The Rigaku Journal
Vol. 13/ number 2/ 1996

CONTRIBUTED PAPERS

X-RAY SCATTERING FROM SURFACES AND INTERFACES AND ITS APPLICATION TO THE CHARACTERIZATION OF CaF_2/Si(111) INTERFACES

J. HARADA

The University of Electro-communications, Chofu 182, Japan

I. TAKAHASHI AND Y. ITOH

Department of Applied Physics, Nagoya University, Nagoya 464-01, Japan

N. S. SOKOLOV, N. L. YAKOVLEV, Y. SHUSTERMAN AND J. C. ALVAREZ

loffe Physico-Technical Institute, St. Petersburg 194021, Russian Federation

A survey of X-ray scattering techniques developed so far is presented keeping in mind that the appearance of the next generation of synchrotron radiation sources makes such techniques one of the promising probes for *ex situ* and *in situ* characterization of the surface and the interface of an epitaxially grown crystal. On the basis of the intensity formula given by one of the present authors [J. Harada, Ultramicroscopy 52 (1993) 233], it is shown that diffuse scattering associated with the crystal truncation rod is closely related to the local atomic arrangement on a surface. Our current X-ray scattering studies on CaF_2/Si(111) films grown by the MBE method are presented and the growth condition of the four types of interface structure found in CaF_2/Si(111) is discussed. A hydrogen-terminated Si(l 1 1) surface was found to be a promising substrate for the low-temperature growth of CaF_2 films.

1. Introduction

Because of the extremely weak interaction of X-rays with materials compared with electrons, X-ray diffraction techniques might be considered to be less effective for the characterization of a crystal surface, compared with, for example, LEED and RHEED. However, several distinct advantages of X-rays need to be considered: X-ray diffraction provides quantitative structural information on an atomic scale with respect to the surface and interface; the data analysis can be carried out straight away on the basis of the kinematical theory of diffraction, which is free from the complications associated with multiple scattering, seen in the cases of LEED and RHEED; X-ray techniques are nondestructive. Certain deficiencies associated with X-ray diffraction techniques can be removed by using synchrotron radiation sources and further improvements in both precision and range of application are possible with the appearance of the next generation facilities. It is thus timely to promote a better understanding of a number of fundamental problems yet to be solved in the even of X-ray scattering from crystal surfaces and interfaces, and also to determine the range of application in the characterization of epitaxial films grown by MBE, MOCVD and other methods.

In this paper we firstly review our X-ray scattering technique developed so far as one of the promising probes for the characterization of growth surfaces and interfaces [1-4] and then we present structural study of CaF_2/Si(111) films grown by the MBE method. This is one of our recent application studies of X-ray scattering, in which we attempt to make clear the relationship between the various structures so far reported for the CaF_2/Si(111) interface [5-10] and their crystal growth conditions [11-13].

2. Observation of CTR Scattering

Our X-ray diffraction technique in the studies of interfaces is simple oscillation photography using imaging plates in combination with a synchrotron

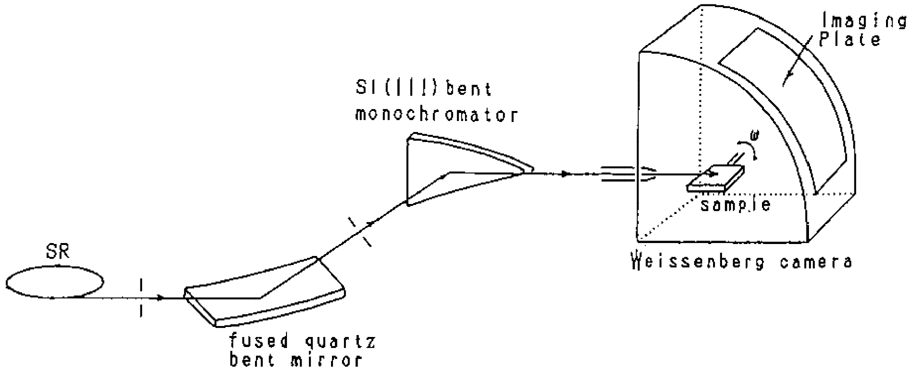

Fig. 1 Experimental arrangement for the observation of X-ray surface scattering by using an imaging plate in conjuction with synchrotron radiation.

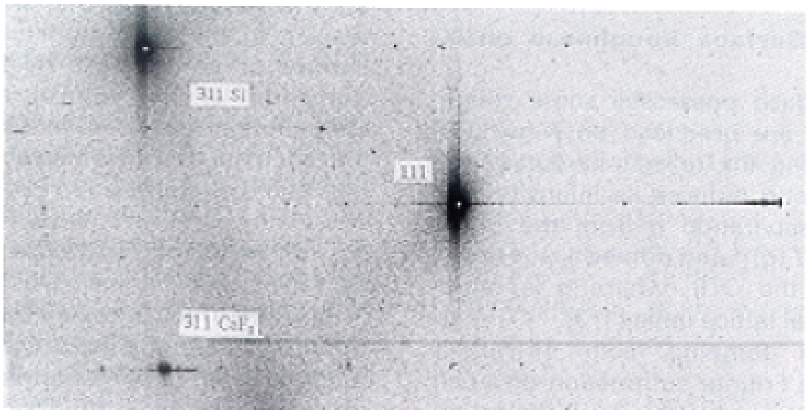

Fig. 2 Oscillation photograph taken from a CaF_2/Si(111) surface with one hour exposure time. The needle-like shaped scattering from each Bragg point is the CTR scattering and that from the direct spot shows the change of reflectivity with scattering angle.

radiation source [2]. The imaging plate is a kind of two-dimensional area detector which has been developed by Fuji Photo Film Co. It has several advantages such as high detective quantum efficiency and a wide dynamic range of 1-10^5 and so on. It will be referred to as IP, hereafter. We also use a four-circle diffractometer with an analyzer crystal of Si(111) for high precision measurements [14]. A schematic diagram of the experimental setup, installed at BL–6A_2 of Photon Factory, KEK (Tsukuba) is shown in Fig. 1. It consists of a bent mirror, a bent Si(111) monochromator and an oscillation camera. Since four IP cassettes of different radius and also several collimators of different sizes are provided, it is possible to select a suitable combination to fit the desired resolution in reciprocal space. We have used the Fuji BA100 system for read-out of image data from an exposed IP so that the pixel size of read-out data is 0.1 x 0.1 mm^2 [2].

A typical example of observation of surface scattering by using an IP, the result obtained from a B-type CaF_2 film on a Si(111) surface, is shown in Fig. 2. The photograph was taken by oscillating the sample around the [112] crystallographic axis from almost zero angle (ω=O) up to the 311 Si Bragg angle during one hour exposure. On the figure the three needle-like shaped scatterings elongated from each Bragg spot along the direction perpendicular to the crystal surface are the crystal truncation rod (CTR) scatterings. We can also see the change of reflectivity with scattering angle near the direct spot. In general mirror reflection-type CTRS, such as the CTR through the 111 Bragg point and the reflectivity curve in Fig. 2, provide the information about the stacking of atomic layers along the direction normal to the surface, while non-mirror reflection-type CTRs are sensitive to the lateral arrangement of atoms in the interface as well. Fairly strong diffuse scatterings seen around each Bragg point are thermal diffuse scattering (TDS) due to low frequency acoustic phonons in bulk Si crystals. The thermal diffuse scattering contribution is readily calculated provided that elastic constant data are available. Thus, the comparison of the CTR intensity with TDS makes it possible to convert the intensity into absolute units, where "absolute units" means that the intensity is converted to a ratio of the intensity of the incident X-ray beam. The observation of CTR scattering from a Si(111) sample on such an absolute scale showed excellent agreement with the predictions based on the kinematical diffraction theory [4]. Thus, the approximation based on the kinematical diffraction theory was justified for predicting CTR scattering by this experiment. Furthermore, it became possible to estimate the coverage of an epitaxial film on any substrate crystal as the CTR scattering from the substrate can be used as the reference scattering.

3. Effects of Surface Roughness on X-Ray Scattering

If a crystal surface possesses some roughness, two effects are produced on X-ray CTR scattering, including the reflectivity curve. The sharp CTR scattering reduces its intensity with the increase of separation *q* from the Bragg point by a factor $|\Gamma(q)|^2$ and diffuse scattering is generated along the CTR, where *q* is represented in reciprocal lattice units [1, 3].

The roughness damping factor $|\Gamma(q)|^2$ is given by a simple Fourier summation of a pair correlation function $<\gamma_p\gamma_p>$, where γ_p is the coverage of the terrace with step height *p* on a surface, i.e.,

$$\Gamma|(q)|^2 = \sum_{p=0} \left\langle \gamma_p \gamma_p \right\rangle \exp(2\pi ipq), \text{ With}$$

$$\sum_{p=0} \gamma_p = 1 \tag{1}$$

The Debye-Waller-like factor, $\exp(-4\pi^2(\Delta p^2)q^2)$ is often used instead, for the analysis of CTR, but it is an approximation for a Gaussian distribution of γ_p around the average step height, if interpreted on the basis of Eq. (1). This approximation is usually valid only for the limited range of small q as discussed in Ref. [1]. In the analysis of the surface and the interface roughness of CaF_2/Si(111), therefore, we employed a formula given in Refs. [15, 16], where the atomic concentration near the surface and the interface is approximated to recover to the bulk value in an exponential form, so that two parameters were introduced.

On the other hand, the diffuse scattering due to surface roughness in give as

$$I(q_x, q_y, q_z) = N\gamma_0(1-\gamma_0) f(K)^2 \sum_m \sum_n \alpha_{mn}, \quad \times \cos\left[2\pi(mq_x + nq_y)\right] \tag{2}$$

where N is the number of the effective lattice sites illuminated by X-rays, γ_0 the coverage of the top surface and α_{mn} the Warren-Cowley short range order (SRO) parameters defined for the atomic arrangement of a surface. Eq. (2) is of exactly the same form as that of the SRO diffuse scattering for a binary alloy system [17] except for the two-dimensional nature in the reciprocal lattice. The intensity distribution of the diffuse scattering forms diffuse columns along the direction perpendicular to the surface in the reciprocal lattice. It is expected from Eq. (2) that the diffuse intensity does not decrease so rapidly with the increase of q_Z. From Eq. (2) we see that we can obtain the SRO parameters with respect to the local atomic arrangement on a surface or an interface by taking the Fourier transform of the diffuse scattering [181. It should be noted here that Eq. (1) is valid within a framework of the two-level model for the surface and the interface [3].

4. Growth of Epitaxial Films of CaF_2/Si(111)

Recently much attention has been paid to the growth of heteroepitaxial CaF_2/Si(111) from the point of view of fundamental science and also in a variety of application for industrial use, because this interface consists of the ionic CaF_2 crystal and the covalent Si substrate. The growth of epitaxial films of CaF_2 on a Si(111) substrate is, however, relatively easy by means of molecular beam epitaxy (MBE), owing to the close lattice matching: 0.6% mismatch at room temperature. Our samples were grown by using several MBE systems of the A.F. Ioffe Physico-Technical Institute. After chemically cleaning the surface, the Si(111) wafer is heated up to 1250°C for 1 min in the growth chamber. After confirming the surface cleanness by the appearance of sharp 7x7 reflections in the high-energy electron diffraction (RHEED) pattern, we start the layer-by-layer growth by evaporating CaF_2 molecules on the structure and monitoring the RHEED oscillations. It turned out that the following two-step growth technique is most effective in preparing a variety of samples.

In this technique we deposit first a few molecular layers at some initial substrate temperature and then the succeeding layers at different substrate temperatures. We examined two different temperatures for making such a buffer layer: one at 750-770°C as a high-temperature growth mode and another at less than 200°C as a low-temperature growth mode. It is possible to grow the main part of the film at any substrate temperature, if it is below 700°C. But we have selected mostly two different temperatures; 500-700°C in one case and less than 200°C in another. As a general tendency, the low-temperature growth of the main film enables one to grow thicker CaF_2 layers, due to the smaller lattice mismatch with the Si substrate than that of high-temperature growth at 500-700°C. Using this two-step growth technique, we can obtain for example, 12 nm pseudomorphic $_{\mathrm{CaF2}}$ layers which correspond to 38 TL (triple layers) of CaF_2. However, needless to say, it is essential to prepare firstly, a good quality thin buffer layer, in order to grow CaF_2/Si(111) epitaxial films with good quality.

5. X-Ray Characterization of CaF_2/Si(111) Epitaxial Films

Two epitaxial relations exist between the CaF_2 film and the Si(111) substrate. As illustrated in Fig. 3 they are referred to as type-A and type-B structures, depending on whether the CaF_2 film is grown in the same orientation or in the opposite orientation, with a 180° rotation about the surface normal to that of the Si substrate [19, 20]. It is easy to distinguish these two types of epitaxial relation by looking at an oscillation photograph. The structural parameters that can be determined from X-ray analysis are the interface spacing d and the lateral atomic stacking between the CaF_2 film on the Si substrate as well as the interlayer spacing, a_1 of the CaF_2 film. In this paper we define the interface spacing d (in Å) as the distance from the middle of the top Si double layer to the first Ca layer in the CaF_2 film as shown in Fig. 3.

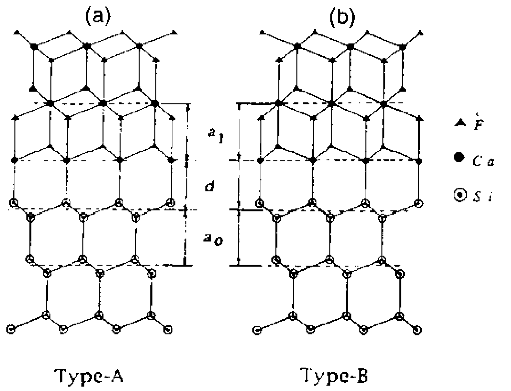

Fig. 3 Two types of epitaxial relations of the CaF_2/Si(111) interface: (a) for type-A and (b) for type-B. The notations of interlayer spacings are shown.

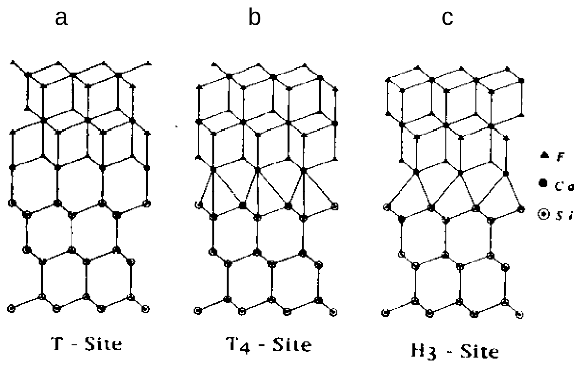

Fig. 4. Three possible atomic sites for Ca atoms at the interface of type-A epitaxial films: (a), (b) and (c) for the T, T_4 and H_3 site, respectively. The same atomic sites occur in type-B epitaxial films. CaF_2 molecules are illustrated to be dissociated to CaF.

In Fig. 4 the lateral atomic configuration at the interface based on a type-A film is schematically shown. This is the same for a type-B film. As illustrated there are three possible high-symmetry sites on the Si substrate: the site at the top Si atom on the first Si layer, the site on the three-fold symmetry site at the top of the second Si layer and the site above the hollow site with three-fold symmetry at the top of a third Si layer. They are referred to as T site, T_4 site and H_3 site, respectively. In the figure CaF is illustrated as to be dissociated from CaF_2 molecules at the interface based on the results confirmed so far for type-B samples [6, 7, 9, 11, 21].

Surfaces and interfaces are not necessarily ideally flat. We, therefore, need another two parameters characteristic of each, as discussed in Sections 3 and 4: that is the relative concentration of molecules at the surface and the interface ρ_i and the characteristic depth of the region near the surface and the interface ξ_i, where the suffix *i* stands for surface or interface. Those parameters are included in the calculation of the structure factors $F_{Si}(K)$ and F_{CaF2},(K) respectively, for the Si substrate and the CaF_2 film [15].

On the basis of the kinematical diffraction theory the intensity profile of Si-CTR will be modulated by the existence of the CaF_2 film as [22]:

$$I_{CTR}(K)=|F_{Si}(K)+ QF_{CaF2}(K)\exp(iKd)|^2, \qquad (3)$$

Table 1 Parameters refined by three CTRs for the sample of (CaF_2, 10 nm 10°C/CaF_2, 2nm 750°C/Si(111)).

CaF_2/Si(111) interface		
Interface spacing	d	4.580 Å
Atomic site	T, T_4 or H_3 site	T site
CaF_2 film		
Lattice parameter	a_1	3.174 Å
Number of layers	n	37
Quality of crystal	Q or (δ^2)	0.0619 $Å^2$
Interface roughness		
Concentration	ρ_i	99.1%
Characteristic depth	ξ_i	2.322 Å
Surface roughness		
Concentration	ρ_i	35.1%
Characteristic depth	ξ_i	5.422 Å

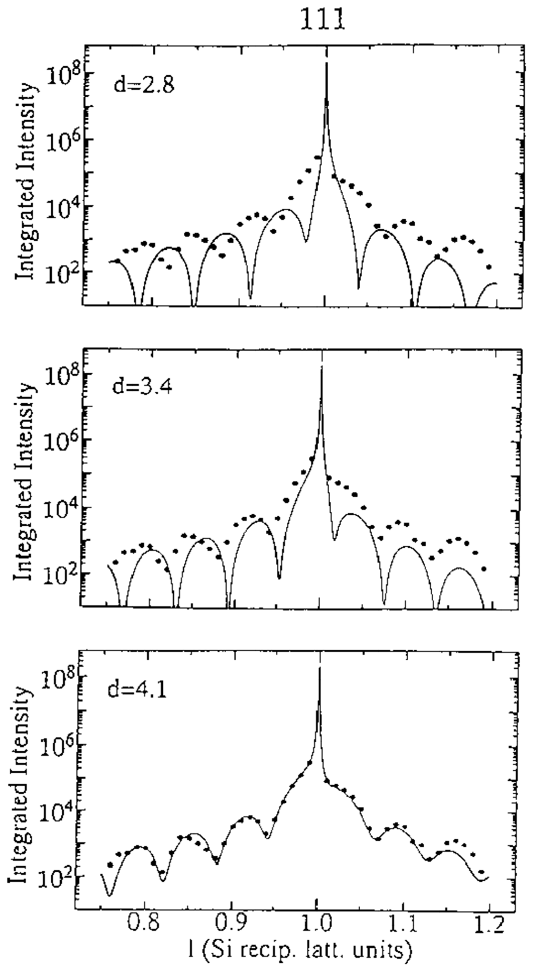

Fig. 5 Comparison of the intensity modulation of the Si(111)-CTR due to type-A epitaxial CaF_2 films with calculations. Solid curves are calculations based on three different interface spacings *d* (in Å), where all other parameters are fixed to the same values. By this fitting the sample is identified to be a type-A film with a long interface of d=4.10 Å.

where d is the interface spacing defined in Fig. 3 and Q is a parameter we introduced to describe the crystalline quality of the CaF_2 film representing the coherent contribution from the CaF_2 films to the CTR. Q may be given to be in the form of the static Debye-Waller factor, $\exp[-2\pi^2<\delta^2>(\sin\theta/\lambda)^2]$, $<\delta^2>$ being the mean squares static displacement due to some irregularity in the atomic arrangement such as defects in the film [16].

The number of parameters we can refine in the X-ray analysis is, therefore, all together eight in addition to the parameter representing the lateral site which is shown in Table 1. Our analysis showed that all the parameters are well determined by using a least squares fitting procedure, when several CTR intensity profiles including both mirror- and nonmirror-type CTR, are analyzed simultaneously. In Figs. 5 and 6 we demonstrate two examples to show how CTR intensity profiles are sensitive to the parameters of interface spacing d and atomic site, where we selected data one each for type-A and type-B samples.

One of the results obtained from such a simultaneous analysis of three CTR intensity profiles is listed in Table 1 where the growth condition of the sample is (CaF_2, 10nm 10°C/CaF_2, 2nm 750°C/Si(111)) so that the sample is of type-B epitaxy. The average lattice spacing of a CaF_2 film normal to the surface is 3.174 Å, which is slightly larger than that of the bulk crystal (3.155 Å). A slight expansion of lattice spacing of the CaF_2 film along the normal to the surface means that the film is deformed in pseudomorphic structure, as the result of matching the lateral lattice spacing to that of the Si substrate [23]. This value is in good agreement with the prediction based on Poisson's expansion. The mean-square static displacement (δ^2) is 0.0619 $Å^2$, indicating good crystalline quality of the sample. For the roughness parameters at the interface we have ρ_i=99.1% with ξ_i=2.322 Å (less than the lattice spacing of Si), ensuring a very high quality of the interface for this film. On the other hand, ρ_s at the surface is given to be 35.1% with ξ_s=5.422 Å. ξ_s is larger than the lattice parameter, indicating that the

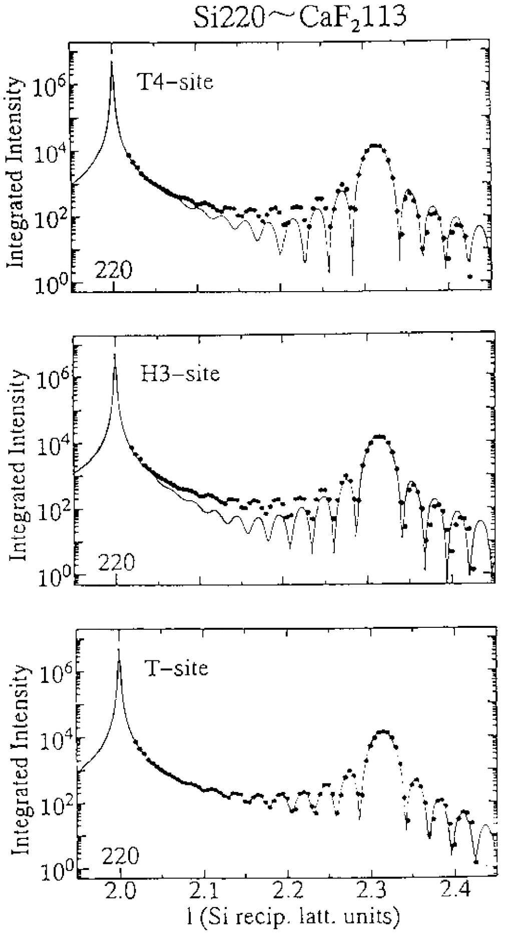

Fig. 6 Comparison of the intensity modulation observed along the line from the Si 220 Bragg point to the CaF$_2$ 113 point with calculations. Solid curves are calculations based on three different atomic sites, where all other parameters are fixed to the same values. This sample is identified to be type-B film with a long interface of d=4.60 Å.

rough region at the surface is more than 1 ML (monolayer). The density at the *n*th CaF$_2$ layer is calculated as 35% at n=37, 64% at n=36, 80% at n=35, 90% at n=34 and almost 100% for less than n=33. The interface distance d=4.583 Å indicates the sample to be of “long” interface. As discussed in Ref. [23] this value is too long to accept as a physically reasonable structure. The detailed structure has not yet been understood although it has been suggested that there may be another layer in this interface. X-ray scattering is not sensitive enough to reveal its details at this stage.

6. The Interface Structures of Epitaxial Films and Their Growth Conditions

We summarize here the results obtained for all the samples we have examined by using X-ray CTR scattering in connection with their growth conditions. First of all we can say that it is possible to grow both types of epitaxial films, type-A and type-B films, by using the two-step growth technique. In general we can obtain type-A epitaxial films if a thin buffer layer is prepared first at a temperature less than around 200°C regardless of the temperature at which the main part of the film is grown. As for type-B films, we can also obtain them if we prepare a thin buffer layer at a high temperature, something like 750-770°C. This is also independent of the temperature for the growth of the main part of the film.

The interface distances d observed are classified into two groups, depending crucially on the temperature of the second growth step at which the main part of CaF$_2$ film is deposited. That is, d=2.82-2.87 Å, for one group of samples grown at a temperature above 600°C and d=4.2-4.6 Å for another group obtained at a temperature lower than 200°C. Those two structures may be referred to as “short” and “long” interface films or interface structures. The existence of such structures having “short” and “long” interfaces is in agreement with what Lucas et al. [8] have pointed out for type-B films, although the relationship with their growth process has not been clarified. Instead they found that the relatively thin type-B samples of “short” interface are unstable and transform into films with “long' interface with time.

The existence of such an interesting transformation was confirmed for type-B films by our study but we revealed that it depends not only on aging time but also on the growth temperature of the main part of the film. Our recent test of two structures showed very interesting results, which were made with 5 ML by initial growth at 700°C and followed by 32 ML growth at 20°C in one case and at 500°C in the other case. Both of the as-grown films were confirmed to be of “short” interface, but the former had changed into that of “long” interface while the latter sample kept a “short” interface after three weeks. With other additional evidence we come to the conclusion that the transformation from “short” to 'long" interface originates from the quality of the film. We interpreted that the film formed at a low temperature is usually unstable, because it contains many point defects, presumably vacancies. The defects may diffuse to the

Table 2 Four possible interface structures of CaF_2/Si(111) and their crystal growth conditions.

Two-step growth		Structure			
First step a few layers	Second step main layers	Type A or B	Short or Long	Site of the Ca atom	References
Low temp.	Low temp.	A	Long	T site	[25]
Low temp.	High temp.	A	Short	Unknown	
High temp.	Low temp.	B	Long	T site	[26]
High temp.	High temp.	B	Short	T_4 site T_4 site + H_3 site	[5,6,8] [10]

interface with time and finally cause atomic rearrangement at the interface [24].

As far as the lateral atomic configuration at the interface is concerned, many studies have so far been performed, but only for the type-B films with "short" interface. There are three reports concluding that the high-symmetry site on the substrate is the T_4 site, by ion scattering experiments [5, 6] and by X-ray CTR analysis [8], and one report that a mixture of T_4 and H_3 sites is involved by X-ray standing wave analysis [10]. Our examinations for both the type-A and type-B films with "long" interface showed different structure as seen from Fig. 6, in which the non-mirror-type CTR scattering is reproduced only by the configuration due to a T site [9, 25]. Similarly, the best fit to the observations was also obtained for the T site, for a type-A sample. The relationships between the interface structures of CaF_2/Si(111) films and their growth processes are summarized in Table 2.

An interesting point seen in our data is that there is a significant variation in the interface distances d observed; the short interface distance d is distributed from 2.835 to 3.24A depending on the sample and there is some correlation with crystalline quality Q and also with its life time until the change to the "long" interface. We have observed that the interface distance is getting shorter for annealed samples, independent of whether the sample is of type-A or type-B. This observation would be related to the XPS result that there are Si-F bonds at the interface formed at low temperature and depletion of interfacial fluorine occurs when the CaF_2 layer is annealed [26]. We can also understand the reason why the interface distances so far reported are not in good agreement with one other.

7. Related Topics to the Growth of CaF_2/Si(111) Films

In order to see the influence of Si(111) 7x7 reconstruction on the quality of an epitaxial film, an attempt was made to grow a CaF_2 film of 15 ML thickness on a hydrogen-terminated Si(111) l x l surface. The analysis of the CTR profile near the Si 111 Bragg reflection showed that the structure was of type B with short interface and furthermore it was very stable even for four months after MBE growth. This result differs from the report given by Lucas et al. [8] that the characteristic life time is very short and less than one day for similar thin films grown on a Si(111)7x7 surface. This result suggests that there is a strong influence of H termination on the stability of the structure of the short interface.

Acknowledgements

This work was supported by the Photon Factory, KEK under the proposal No. 93-G268 and also the Grants-in-Aid for Scientific Research on Priority Areas, Nos. 030243105 and 04227105 from the Ministry of Education, Science and Culture, Japan. The authors are most grateful for the support by the Japan-FSU Scientists Collaboration Project in Physics for 1994 of the JSPS. Russian scientists wish to express their gratitude for support from the International Science Foundation Grant No. NUL000 and the Grant of the Russian Foundation for Fundamental Studies No. 95-02-04141-a. The computer calculations were mostly performed by using the Nagoya University Computing Center. The facilities of the Information Processing Center of the University of Electro-communications was also most helpful.

References

[1] J. Harada, Acta Cryst., **A48**, 764 (1992).

[2] T. Shimura and J. Harada, J. Appl. Cryst., **26**, 151 (1993).

[3] J. Harada, Ultramicroscopy, **52**, 233 (1993).

[4] T. Shimura and J. Harada, Physica, **B198**, 195 (1994).

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

[6] M. Katayama, B. V. King, E. Nomura, and M. Aono, Progr. Theoretical Phys. Suppi., **106**, 315 (1991).

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

[8] A. C Lucas, D. Loretto, and G. C. L. Wong, Phys. Rev., **B50,**14340 (1994).

[9] N. S. Sokolov, T. Hirai, K. Kawasaki, S. Ohmi, K. Tsutui, S. Furukawa, 1. Takahashi, Y. Itoh, and J. Harada, Jpn. J. Appl. Phys., **33**, 2395 (1994).

[10] J. Zegenhagen and J. P. Patel, Phys. Rev., **B41**, 5315 (1990).

[11] L. J. Schowalter and R. W. Fathauer, J. Vac. Sci. Technol., **A4**,1026 (1986).

[12] H. Mizukami, A. Ono, K. Kawasaki, S. Ohmi, K. Tsutui, and S. Furukawa, Mater. Res. Symp. Proc., **237**, 1394 (1992).

[13] N. S. Sokolov, S. V. Novikov, and N. L. Yakovlev, Proc. lnt. Conf. on Insulating Films on Semiconductors, Liverpool, April, p. 203 (1991).

[14] N. Kashiwagura, Y. Kashihara, M. Sakata, J. Harada, S. W. Wilkins, and A. W. Stevenson, Jpn. J. Appl. Phys., **26**, L2026 (1987).

[15] Y. Kashihara, K. Kawamura, N. Kashiwagura, and J. Harada, Jpn. J. Appi. Phys., **26**, L1029 (1987).

[16] T. Shimura and J. Harada, Proc. 2nd ROC-Japan Joint Seminar on Crystallography, Taipei, p. 29 (1992).

[17] J. M. Cowley, Diffraction Physics, 2nd ed. (North-Holland, Amsterdam, 1981).

[18] L. Schwartz and J. B. Cohen, Diffraction from Materials, 2nd ed. (Springer, Berlin, 1987).

[19] C. C. Cho, H. Y. Liu, B. E. Grande, T. S. Kim, and Y. Nishioka, J. Vac. Sci. Technol., **A10**, 769 (1992).

[20] S. Omi, K. Tsutsui, and S. Furukawa, Jpn. J. Appl. Phys., **33**, 1121 (1994).

[21] J. L. Batstone, J. M. Pillips, and E. C. Hunke, Phys. Rev. Lett., **60**, 1394 (1988).

[22] I. K. Robinson, and D. J. Tweet, Rep. Progr. Phys., **55**, 599 (1992).

[23] C. A. Lucas and D. Loretto, Appl. Phys. Lett., **60**, 2071 (1992).

[24] N. L. Yakovlev, J. C. Alvarez, Yu. V. Shusterman, N. S. Sokolov, Y. Itoh, 1. Takahashi, and J. Harada, Extended Abstract of Symposium on Nanostructures, St. Petersburg, June (1995).

[25] Y. Itoh, 1. Takahashi, A. lchimiya, J. Harada, and N. S. Sokolov, J. Crystal Growth, in press.

[26] M. A. Olmstead, R. L. G. Uhberg, R. D. Bringam, and R. Z. Bachrach, Phys. Rev., **B35**, 7526 (1987).

(This paper was originally carried in the Journal of Crystal Growth, Vol. 163 (1996) 31-38. It was reprinted here by the courtesy of ELSEVIER SCIENCE B. V., its copyrighter and Dr. J. Harada, its author, who currently works at Rigaku Corporation as Director of X-ray Research Lab.)