW for films grown at 370 °C, is larger than the value of 0.262 nm determined by Tromp *et al.* with MEIS for 1 TL CaF_2 grown at 770 °C[12] (the outward relaxation of the outermost Si layer of 0.0125 nm observed by MEIS is included in the 0.262 nm as it cannot be determined by XSW). This larger interface spacing can be explained by an incomplete dissociation of the CaF_2 molecules at lower temperatures, or by relaxation of the topmost Si plane. This results in CaF and CaF_2 domains, with an increased interface spacing in CaF_2 areas (c.f. Fig. 3).

In this paper, we present an application of XSW employing XPS to study the structure of a buried interface. This technique is not restricted to one particular system. Most heteroepitaxial systems involving disparate materials show clear CLS of atoms at the interface. Even the position of surface atoms may be determined by XSW, if the CLS of the surface atoms is sufficiently large to be experimentally resolved. Thus using a high-resolution photoelectron spectrom-

eter in conjunction with a third generation synchrotron radiation source opens the possibility to determine surface and interface structures with the accuracy of XSW but reduced ambiguities. In addition we stress that this technique is important to study buried interfaces whose structure may differ from uncovered monolayers. For instance, we observed a strong coverage dependence for the structure of CaF_2 submonolayers on Si(111) with XSW.[24]

In conclusion, the CaF_2/Si(111) interface grown at 370 °C consists of a mixture of CaF and CaF_2. The atoms at the interface itself are well ordered with Ca adsorbed on T_4 sites. Even at these low temperatures the majority of the interface consists of CaF. These results contradict previous publications assuming the need for high growth temperatures to establish a well-ordered interface structure.[3,12] Therefore, CaF_2 films with high crystalline quality can be grown on Si(111) at rather low temperatures, avoiding problems with inhomogeneous growth of CaF_2 films at high temperatures.[13]

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[1] M. A. Olmstead, *Thin Films: Heteroepitaxial Systems* (World Scientific, Singapore, 1999), Chap. 5, p. 211.

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

[3] J. Zegenhagen and J. R. Patel, Phys. Rev. B **41**, 5315 (1990).

[4] H. Ishiwara and T. Asano, Appl. Phys. Lett. **40**, 66 (1982).

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

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

[7] J. D. Denlinger, E. Rotenberg, U. Hessinger, M. Leskovar, and M. A. Olmstead, Phys. Rev. B **51**, 5352 (1995).

[8] E. Rotenberg, J. D. Denlinger, M. Leskovar, U. Hessinger, and M. A. Olmstead, Phys. Rev. B **50**, 11 052 (1994).

[9] C. A. Lucas, G. C. L. Wong, and D. Loretto, Phys. Rev. Lett. **70**, 1826 (1993).

[10] C. A. Lucas, D. Loretto, and G. C. L. Wong, Phys. Rev. B **50**, 14 340 (1994).

[11] K. G. Huang, J. Zegenhagen, J. M. Phillips, and J. R. Patel, Phys. Rev. Lett. **72**, 2430 (1994).

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

[13] J. Wollschläger, H. Pietsch, and A. Klust, Appl. Surf. Sci. **130-132**, 29 (1998).

[14] C. Cho, H. Liu, B. Gnade, and T. Kim, J. Vac. Sci. Technol. A **10**, 769 (1992).

[15] M. Watanabe, T. Funayama, T. Teraji, and N. Sakamaki, Jpn. J. Appl. Phys., Part 2 **39**, L716 (2000).

[16] M. Watanabe, Y. Iketani, and M. Asada, Jpn. J. Appl. Phys., Part 2 **39**, L964 (2000).

[17] F. Bassani, I. Mihalcescu, J. C. Vial, and F. A. d'Avitaya, Appl. Surf. Sci. **117/118**, 670 (1997).

[18] J. Zegenhagen, Surf. Sci. Rep. **18**, 199 (1993).

[19] C. Sánchez-Hanke, V. Eteläniemi, A. Hille, G. Materlik, and E. G. Michel, Surf. Sci. **482-485**, 1283 (2001).

[20] E. Rotenberg and M. A. Olmstead, Phys. Rev. B **46**, 12 884 (1992).

[21] G. C. L. Wong, C. A. Lucas, D. Loretto, A. P. Payne, and P. H. Fuoss, Phys. Rev. Lett. **73**, 991 (1994).

[22] S. Ohmi, K. Tsutsui, and S. Furukawa, Jpn. J. Appl. Phys., Part 1 **33**, 1121 (1994).

[23] K. G. Huang, J. Zegenhagen, J. M. Phillips, and J. R. Patel, Physica B **221**, 192 (1996).

[24] A. Klust, Ph.D. thesis, Universität Hannover, Berlin, 2001.