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LETTER TO THE EDITOR

Macrosteps on $CaF_2(111)$

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Abstract

Growth topographies of $CaF_2(111)$ after molecular beam growth of CaF_2 at $T = 1055$ K for different saturation ratios $S > 1$ and layer thickness were inspected by atomic force microscopy (AFM). Growth steps one triple layer high run mostly in $\langle 110 \rangle$ directions, where those of type I prevail. Macrosteps resulting from a step bunching of triple layer steps are observed only for the $\langle 110 \rangle$ directions. Macrosteps resulting from a pile-up of type I triple layer steps are steeper than those from type II steps. This can be attributed to a theoretically predicted attractive interaction between type I steps at distances closer than 1 nm.

1. Introduction

CaF_2 is a material of great current interest. Thin epitaxial layers are deposited on semiconductor materials, above all on Si, as protecting and buffer layers [1]. Large crystals are grown to fabricate optical components for the 157 nm lithography [2]. Of great importance in such applications is the degree of surface perfection. Often a very smooth surface is required to allow further epitaxial growth of semiconductors on CaF_2/Si or to prevent the scatter of light beams at surface imperfections [3].

In a broader research project we are currently investigating the growth and evaporation of CaF_2, both from experimental and from theoretical viewpoints. Among these investigations we have performed atomic force microscopic (AFM) studies of the development of the surface topography of $CaF_2(111)$ from room temperature up to free evaporation [4] and of the {111} faceting occurring at polished $CaF_2(100)$ [5], as well as theoretical studies of the adsorption and surface diffusion of the CaF_2 molecule on $CaF_2(111)$ [6]. Further studies of growth and evaporation of $CaF_2(111)$ by molecular beam methods are in progress and will be published

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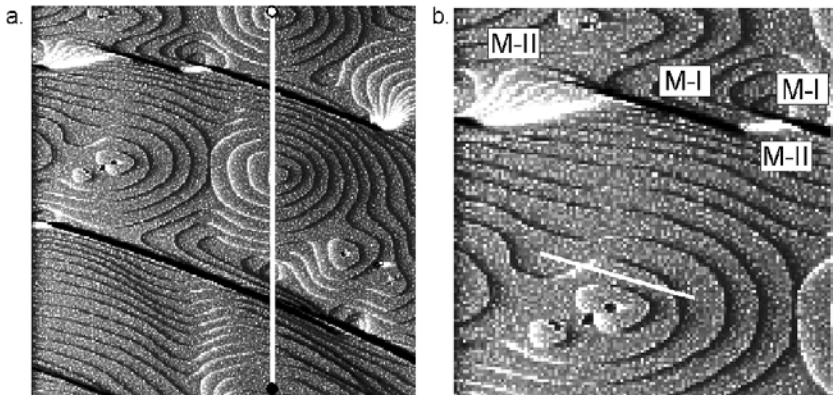

Figure 1. (a) Surface topography (1600×1600 nm^2) after deposition of about 3000 triple layers of CaF_2 on $CaF_2(111)$ at $T = 1055$ K and for a saturation $S = 354$; (b) detail of (a); the white line indicates a [110] direction; M-I and M-II denote macrosteps parallel to type I and type II steps, respectively.

elsewhere [7]. These studies should also yield insight into the degree of surface perfection of the crystals inspected by AFM.

One aspect of these investigations will be discussed in the present letter. A recent theoretical investigation by Puchin *et al* [8] published in this journal was concerned with the theoretical modelling of steps on the (111) surface of CaF_2. These authors studied, among other things, the atomic structure of steps one triple layer (0.315 nm) high in $\langle 110 \rangle$ directions. Crystallographically, two different types, I and II, depending on the direction of the descent from the higher to the lower terrace, must be distinguished [4]. Type I, which can be described as having a small {110} mini-facet at the step edge, has the lower step energy of 0.25 nJ m^{-1} compared to 0.35 nJ m^{-1} calculated for type II. Type I should therefore be more stable. This theoretical result was confirmed by our experimental studies, which showed that one of these step types, probably type I, is strongly preferred on approaching thermodynamic equilibrium [4].

Puchin *et al* [8] studied, in addition, the interaction between steps of type I on the one hand and that between steps of type II on the other hand. They found an attractive interaction between type I steps and a repulsive one between steps of type II. They concluded from this that an aggregation of type I steps into higher steps should yield a gain in surface stability. Exactly this has been found in our growth experiments with CaF_2. Figure 1 shows a typical growth topography of a $CaF_2(111)$ surface, which was obtained after deposition of about 3000 triple layers (TL) of CaF_2 corresponding to a mean layer thickness of ≈ 0.95 μm at $T = 1055$ K and a saturation ratio $S = j_{on}/j_s = 354$. Here, j_{on} is the impinging molecular flux, while j_s is the saturation flux at the crystal temperature. Figure 1 shows growth hills (pyramids) made up off concentric, closed steps one TL high. These closed steps predominantly have a triangular shape with rounded corners. They were probably formed by repeated two dimensional nucleation at edge dislocations in the centres of the growth hills with a component of the Burgers vector parallel to the surface. The mean step distance in the growth hills amounts to about 70 nm. In the centres of some of these growth pyramids a small hole is visible, which was probably created during re-evaporation of some material in the short quenching period at the end of the growth experiment. The holes may be formed via two dimensional hole nucleation at the dislocations. This marginal evaporation does not adulterate, apart from a small shift of the step edges in the direction of the higher terraces, the growth topographies, once created, substantially.

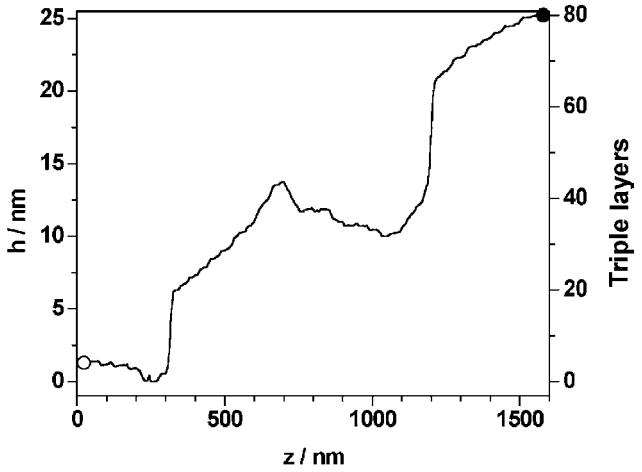

Figure 2. The surface profile along the white line in figure 1(a).

In addition to the one TL high steps of the growth hills, macrosteps can also be recognized, which run in figure 1(a) diagonally from the lower right to the upper left across the surface. These macrosteps result from the different heights of the growth topographies on both sides of the macrosteps; see the height profile in figure 2. Usually, one TL high steps from neighbouring growth pyramids with opposite descent from the higher to the lower terrace coalesce and annihilate each other. This can be seen at the two growth pyramids in the centre of figure 1(a). However, such an annihilation cannot be achieved when there is a surplus of one type of steps, as is the case between surface parts of different mean heights. In this case a pile-up of triple layer high steps to macrosteps or small facets should occur.

Due to the shadowing in the image processing of the force image of figure 1 in the AFM at the macrosteps, dark and bright parts (marked as M-I and M-II, respectively) can be distinguished. The dark parts of these macrosteps run parallel to corresponding triple layer steps at the edges of the triangular growth hills with the same direction of descent from the higher to the lower terrace. The brighter parts of the macrosteps exhibit an angle of about 120° to the darker parts. They run parallel to the shorter straight step edges at the rounded islands. Obviously, the darker parts of the macrosteps have smaller widths than the brighter ones. While in the brighter parts one triple layer high steps can be partly resolved, this is not the case in the darker parts. In correspondence with the theoretical results of Puchin *et al* [8] it can therefore be concluded that the narrower, darker parts of the macrosteps correspond to a pile-up of $\langle 110 \rangle$ steps of type I and the wider, brighter parts to those of type II, which have the tendency to repel each other. However, this tendency seems to be partly suppressed because of spatial restrictions.

For a more thorough investigation of the pile-up effect we have determined inclination angles of the parts of the macrosteps, which are built up of $\langle 110 \rangle$ type I steps, by determining height profiles perpendicular to the steps. The inclination angles of the macrosteps with respect to the basic (111) surface were calculated from the width and the heights of these steps. Altogether 52 macrosteps were analysed. The results of this analysis are compiled in the histogram in figure 3.

The calculations of Puchin *et al* [8] were performed for different facets, i.e. for different terrace widths between one TL high $\langle 110 \rangle$ steps of type I. Small sections of these different facets are shown in figures 4(a)–(e) in a view onto $(\bar{1}01)$, i.e., a side view. The facets can be characterized by the angle they form with the basic (111) surface. These angles as well as the

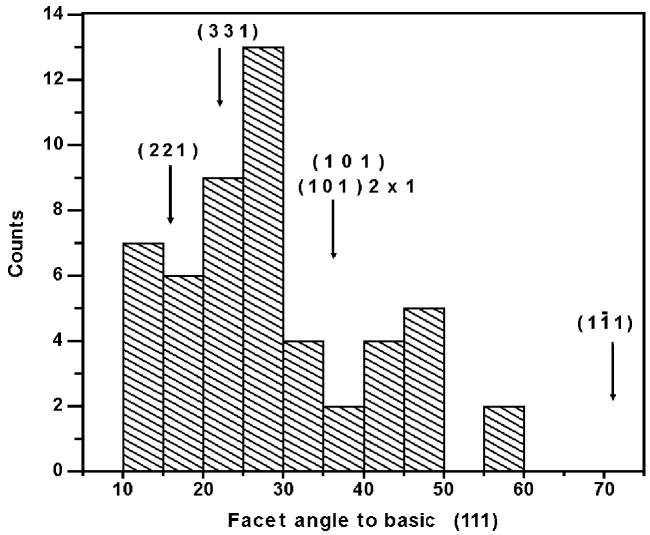

Figure 3. A histogram of inclination angles of ⟨110⟩ macrosteps of type I.

notation for the facets are also indicated in the histogram in figure 3. According to the above mentioned theoretical calculations the reconstructed (101) 2×1 configuration (figure 4(c)) with a facet angle of 35.3° should be energetically favoured. This reconstructed surface consists of 2 TL high type I steps. The surface energy of this surface is lower by 0.14 nJ m^{-2} than that of the normal (101) surface (figure 4(b)). Puchin *et al* attributed this to the fact that the 2×1 surface is composed of small most stable {111} facets. A clear indication of the preference for this type of facet is, however, not found. The distribution of facet angles (figure 3) rather shows a minimum at this value. It should be noted in addition that in none of our growth experiments were isolated steps of height 2 TL observed. This is in contrast to the case for alkali halide crystals where double steps are common [9], as can also be substantiated theoretically [10]. Since dislocations are assumed to act as the sources of steps, these differences may be explained by the unequal crystallographic appearances of dislocations in the two lattice types.

Also 'pure' $(1\bar{1}1)$ facets at an angle of 70.5°, which are the steepest facets possible, are not observed. Yet some facets with inclination angles greater than 40° are found, which may indicate a tendency to such a step bunching. Altogether, the measured facet or macrostep angles show a broad distribution. This may be attributed to the fact that in these facets there is not a homogeneous distance for one TL high steps but a scatter of these distances. An atomic resolution of the closely neighbouring one TL high steps in the facets was not possible. In this connection it should be mentioned that uncertainties in the determinations of the facet angles may be also caused by the AFM measurements themselves. For some of these facets forward as well as backward scans were performed, which showed mean differences in the inclination angles of about 3.5°. Quite generally, the measured facet angles depend to some extent on the scan direction. Such errors are a usual phenomenon in AFM measurements (see also [9]).

Summarizing the results of our investigations it can be stated that the conclusions of the theoretical investigations of Puchin *et al* [8], especially the fact that type I steps attract each other at low step distances, while type II steps have a repulsive interaction, are nicely confirmed. The consequence of the attractive interaction is that step bunches of this type occur when type I steps are hindered to annihilate with steps of type II, because type I steps dominate at the peripheries of two growth regions. Stronger growth may occur at more active centres in the growth hills, which may lead to lower step distances and, also, to higher condensation

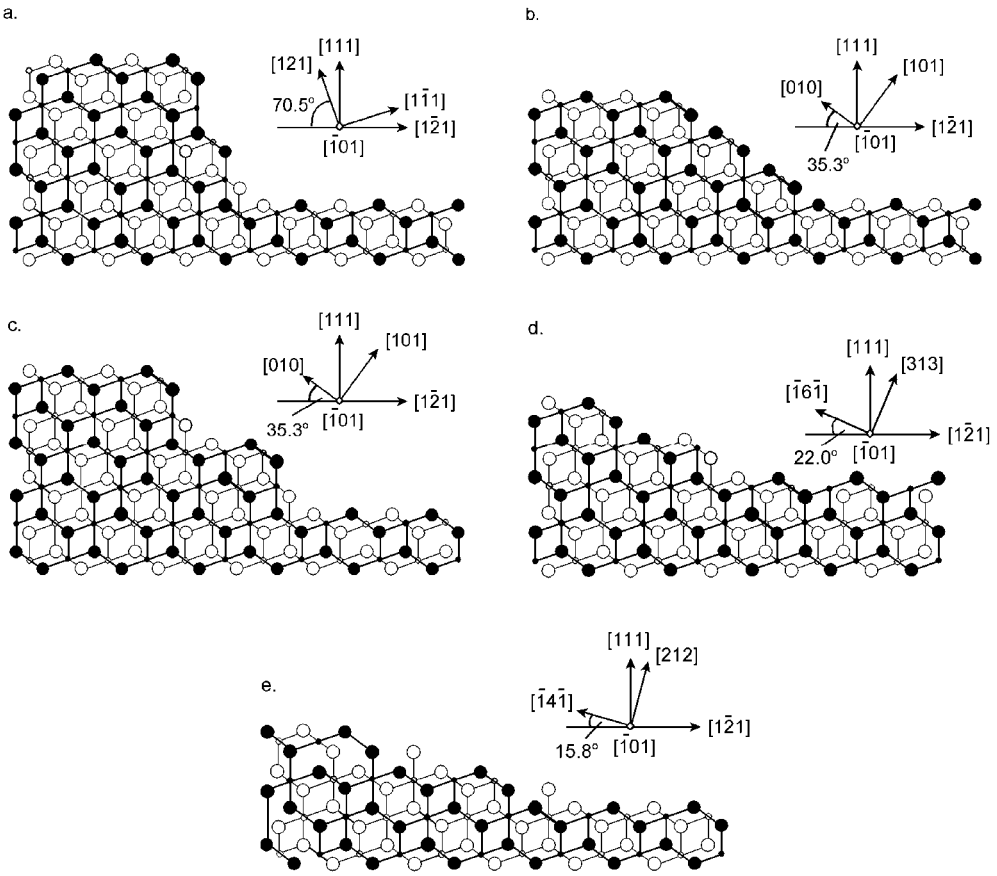

Figure 4. Schemes of different arrangements of one TL high [$\bar{1}$01] type I steps into macrosteps and facets, respectively—compare [8]; (a) (1$\bar{1}$1), (b) (101), (c) (101) 2 × 1, (d) (313), (e) (212). Here, only unrelaxed steps are shown. Inclination angles with respect to the basic (111) surface are indicated. The dark and bright circles represent ions from different layers lying alternately in the [$\bar{1}$01] direction. Calcium and fluorine ions are plotted as small and large circles respectively.

coefficients in these regions. Another reason for a pile-up is the decrease of the step velocity caused by the presence of impurities.

References

[1] Sinharoy S 1990 *Thin Solid Films* **187** 231
[2] Bloomstein T M, Horn M W, Rothschild M, Kunz R R, Palmacci T and Goodman R B 1997 *J. Vac. Sci. Technol.* **15** B2112
[3] Stenzel E, Gogoll S, Sils J, Huisinga M, Johansen H, Kästner G, Reichling M and Matthias E 1997 *Appl. Surf. Sci.* **109/110** 162
[4] Engelhardt J B, Dabringhaus H and Wandelt K 2000 *Surf. Sci.* **448** 187
[5] Deuster V, Schick M, Kayser Th, Dabringhaus H, Klapper H and Wandelt K 2003 *J. Cryst. Growth* **250** 313
[6] Dabringhaus H and Wandelt K 2003 *Surf. Sci.* **526** 257
Dabringhaus H and Wandelt K 2003 *Surf. Sci.* **526** 273
[7] Schick M, Dabringhaus H and Wandelt K 2004 in preparation
[8] Puchin V E, Puchina A V, Huisinga M and Reichling M 2001 *J. Phys.: Condens. Matter* **13** 2081
[9] Ostadrahimi A H, Dabringhaus H and Wandelt K 2002 *Surf. Sci.* **521** 139
[10] Lacman R 1965 *Coll. Int. Centre Nat. Rech. Sci.* **152** 1