

## Restrained relaxation of stress in a MBE-grown thin film of $\text{CaF}_2$ on (111) silicon

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A rhombohedral symmetry of  $\text{CaF}_2$ , grown by MBE on (111)Si to a thickness of 30 nm was found with the help of RBS and ion channeling measurements. This symmetry is caused by hampered stress relaxation and the build-up of planar strain of tensile type due to different thermal expansion coefficients of the deposit and the substrate on the one hand, and dislocation pinning during the cooling process of the sample, on the other. The strain field forces the epitaxial film to a rhombohedral instead of cubic structure, and a total misfit of 1.2% is generated, instead of the common 0.6%.

*Keywords:* Molecular Beam Epitaxy; Dielectric fluoride films; Epitaxial growth; Thin films; Heteroepitaxy, silicon.

### 1. Introduction

The continued interest in the growth of epitaxial thin films of alkaline-earth fluorides is motivated by potential applications e.g. in light emitters by virtue of the incorporation of rare-earth elements, and solid-state microcavity lasers [1-3]. Growth of these insulating materials on silicon substrates offers potential compatibility with Si-based technology.

The heteroepitaxy of insulators on Si offers a number of attractive opportunities for industrial applications, including silicon-on-insulator (SOI) and three-dimensional device structures, and is also attractive for hot electron devices, optoelectronic devices, and appropriate buffer layers upon semiconductors in the structures such as GaAs on Si [4, 5].

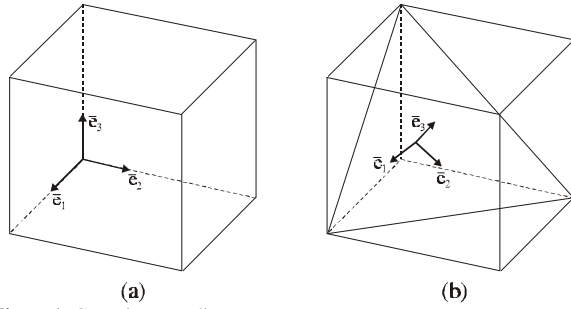
Two classes of insulating materials have been shown to grow epitaxially on Si when deposited by MBE. They are alkaline-earth fluorides ( $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  as well as mixtures thereof), and lanthanide trifluorides (e.g.  $\text{LaF}_3$ ). The  $\text{CaF}_2/\text{Si}$  system has received particular attention because of the compatible crystal structure and small lattice constant mismatch (0.6% at room temperature) of the two materials. With a band gap of approximately 12 eV,  $\text{CaF}_2$  is an excellent insulator. Its relatively large dielectric constant of  $\epsilon = 6.8$  also makes it attractive for device applications, as e.g. gate insulators, and the dielectric memory devices.

Strain and stress in heteroepitaxial thin film systems are a natural consequence of lattice misfit and different thermal expansion coefficients of the participating materials. On the other hand, the development in the field of microelectronics is producing ever higher integration densities, and there are successful attempts to realize a three dimensional integration. In this concept, several levels of semiconducting material containing microelectronic circuits are piled-up and separated by dielectric layers for electrical isolation. However, the fabrication of semiconducting devices is based on a highly perfect crystalline material, which means that the semiconducting active layer must be monocrystalline and free of crystal defects, like dislocations, stacking faults, or twins.

As a consequence, epitaxial growth is needed for all steps of material stacking, including semiconductors, insulators and metals. Practically, epitaxial growth of different materials is the "conditio sine qua non" for a real three-dimensional integration [4]. Possible candidates to fulfill this condition in Si- microelectronics are refractory metal silicides as a conducting material and  $\text{CaF}_2$  as an appropriate insulator [6]. In the present paper we investigate the properties of thin  $\text{CaF}_2$  films grown epitaxially by MBE on {111}-oriented Si substrates, particularly with respect to the epitaxial quality and strain behavior.

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**Figure 1.** Cartesian coordinate systems  
 a)  $\bar{e}_1 \parallel [100], \bar{e}_2 \parallel [010], \bar{e}_3 \parallel [001]$  ;  
 b)  $\bar{e}_1 \parallel [2\bar{1}\bar{1}], \bar{e}_2 \parallel [01\bar{1}], \bar{e}_3 \parallel [111]$ .

**2. Basic considerations**

The earth alkaline fluorides can be considered as a material class especially appropriate for heteroepitaxial growth on Si substrates because their crystal structure is very similar to the structure of Si (diamond type, point group  $m\bar{3}m$ ).

Within the group of earth alkaline fluorides,  $\text{CaF}_2$  is the substance with the smallest lattice parameter of 0.5464 nm at room temperature [6]. The lattice constant of silicon is  $a_0 = 0.5431$  nm, indicating that no lattice matching between silicon and earth alkaline fluorides exists (Table 1).

An epitaxial layer of  $\text{CaF}_2$  on Si will either grow pseudomorphically without misfit dislocations, or is relaxed with the formation of a misfit dislocation network [7]. In the former case, the epilayer should not be cubic due to strain in the film, while in the latter case the  $\text{CaF}_2$  layer will have its bulk crystal structure with the point symmetry  $m\bar{3}m$ . It is clear that the first case can be realized only for a layer thickness smaller than a so called critical value. The symmetry decrease can be found by using Curie's principle: The strain field in the crystal layer is caused by a planar stress field  $\overset{2\rightarrow}{s}$  having the symmetry  $\frac{\infty}{m}$  (the  $\infty$ -fold symmetry axis is parallel to the layer normal).

The point symmetry group of the strained layer is given by the intersection of the point symmetry of the unstrained crystal and the point symmetry of the stress field: For epitaxy of  $\text{CaF}_2$  ( $m\bar{3}m$ ) on Si(100) one obtains as the symmetry of the epitaxial layer

$$m\bar{3}m \cap \frac{\infty}{m} \Big|_{\infty / \langle 100 \rangle} = 4/mmm.$$

In the case of the {111}-oriented Si substrates the symmetry of the epitaxial film is

$$m\bar{3}m \cap \frac{\infty}{m} \Big|_{\infty / \langle 111 \rangle} = \bar{3}m.$$

Consequently, in the first case the epitaxial layer is tetragonal, and in the second one rhombohedral under

pseudomorphic growth conditions. Of course, if a symmetry decrease takes place, for example from cubic to tetragonal ( $m\bar{3}m \rightarrow 4/mmm$ ), most of the atomic distances as well as crystallographic directions will be changed with regard to the ideal bulk material.

In what follows we give an exact calculation of the strain perpendicular to the interface,  $\in_{\perp}$  and the angle deviation of the crystallographic directions,  $J_{[uvw]}$ , for a strained layer system  $\text{CaF}_2/\text{Si}(111)$  in the case of pseudomorphic epitaxial growth.

**3. Determination of  $\in_{\perp}$  and  $J_{[uvw]}$**

The state of strain is considered to be a result of a planar stress field  $\overset{2\rightarrow}{\sigma}$  :

$$\overset{2\rightarrow}{\in} = \overset{2\rightarrow}{S} \overset{2\rightarrow}{\sigma} ; \quad \overset{2\rightarrow}{\sigma} = \begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (1)$$

Here the components of  $\overset{2\rightarrow}{\sigma}$  and  $\overset{2\rightarrow}{\in}$ , are described in a Cartesian coordinate system (CS) with the unit vectors being parallel and perpendicular to the layer normal, for example  $\bar{e}_1 \parallel [2\bar{1}\bar{1}], \bar{e}_2 \parallel [01\bar{1}],$  and  $\bar{e}_3 \parallel [111]$  in the given case (see Fig. 1). Due to the symmetry reasons, the strain field tensor  $\overset{2\rightarrow}{\in}$  in this Cartesian CS will take up the form

$$\overset{2\rightarrow}{\in} = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \in_{\perp} \end{pmatrix} \quad (2)$$

in which  $\beta$  is the lattice misfit in the epitaxial system calculated as  $\beta = (a_d - a_s)/a_s$ , the  $a$ 's are the lattice constants of the deposit (d) and the substrate (s), respectively; and  $\in_{\perp}$  means the strain component perpendicular to the layer interface.

If the tensor components of  $\overset{4\rightarrow}{S}$  (or  $\overset{4\rightarrow}{C} = \overset{4\rightarrow}{S}^{-1}$ ) are known, the strain component  $\in_{33} = \in_{\perp}$  can be calculated from the condition  $\sigma_{33} = 0$  (see equation (1)) by using

$$\overset{4\rightarrow}{\sigma} = \overset{4\rightarrow}{C} \overset{4\rightarrow}{\in} ;$$

$$0 = \sigma_{33} = C_{33ik} \hat{I}_{ik}; \quad i, k = 1 \dots 3$$

or simpler in Voigt's matrix notation [8] together with (eq. 2)

$$\begin{aligned} 0 &= \mathbf{s}_3 = C_{3v} \mathbf{e}_v; \quad v = 1 \dots 6 \\ &= (C_{31} + C_{32})\mathbf{b} + C_{33}\hat{\mathbf{l}} \wedge; \\ &= -\mathbf{b}(C_{31} + C_{32})/C_{33} \end{aligned}$$

Unfortunately, the components  $C_{mm}$  usually are given by the tensor components with respect to a coordinate system with unit vectors parallel to [100], [010], and [001] directions. Thus to transform the components of a fourth rank tensor according to

$$C'_{ijkl} = a_{im}a_{jn}a_{ko}a_{lp}C_{mnop}$$

is a tedious work. A simpler way to arrive at the result is to calculate in the Cartesian CS, as shown in Fig. 1, characterized by  $\bar{\mathbf{e}}_1 // [100]$ ,  $\bar{\mathbf{e}}_2 // [010]$ ,  $\bar{\mathbf{e}}_3 // [001]$  instead of CS with  $\bar{\mathbf{e}}_1 // [2\bar{1}\bar{1}]$ ,  $\bar{\mathbf{e}}_2 // [01\bar{1}]$ ,  $\bar{\mathbf{e}}_3 // [111]$ .

The transformation  $\overset{2\rightarrow}{\epsilon}' \rightarrow \overset{2\rightarrow}{\epsilon}$  provides

$$\overset{2\rightarrow}{\epsilon} = \frac{1}{3} \begin{pmatrix} 2\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} \\ -\beta + \epsilon_{\perp} & 2\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} \\ -\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} & 2\beta + \epsilon_{\perp} \end{pmatrix} \quad (3)$$

in the Cartesian CS given by the crystal axes, or in Voight's notation

$$\overset{2\rightarrow}{\epsilon} = \frac{1}{3} \begin{pmatrix} 2\beta + \epsilon_{\perp} \\ 2\beta + \epsilon_{\perp} \\ 2\beta + \epsilon_{\perp} \\ 2(-\beta + \epsilon_{\perp}) \\ 2(-\beta + \epsilon_{\perp}) \\ 2(-\beta + \epsilon_{\perp}) \end{pmatrix}.$$

Using Hook's law in the matrix form  $\overset{2\rightarrow}{\sigma} = \overset{2\rightarrow}{\tilde{C}} \overset{2\rightarrow}{\epsilon}$  we find for a cubic crystal (see Kittel [9])

$$\overset{2\rightarrow}{\sigma} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix}.$$

$$\overset{2\rightarrow}{\epsilon} = \frac{1}{3} \begin{pmatrix} (2\mathbf{b} + \epsilon_{\perp})(C_{11} + 2C_{12}) \\ (2\mathbf{b} + \epsilon_{\perp})(C_{11} + 2C_{12}) \\ (2\mathbf{b} + \epsilon_{\perp})(C_{11} + 2C_{12}) \\ 2(-\mathbf{b} + \epsilon_{\perp})(C_{44}) \\ 2(-\mathbf{b} + \epsilon_{\perp})(C_{44}) \\ 2(-\mathbf{b} + \epsilon_{\perp})(C_{44}) \end{pmatrix}$$

and from the condition  $\sigma'_{33} = 0$  after having carried out the transformation of  $\overset{2\rightarrow}{\sigma}'$  to  $\overset{2\rightarrow}{\sigma}$ :

$$\begin{aligned} \frac{1}{3}(2\beta + \epsilon_{\perp})(C_{11} + 2C_{12}) + \frac{4}{3}(-\beta + \epsilon_{\perp})C_{44} &= 0 \\ \epsilon_{\perp} &= \frac{-2 + 4C_{44}/(C_{11} + 2C_{12})}{1 + 4C_{44}/(C_{11} + 2C_{12})} \cdot \beta. \end{aligned} \quad (4)$$

Using the values  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  for  $\text{CaF}_2$  measured by Ho and Ruoff [10] the strain in normal layer direction results in

$$\epsilon_{\perp} = -0.9399\beta. \quad (5)$$

With the knowledge of  $\overset{2\rightarrow}{\epsilon}$  in the Cartesian CS (eq. (3)), it is possible to calculate the change of any crystallographic direction  $[uvw]$ . As the result of the strain field  $\overset{2\rightarrow}{\epsilon}$ , the lattice vector  $\bar{\mathbf{R}} = [uvw]$  will be modified by a small vector

$$\bar{\rho}_{[uvw]} = \overset{2\rightarrow}{\epsilon} \cdot \bar{\mathbf{R}}$$

giving

$$\bar{\rho}_{[uvw]} = \frac{1}{3} \begin{pmatrix} 2\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} \\ -\beta + \epsilon_{\perp} & 2\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} \\ -\beta + \epsilon_{\perp} & -\beta + \epsilon_{\perp} & 2\beta + \epsilon_{\perp} \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix} \quad (6)$$

Consequently, the angle deviation of the crystallographic direction  $[uvw]$  due to the strain field is given by the angle between  $\bar{\mathbf{R}}$  and  $\bar{\mathbf{R}} + \bar{\rho}$ :

$$J_{[uvw]} = \arccos \frac{\bar{\mathbf{R}} \cdot (\bar{\mathbf{R}} + \bar{\rho})}{|\bar{\mathbf{R}}| \cdot |(\bar{\mathbf{R}} + \bar{\rho})|}. \quad (7)$$

**Table 1.** Crystal properties of CaF<sub>2</sub> and Si.

	Crystal symmetry	Lattice constant	Lattice misfit		Thermal expansion coefficient
			300 K	700 K	
CaF <sub>2</sub>	Cubic fluorite	5.4640 Å	0.6%	2.16%	1.9 · 10 <sup>-5</sup> K <sup>-1</sup>
Si	Diamond	5.4308 Å			2.5 · 10 <sup>-6</sup> K <sup>-1</sup>

In particular it follows, for example, from eq. (6) with  $[uvw]$  being  $[110]$ , by multiplication

$$\rho_{[110]} = \frac{1}{3} \begin{pmatrix} \beta + 2\epsilon_{\perp} \\ \beta + 2\epsilon_{\perp} \\ -2\beta + 2\epsilon_{\perp} \end{pmatrix}$$

and

$$\vartheta_{[110]} = \arccos \frac{2[1 + \frac{1}{3}(\beta + 2\epsilon_{\perp})]}{\sqrt{2} \cdot \sqrt{2[1 + \frac{1}{3}(\beta + 2\epsilon_{\perp})]^2 + \frac{4}{9}(-\beta + \epsilon_{\perp})^2}} \quad (8)$$

#### 4. Experimental results

For the growth process,  $\{111\}$ -oriented Si substrates were cleaned and covered with a thin volatile oxide layer by a procedure after Ishizaka and Shiraki [11]. The MBE growth was carried out in a custom-built MBE-reactor by molecular evaporation of CaF<sub>2</sub> from a Knudsen cell. Prior to deposition, the substrate was heated by a direct current flow to 1100 °C for a short time in order to remove the protective oxide.

During the evaporation (1 nm/min), the substrate temperature was kept at about 700 °C. The evaporation was started after the detection of a (7 x 7) reconstruction on the  $\{111\}$ Si surface by RHEED (beam voltage of 20 kV) and operated until a film thickness of 30 nm was reached. The epitaxial relationship for CaF<sub>2</sub> growth on Si

$$\{111\}_{\text{CaF}_2} \parallel \{111\}_{\text{Si}}; \quad \langle 110 \rangle_{\text{CaF}_2} \parallel \langle 110 \rangle_{\text{Si}}$$

has also been found by this method. Using 4He<sup>+</sup>-ions of 1.2 MeV energy, RBS and ion channeling measurements were carried out in order to characterize the epitaxial CaF<sub>2</sub> layer. In our RBS measurements (Figure 2), we find a  $\chi_{\text{min}}$ -value of about 5%, demonstrating a good crystallographic quality of the epitaxial film. The channeling experiments dismantle an increase of 0.32° for the angle between the  $\langle 110 \rangle$  directions and the  $[111]$  surface normal. For cubic crystals, this angle has to be exactly 35.26°.

If only pseudomorphic growth would be responsible, the epitaxial film after cooling down to room temperature would suffer from a compressive strain, indicated by a smaller angle than the 35.26° between  $\langle 110 \rangle$  and  $\langle 114 \rangle$

with respect to the  $[111]$  surface normal according to Fig. 3.

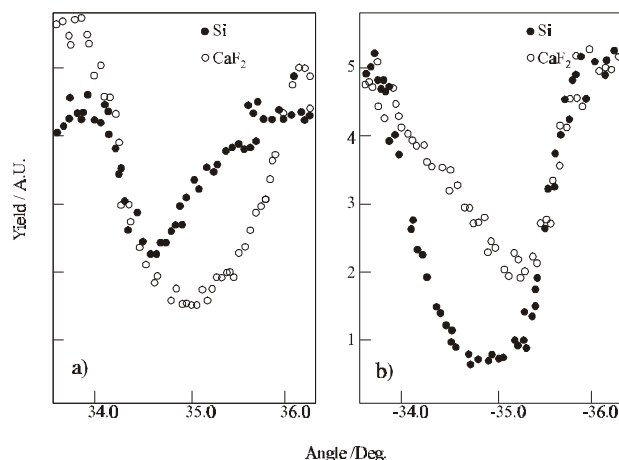
If misfit dislocations are not formed, the angle misalignment would have the theoretical value of 0.315° as found by applying eqs. (5) and (8) and a misfit value of  $b=0.0061$ . Given the lattice constant of the deposit larger than that of the substrate (Tab. 1), this misalignment angle reduces the value of the cubic crystal. The fact that our experimental results show an increase of 0.32° instead of the expected reduction, proves that this epitaxial layer is not compressed but stretched. In other words, no pseudomorphic growth has taken place.

#### 5. Conclusions

The experimental results can be understood in terms of the different thermal expansion coefficients of the deposit and the substrate, respectively. For Si the thermal expansion coefficient  $\alpha$  is 2.5 · 10<sup>-6</sup> K<sup>-1</sup>, the respective value for CaF<sub>2</sub> is much higher, namely 1.9 · 10<sup>-5</sup> K<sup>-1</sup>. Further, the  $\alpha$  of CaF<sub>2</sub> depends on the temperature: it increases with increasing temperature as  $\alpha(T) = 1.885 \times 10^{-5} + 1.67(T-T_0) \times 10^{-8} + 5.5(T-T_0)^2 \times 10^{-12}$  [12], while that of Si is constant in the considered temperature range.

Taking this fact into account, one finds an actual misfit value of  $b = 2.16\%$  for the system CaF<sub>2</sub>/Si at the growth temperature of 700 °C. From the experimental result, namely that the angle misalignment of the  $\langle 110 \rangle$  rows is pointing into the opposite direction as it would have been expected for pseudomorphic growth, we could conclude that the layer thickness of 30 nm in our experiment is larger than the critical value at growth temperature. Indeed this value has been found to be about 12 nm.

During the growth process, which starts pseudomorphically, the epitaxial CaF<sub>2</sub> layer must later relax by forming a dislocation network which compensates for the planar stress. Prior to this relaxation, the epitaxial layer must have been rhombohedral, characterized by a ratio  $|\langle 111 \rangle| / |\langle 100 \rangle| > \sqrt{3}$  due to compressive stress in the film. After relaxation, the deposited layer of CaF<sub>2</sub> is cubic according to its bulk crystal structure. Now the ratio of  $|\langle 111 \rangle|$  and  $|\langle 100 \rangle|$  is exactly  $\sqrt{3}$ . We note that the number of dislocations affecting the lattice matching is given by the actual misfit of 2.16% at 700 °C. This means, one dislocation exists for about 50 lattice planes perpendicular to the interface.



**Figure 2.** RBS and ion channeling of the heterostructure  $\text{CaF}_2/\text{Si}(111)$  measured in  $\{110\}$  planes over: a)  $\text{CaF}_2\langle 110 \rangle/\text{Si}\langle 114 \rangle$ ; b)  $\text{CaF}_2\langle 114 \rangle/\text{Si}\langle 110 \rangle$ . • Si; ○  $\text{CaF}_2$ . Film thickness  $d = 30 \text{ nm}$ .

During the cooling process from  $700^\circ\text{C}$  to room temperature, the different thermal expansion coefficients of Si and  $\text{CaF}_2$  cause an increasing planar stress of tensile type, moving dislocations to relieve the layer stress. However, this ability to move freely dislocations requires sufficiently high temperatures. At some moment between growth and room temperature, this mobility is no longer sustained. The dislocations are then pinned, the stress due to the difference of thermal expansion coefficients cannot be disarmed, and a tensile strain will now build up.

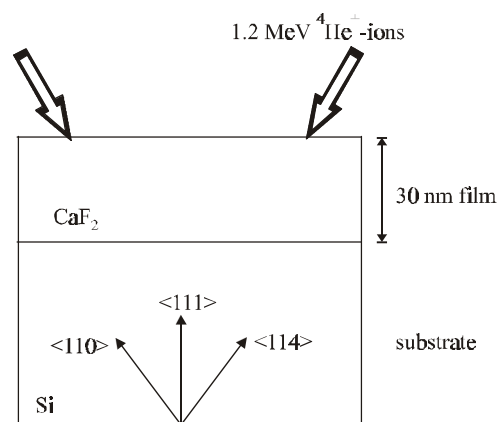
This strain field causes the fact that the symmetry of the epitaxial layer is not cubic at the end but rhombohedral with a  $|\langle 111 \rangle|/|\langle 100 \rangle|$  ratio smaller than  $\sqrt{3}$  in contrast to what would have been expected for a pseudomorphic growth. From the measured angle misalignment of  $0.32^\circ$  (as mentioned above), one gets an additional misfit of 0.6%. This brings the actual misfit in the strained  $\text{CaF}_2$  epitaxial layer on the Si-wafer to a value of 1.2% instead of 0.61% given in Table 1.

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**Figure 3.** Crystallographic orientations and ion-beam direction in RBS experiments. • Si; ○  $\text{CaF}_2$ .

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