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Morphology and texture evolution of nanostructured CaF₂ films on amorphous substrates under oblique incidence flux

C Gaire, P Snow, T-L Chan, W Yuan, M Riley, Y Liu, S B Zhang, G-C Wang and T-M Lu

Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180, USA

E-mail: gairec@rpi.edu

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Abstract
The morphology and biaxial texture of vacuum evaporated CaF₂ films on amorphous substrates as a function of vapour incident angle, substrate temperature and film thickness were investigated by scanning electron microscopy, x-ray pole figure and reflection high energy electron diffraction surface pole figure analyses. Results show that an anomalous [220] out-of-plane texture was preferred in CaF₂ films deposited on Si substrates at <200 °C with normal vapour incidence. With an increase of the vapour incident angle, the out-of-plane orientation changed from [220] to [111] at a substrate temperature of 100 °C. In films deposited with normal vapour incidence, the out-of-plane orientation changed from [220] at 100 °C to [111] at 400 °C. In films deposited with an oblique vapour incidence at 100 °C, the texture changed from random at small thickness (5 nm) to biaxial at larger thickness (20 nm or more). Using first principles density functional theory calculation, it was shown that [220] texture formation is a consequence of energetically favourable adsorption of CaF₂ molecules onto the CaF₂(110) facet.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Epitaxial CaF₂ films grown on single crystal substrates have been used extensively as buffer layers for the growth of a variety of semiconductor films [1–8] used for microelectronic, optoelectronics, and solar cell applications because of their high band gap ($E_g = 12.1$ eV), low permittivity ($\varepsilon = 8.4$), and chemical robustness. Recently, it was shown that a biaxially textured ([111] ⟨121⟩ oriented) CaF₂ film [9] could be deposited on an amorphous substrate using an oblique angle deposition (OAD) technique. Such biaxially textured fluoride films on amorphous substrates are particularly attractive from a technological point of view because highly oriented semiconductor films, for example Ge [10] and CdTe [11], can be heteroepitaxially grown on them.

In this paper, we present the detailed results of scanning electron microscopy (SEM), x-ray pole figure analyses and reflection high energy electron diffraction (RHEED) surface pole figure analyses of the morphology and texture of vacuum evaporated CaF₂ films on amorphous substrates at temperature $T = 100–400$ °C, for thickness $d = 5–500$ nm and vapour incidence angle with respect to substrate normal $\alpha = 0^\circ–80^\circ$. It was found that for the CaF₂ films with $\alpha = 0^\circ$, $T < 200$ °C, the preferential out-of-plane orientation is [220]. With an increase in $\alpha$, the [220] texture orientation was observed to tilt towards the incident vapour direction leading to a [111] orientation normal to the substrate plane. At $T = 400$ °C and $\alpha = 0^\circ$, the film has a [111] orientation. We also present the results of adsorption energy calculation for CaF₂ molecules on different surfaces of CaF₂ crystals using first principles density functional theory (DFT). The energetics of the facet formation at the tip of the CaF₂ column and a possible explanation for the observed [220] texture are discussed in detail.
2. Methods

2.1. Experimental details

CaF$_2$ films were deposited on native oxide coated Si(100) substrates using the OAD technique. Four sets of films were made and the conditions are summarized in table 1. In the first set, the value of $\alpha$ was varied (0°, 15°, 30°, 45°, 60°, 70°, 75° and 80° with respect to the substrate normal) keeping $T = 100$ °C and $d = 500$ nm. In the second and third sets, the value of $T$ was varied (100, 200, 300 and 400 °C) keeping $\alpha = 0^\circ$ and 70°, respectively. In the fourth set of films, the value of $d$ was varied (5, 20, 40, 80 and 200 nm) keeping $\alpha = 65^\circ$ and $T = 100$ °C. All the other deposition conditions were similar: source–substrate distance 25 cm, base pressure 2 $\times$ 10$^{-8}$ Torr, average deposition pressure 5 $\times$ 10$^{-2}$ Torr and the normal deposition rate 13 nm min$^{-1}$. The temperatures were measured on the front surface of the samples. A field emission scanning electron microscope (SEM, Carl Zeiss Supra 1550) was used to study the microstructure of the CaF$_2$ films. The film texture was studied through x-ray diffraction and x-ray pole figure analyses using a Bruker D8 Discover diffractometer (wavelength = 0.154 05 nm) with an area detector. The thickness dependent texture was studied using the reflection high energy electron diffraction (RHEED) surface pole figure technique [12, 13].

2.2. Theoretical model

We carried out first principles total energy calculations to compare the adsorption of CaF$_2$ molecules and nucleation of small islands on CaF$_2$(111) and CaF$_2$(110) surfaces. Our calculations are based on density functional theory (DFT) [14, 15] using the VASP (Vienna ab initio simulation) [16, 17] package with PAW (projector augmented wave) [18] pseudopotentials. We used the generalized gradient approximation and the PBE (Perdew–Burke–Ernzerhof) [19] functional for the exchange–correlation energy. We chose a plane wave cutoff of 400 eV. All the structures were optimized to a local energy minimum with forces on each atom less than 0.25 eV nm$^{-1}$. We used a periodically repeating supercell containing 1.2 nm of vacuum space to model the CaF$_2$ surface. For the calculation on CaF$_2$(111) and CaF$_2$(110) surfaces, a (5 x 5) unit cell with a slab thickness of 12 atomic layers and a (3 x 3) unit cell with a slab thickness of 10 atomic layers were used, respectively. Our CaF$_2$(111) slab has similar size and number of atoms compared to our CaF$_2$(110) slab. The size of the calculation domain is large enough to minimize the interaction of the adsorbed molecules between periodic images. Only the Gamma point was used for the Brillouin zone integration, which is sufficient to converge the total energy for the large unit cells used in our calculations.

<table>
<thead>
<tr>
<th>Vapour incident angle ($\alpha$) (deg)</th>
<th>Substrate temperature ($T$) (°C)</th>
<th>Film thickness ($d$) (nm)</th>
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<tbody>
<tr>
<td>0–80</td>
<td>100</td>
<td>500</td>
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<tr>
<td>0</td>
<td>100–400</td>
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<td>100–400</td>
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<tr>
<td>65</td>
<td>100</td>
<td>5–200</td>
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3. Results and discussion

3.1. Biaxial texture formation with vapour incident angle

3.1.1. Film morphology: Figures 1(a), (c) and (e) show the top view and figures 1(b), (d) and (f) show the corresponding cross section SEM images of the first set of CaF$_2$ films deposited at $\alpha = 0^\circ$, 45° and 80°. ((a), (c) and (e)) Top view images of the films. The vapour incidence direction in the top view images is from left to right as indicated by the arrow in (c) and (e). ((b), (d) and (f)) Corresponding cross section images showing isolated rods. In the cross section images, approximate directions of $\alpha$ and $\beta$ are shown. The sample cracking direction for taking cross section images is the same as the incident vapour direction.

![Figure 1](image-url)
and α, respectively. It was determined that the CaF2 films have preferential out-of-plane orientation. To see if these films are biaxially oriented (having both out-of-plane and in-plane alignments), we conducted x-ray pole figure measurements for both (220) and (111) diffraction peaks. Figures 4(a)–(c) show the x-ray pole figures constructed from the (220) diffraction peaks of the x-ray spectra from samples α = 0°, 30° and 60°, respectively. Likewise, figures 4(d)–(f) show the corresponding pole figures for the (111) diffraction peaks. As seen in the pole figures, all the films (including the normally deposited ones) are biaxially textured because there are distinct poles with some dispersion. The in-plane dispersion for normally deposited film is 60° ± 5° and that for films deposited at higher angles ranges of the order of 10° ± 5° to 15° ± 5° where the ±5° error is because of the 5° step size in the azimuthal direction for data acquisition. The {220} poles shown in figure 4(a) and the {111} poles shown in figure 4(d) are similar to the projection of theoretical {220} and {111} poles along the [220] direction of a cubic crystal. This implies that the [220] direction is normal to the substrate plane. In figure 4(d), the (111) and (111) poles are each 35° ± 3° away from the centre. Note that this angle is close to the theoretical angle between [220] and [111] directions which is 35.24°. When α is increased, the central (220) pole shifts towards the vapour incident direction. As a result, the (111)
Figure 4. (220) x-ray pole figures of the first set of CaF₂ films grown at (a) $\alpha = 0^\circ$, (b) $\alpha = 30^\circ$ and (c) $\alpha = 60^\circ$. Corresponding (111) x-ray pole figures of CaF₂ samples grown at (d) $\alpha = 0^\circ$, (e) $\alpha = 30^\circ$ and (f) $\alpha = 60^\circ$. Transition from (220) to (111) texture can be seen. The wide white arrows indicate the projection of the vapour flux direction on the substrate plane. The small intense poles in each figure are from the Si substrate.

Figure 5. (a) The (220) and (111) texture tilt angles from substrate normal as a function of $\alpha$ for the first set of films. Positive and negative values of texture tilt angles correspond to tilting towards and away from the vapour incidence direction, respectively. For comparison, the column tilt angle, $\beta$, is also shown (with negative number assigned to the column angle when vapour is incident at $0^\circ$, for the continuation of the curve). (b) The crystallographic directions are shown for $\alpha = 45^\circ$. The pole starts to move towards the centre. For example, when $\alpha = 30^\circ$ and $60^\circ$, the [220] direction is tilted by $10^\circ \pm 1^\circ$ and $24^\circ \pm 2^\circ$, respectively towards the incident flux; the [111] direction is tilted by $25^\circ \pm 2^\circ$ and $11^\circ \pm 1^\circ$, respectively away from the incident flux. Figure 5 summarizes this behaviour for the first set of films. From figure 5(a) it can be seen that as $\alpha$ is increased from $0^\circ$ to $80^\circ$, the [220] out-of-plane orientation changes from near normal to $35^\circ \pm 3^\circ$ towards the incident vapour direction while the [111] orientation changes from $35^\circ \pm 3^\circ$ away from the incident vapour direction to near normal. The angle between the [220] and [111] orientations is maintained at $35^\circ \pm 3^\circ$. In figure 5(a), the column tilt angle, $\beta$, as a function of $\alpha$ is also plotted. The columns are tilted in such a way that the [111] and [220] directions make $12^\circ \pm 1^\circ$ and $23^\circ \pm 2^\circ$ angles with the column direction. Again, as described in figure 2, the column tilt has a total swing of $35^\circ \pm 3^\circ$ consistent with the texture direction as $\alpha$ is changed from $0^\circ$ to $80^\circ$. Figure 5(b) shows the magnified SEM images of the tip area of the CaF₂ samples grown at $\alpha = 45^\circ$. In this figure, approximate [111], [111] and [220] directions along with column tilt angle are shown. The corresponding directions for the sample deposited at $\alpha = 0^\circ$ are shown by dotted arrows. It is clear that with an increase in $\alpha$, the columns tilted off the substrate normal at $\alpha = 0^\circ$ tend to come towards the vapour incidence direction as indicated by the rotational arrow in figure 5(b). The change in the texture axis with the change in $\alpha$ has been reported on other material such as CdS [24, 25].

3.2. Temperature dependent biaxial texture formation

3.2.1. Deposition at normal vapour incidence. Figure 6(a) shows the x-ray intensity versus $2\theta$ spectra of the second set
of samples deposited at $\alpha = 0^\circ$, $d = 500$ nm and $T = 100\text{--}400^\circ$C. The films have dominant [220] and [111] out-of-plane orientation at $T = 100$ and 400°C, respectively. In the intermediate temperatures (200 and 300°C), the orientation is a mixture of [111], [311], [400] and [331] with slight preference for the [111]. Figure 6(b) shows the x-ray pole figure constructed from the (111) diffraction peak of the sample grown at $\alpha = 0^\circ$; $T = 400^\circ$C. The high intensity (111) pole at the centre and a continuous ring at 70° from the centre indicate that the sample is fibre textured with [111] as the out-of-plane orientation. This observation is consistent with other materials where the texture direction is usually the direction of the lowest energy plane (the (111) plane in fcc) when there is a sufficient surface diffusion during the film deposition. At $\alpha = 0^\circ$; $T = 100^\circ$C, the sample has [220] out-of-plane orientation and the (111) pole figure is similar to figure 4(d). The films deposited at 200 and 300°C have random orientation with a slight preference for [111] out-of-plane orientation. These observations are consistent with earlier reports on the temperature dependent texture formation of CaF$_2$ on glass substrates under normal incidence [26], where it was observed that at $T = 105^\circ$C, the preferential texture was [220] and at $T \geq 200^\circ$C, the texture was [111].

3.2.2. Deposition at oblique vapour incidence. Figure 7(a) shows the x-ray intensity versus 2θ spectrum of the third set of CaF$_2$ samples at $\alpha = 70^\circ$ and $T = 100\text{--}400^\circ$C. At 100°C, the film is [111] oriented (similar to figure 4(f)) and at 400°C, the film is [001] oriented. At 200°C, the film orientation is primarily [111] and at 300°C, the film has relatively strong (111) peak but also contains other peaks such as (220), (311), (400) and (331). At 400°C, the film is [001] oriented. Since the allowed diffraction peak (400) has very small diffraction intensity, it did not show up in the intensity versus 2θ spectrum for the given azimuthal direction where the spectrum was collected. Figure 7(b) shows the x-ray pole figures constructed from the (111) peaks of the CaF$_2$ sample deposited at $T = 400^\circ$C with $\alpha = 70^\circ$. It is clear from this pole figure that at 400°C, the film has a dominant [001] out-of-plane orientation similar to that of the substrate. We suspect that at 400°C, the CaF$_2$ might have grown epitaxially onto the [001] oriented Si substrate at an oblique angle deposition as opposed to the sample deposited at normal incidence ([111] orientation). Because of the geometry in an OAD configuration, part of the substrate surface is shadowed to the incoming vapour. If the oxide layer in the shadowed region is removed, a subsequent diffusion of the CaF$_2$ molecules into these areas (note that $T = 400^\circ$C) causes...
an epitaxial growth to occur. The description of this kind of growth is beyond the scope of the present paper. The samples deposited at \( T = 100 \) and \( 200 \) °C have similar pole figures to the samples discussed earlier in section 3.1 (with \( \alpha = 60^\circ - 75^\circ, T = 100 \) °C) and at 300 °C, the orientation is a mixture of [111], [311], [400] and [331] with slight preference for the [111].

3.3. Biaxial texture evolution with film thickness

The first column in figure 8 shows the RHEED images of the fourth set of CaF\(_2\) films deposited at \( \alpha = 65^\circ \) and \( d = 5, 20, 40, 80 \) and \( 200 \) nm, respectively. The incident vapour directions are labelled by arrows. There are two prominent features in the successive RHEED patterns: the first is the dramatic change in the diffraction pattern as \( d \) increases from \( 5 \) to \( 20 \) nm. The pattern for the \( 5 \) nm sample contains highly diffused rings. This indicates that the film does not have a preferential in-plane or out-of-plane orientation. For \( 20 \) nm thick film, the diffraction pattern consists of broken arcs. This indicates that biaxial texture forms in the film between \( 5 \) and \( 20 \) nm thickness. This observation is consistent with an earlier report on the scaling behaviour of CaF\(_2\) thin films which suggested that the morphological transition of CaF\(_2\) films occurs in a film thickness less than \( 20 \) nm [27].

The second feature is the tilting of the [111] direction about the surface normal. The RHEED patterns are symmetric with the respect to the [111] direction which is tilted off the substrate normal and away from the incident vapour direction by approximately \( 4^\circ, 7^\circ \) and \( 12^\circ \) for the \( 40, 80 \) and \( 200 \) nm thick films, respectively. The change in the texture axis with increasing film thickness has also been reported for CdS [24].

The second column in figure 8 shows the RHEED surface pole figures constructed from the (220) diffraction peaks of the \( 5, 20, 40, 80 \) and \( 200 \) nm thick samples, respectively. The reason for constructing the (220) pole figure as opposed to (111) lies in the fact that the (111) is too close to the shadowing edge of the RHEED patterns. The pole figure of the \( 5 \) nm sample is constructed at the position of the (220) arcs and does not contain distinguishable poles, indicative of a random texture. For \( 20 \) nm thick film, the (202) pole and (022) pole are elongated and merged together due to the large in-plane dispersion. However, with an increase in the film thickness, the poles are more localized. The \( 200 \) nm thick sample contains well localized intensity distribution of (220) poles. Also note that there is a gradual shift in the positions of the (220) poles with the increasing film thickness with the [111] axis tilting away from the incident vapour direction as the film grows. For the \( 200 \) nm thick film the (111) axis is approximately \( (12 \pm 1)^\circ \) off the substrate normal and away from the incident vapour direction. This value is similar to the tilt of the [111] axis in a 500 nm thick film deposited at \( \alpha = 70^\circ \) described in section 3.1. From the RHEED patterns shown in the first column of figure 8, we can also estimate the dispersion angle associated with the (220) arc from its full-width at half-maximum. The average dispersion angle is about \( (30 \pm 5)^\circ \) for \( 20 \) nm thick film and reduces to about \( (14 \pm 2)^\circ \) for \( 200 \) nm thick film. The reduction in the dispersion by a factor of about two indicates that the biaxial texture with smaller out-of-plane dispersion forms as the film grows thicker.

3.4. Orientation selection and anomalous [220] texture

The top view SEM images of the CaF\(_2\) films (figure 1) show clearly faceted columns. The initial growth stage of these films must have gone through formation of inherently random nuclei [28]. This is supported by the RHEED pattern and subsequent (220) surface pole figure constructed from the \( 5 \) nm thick CaF\(_2\) sample deposited at \( \alpha = 65^\circ \) (figures 8(a) and (b)).
planes of lowest crystallographic growth rate. Accordingly, the facetted crystal habit formed by the vertical growth rates of different crystallographic planes. Often a particular texture takes place due to the anisotropy in the growth temperature. Furthermore, from figure 5, it is obvious that the adsorption energy of CaF₂ molecules on the CaF₂ film is high, the adparticle diffusion is high and the impinging admolecules can overcome the kinetic barrier to diffuse through grain boundaries. In this case, the texture of the film consists of the direction of the lowest energy plane [30] and the texture direction should be [111] which is what we observed for normally deposited CaF₂ films at 400°C (see figure 6).

Natural CaF₂ crystals exhibit a cubic habit with [100] facets to form [111] texture or an octahedral habit with [111] facets to form [001] texture. However, when grown under pure conditions, the material does not have a tendency to form a [100] surface resulting in a [111] texture. At T ≤ 100°C, the vacuum evaporated CaF₂ film is expected to have the thermodynamically stable [111] habit and consequently exhibit a [001] texture. Contrary to this expectation, our CaF₂ films exhibited an anomalous [220] texture. We therefore conclude that CaF₂ crystal growth does not follow the texture evolution selection rule [29] at low growth temperature. Furthermore, from figure 5, it is obvious that the [220] orientation of CaF₂ changes direction from near normal to 35° ± 3° towards the incident vapour direction when α is changed from 0° to 80°. This is due to the tendency of the [110] direction of CaF₂ crystals to orient towards the incident vapour direction. As a consequence of this, the [111] orientation, which was originally 35° ± 3° off normal and away from incident vapour direction comes towards the centre (substrate normal). At α = 60°, the [111] direction is 11° ± 1° tilted off the substrate normal and away from incident vapour direction. This observation is similar to the reported [111] texture of CaF₂ at 65° vapour incident angle [9].

One of the possible reasons for the observed anomalous [220] texture could be the strongly ionic nature of the CaF₂ molecule. The CaF₂ surfaces such as [110], [112] and [114] are neutral while the surfaces such as [100], [111] and [113] are charged. Among the charged surfaces [111] is stable, but [100] produces a polarizing electric field in the bulk [33] and makes the surface unstable [30, 34, 35]. Therefore, in the absence of a substantial reconstruction or an adsorption of alien species on the [100] surface, the general designation of the [100] face as the growth face of CaF₂ should be restricted to the case of growth in natural environments [36, 37]. This rules out the possibility of having [111] as the out-of-plane orientation in the CaF₂ film. The other possible scenario of having [100] as the out-of-plane orientation with [111] facets is in sharp contrast to the experimental observation.

The facet formation and the subsequent texture selection are related to the state of the impinging adparticle and its sticking coefficient on the growing surface [38]. The CaF₂ is known to evaporate as a molecule [39, 40] and a measure of the sticking coefficient can be obtained by examining the adsorption energy of CaF₂ molecules on the growing surface. The sticking coefficient is higher when the adsorption energy is higher. To clarify the observed anomalous growth, we compare the adsorption energy of CaF₂ molecules on the CaF₂(110) surface (out-of-plane orientation at α = 0°), and the CaF₂(111) surface (growth direction predicted by the texture evolution selection rule). The results of adsorption energy calculation using DFT are presented in section 3.5.

3.5. Adsorption energy calculation using DFT

The most stable atomic geometry for the CaF₂(111) surface is a bulk-truncated surface terminated by F⁻ atoms. We constructed two atomic models (111-1A and 111-1B) for a CaF₂ molecule adsorbed onto the CaF₂(111) surface. Their optimized geometries are illustrated in the first row in figure 9. The structure 111-1A is made by placing a CaF₂ molecule following the bulk CaF₂ geometry. Since there is an F⁻ atom that forms only one Ca–F bond, we created the structure 111-1B by bending the adsorbed linear CaF₂ molecules such that both F⁻ atoms in the molecule can form two Ca–F bonds. For both atomic models, we found that the optimized structures have one of the F⁻ atoms of the CaF₂(111) surface extracted out.

In order to compare the relative stability of the two models, we evaluated the adsorption energy E_{ad} of a CaF₂ molecule on the CaF₂(111) surface by:

\[ E_{ad} = (E - E_{sub} - n E_{CaF2})/n, \]

where E is the total energy of the system, E_{sub} is the energy of the clean CaF₂(111) substrate, E_{CaF2} is the energy of a free isolated CaF₂ molecule, and n is the number of CaF₂ molecules adsorbed onto the substrate. A more negative E_{ad} implies that the adsorption is energetically favourable. As depicted in figure 10 presented later, the structure 111-1B is more stable than 111-1A by 0.44 eV.

A two-molecule CaF₂ island on the CaF₂(111) surface can be constructed by putting together two CaF₂ molecules both in configuration 111-1B. We call the resultant structure 111-2A. Another possibility is the structure 111-2B, which is built by combining a linear CaF₂ molecule (111-1A) with a bent one (111-1B). From figure 10, we found that the structure 111-2B is lower in energy by 0.30 eV/molecule. As the island grows larger, it is energetically favourable to start forming a (F⁻–Ca₂⁺–F⁻) layer that does not carry a net dipole moment. The structure 111-3 in figure 9 is constructed by adding a CaF₂ molecule in configuration 111-1B to the structure 111-2B.
We carried out a similar study for the CaF$_2$(110) surface. The CaF$_2$(110) surface forms rows of troughs. By following the bulk geometry, we placed a CaF$_2$ molecule onto the trough as illustrated in the second row in figure 9. The models 110-1A, 110-1B, and 110-1C differ only by the placement of the adsorbed F$^-$ atoms. We found that different arrangements of the two F$^-$ atoms on the CaF$_2$(110) surface are similar in energy. Their adsorption energies on the CaF$_2$(110) surface are $-3.25$, $-3.07$, and $-3.24$ eV for the models 110-1A, 110-1B, and 110-1C, respectively. In particular, 110-1A and 110-1C are nearly degenerate with 110-1A slightly lower in energy by 0.01 eV. By adopting the model 110-1A as the building block, it is straightforward to build CaF$_2$ islands on the CaF$_2$(110) surface by packing the linear CaF$_2$ molecules one by one onto the trough, as shown in the second row in figure 9.

We compare the stability of islands on the CaF$_2$(111) and CaF$_2$(110) surfaces by comparing the adsorption energy in figure 10. For small islands ($n = 3$), the adsorption energy on the CaF$_2$(110) ($E_{\text{ad}} = -3.88$ eV) surface is approximately 1 eV per CaF$_2$ molecule lower than that on the CaF$_2$(111) surface ($E_{\text{ad}} = -2.96$ eV). The adsorbed CaF$_2$ molecules on the CaF$_2$(110) surface can follow a nearly bulk geometry. In addition, they lay flat in the troughs of the CaF$_2$(110) surface and do not create a dipole moment to the system. On the contrary, islands on the CaF$_2$(111) surface can carry a dipole moment before a complete layer is formed.

Our study of the adsorption of CaF$_2$ molecules on CaF$_2$ surfaces has important implications on the growth of CaF$_2$ columns. The growth of a CaF$_2$ column starts from a multi-facettted CaF$_2$ grain on the glass substrate. Our results predict that it is most energetically favourable for CaF$_2$ molecules to be adsorbed onto the CaF$_2$(110) facet. Consequently, the CaF$_2$ grain with the (110) facet facing the flux direction should grow the fastest. This is consistent with the experimental SEM and x-ray observation that the growth direction is [220] when the flux has a normal incidence, and the [220] direction tends to follow the direction of the flux. Note that the DFT calculation does not take into account the effect of physical shadowing during growth. In addition, we predict that the topmost tip of the CaF$_2$ columns should correspond to the (110) facet. This is because it is easier for nucleation to take place on the (110) surface. Starting from the nucleation on the (110) tip, there should be a step-flow growth onto the (111) surface on the top of the columns, which has the lowest surface energy but a low nucleation rate.

4. Conclusion

It was shown that the vacuum evaporated CaF$_2$ films on amorphous substrates at temperature less than $200\degree$C have the [220] out-of-plane texture at normal incidence. The dependence of the [220] texture orientation on the vapour incident angle was found such that an originally [220] textured film (in the case of normal deposition) transforms to a [111] textured film at vapour incident angle $\alpha > 70\degree$. The biaxial texture was observed to form at film thicknesses
less than 20 nm under oblique angle incidence without
intentional heating. It was also shown that the texture observed
does not obey the conventional texture evolution selection
rule. The disparity between our observed texture and the
texture evolution selection rule was resolved by comparing the
adsorption energy on the CaF$_2$ surface. It was concluded that it is energetically
most favourable for CaF$_2$ molecules to be adsorbed onto the
facets and hence the [110] direction should grow more
favourably from a randomly oriented CaF$_2$ nuclei in the initial
stage of the film growth.

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