RBS and TEM studies of strain in epitaxially grown CaF_2 on Si(111)

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In recent years strained layers in epitaxial systems relevant for microelectronic applications have found increasing attention. Due to strain effects the lattice parameters in epitaxial films are changed with reference to those of the bulk material. This allows to design material combinations with new physical properties. In all such cases the strain is a result of pseudomorphic growth of an epitaxial deposit having a bulk lattice constant being different from that of the substrate. Thin CaF_2 epitaxial layers were prepared onto (111)-oriented Si substrates by MBE, and investigated by means of Rutherford backscattering (RBS), ion channeling, and transmission electron microscopy (TEM). It has been found that the symmetry of the strained CaF_2 films is decreased to $\overline{3}$m with respect to m$\overline{3}$m of the bulk material. Moiré fringes in TEM micrographs dismantle an inhomogeneous lattice misfit in the epitaxial system. A misfit value of about 1% is determined as compared to the theoretical value of 0.6% at room temperature usually considered.

1. Introduction

Electronics on the nanometer scale is presently in a state of preliminary research. Applications to be considered are certain only when conventional technologies are no longer adequate to cover the growing requirements of a fast going development in microelectronics. Structures of less than 100 nm in lateral size are already feasable and new effects, like ballistic transport, speed up devices and reduce the cost per switching function.

Heterostructure systems in semiconductors, and even including epitaxially growing materials on semiconductors, like metals and insulators, stay in an important row for actual and future research activities [1]. Particularly are present epitaxially growing insulators on silicon a basis for powerful CMOS-structures in the SOI- (semiconductor on insulator) concept.

The epitaxial growth of two different materials always implies mechanical stress between both. In all such cases, the strain is the result of pseudomorphic growth of an epitaxial deposit, having a bulk lattice constant being different from that of the underlying substrate [2].
In the present study, we prepare and investigate thin CaF_2 -films, grown epitaxially on (111)-oriented silicon wafers, using the UHV-technique of molecular beam epitaxy (MBE) for the controlled film growth.

The slight lattice misfit of 0.6% at room temperature between Si and CaF_2 causes *a priori* the generation of strain in the interface. Rutherford backscattering and channeling spectroscopy (RBS) as well as transmission electron microscopy (TEM) is applied to detect this property.

2. Experimental procedure

The growth of thin CaF_2 epitaxial layers on Si substrates was carried out in a custom-built MBE reactor. The basic pressure in the growth chamber was 10^{-7} Pa, during the evaporation 10^{-6} Pa, respectively. CaF_2 deposit material was evaporated from a Knudsen cell containing a graphite crucible. The cell temperature during the evaporation was held at about 900 °C. The {111}-oriented Si substrates, 5 by 15 mm^2 in size, were chemically cleaned and covered with a thin protective oxide layer [3].

After the introduction of the sample into the growth chamber the volatile oxide was removed by heating the sample to about 1150 °C for a few minutes. As soon as the protective oxide is desorbed, the clean Si{111} surface shows the well-known (7 x 7) reconstruction pattern detected by RHEED [4].

The substrate temperature was kept at 700 °C for the growth process to be executed. During the evaporation the growing surface of the sample was observed by RHEED. After cooling to room temperature the epitaxial layer (thickness about 30 nm) was investigated by RBS and channeling measurements using $^4He^+$ -ions with an energy of 1.2 MeV.

TEM images were produced in a high voltage electron microscope at an accelerating voltage of 1 MeV. In order to do this, the samples were cut and etched to provide small discs of 3 mm in diameter, and then prepared by chemical thinning using HF and HNO_3 as an etchant.
The ratio HF : HNO_3 was 2 : 7 for rapid thinning and 1 : 30 for final thinning.

3. Results

The good monocrystalline perfection of the deposited layer is affirmed by RBS measurements. Figure 1 shows a typical RBS plot for random and aligned incident beam, respectively directions of silicon, including an angle of 35.26° with the <111> direction, which is parallel to the substrate normale. The geometrical arrangement of the experiment is schematically shown in figure 2.

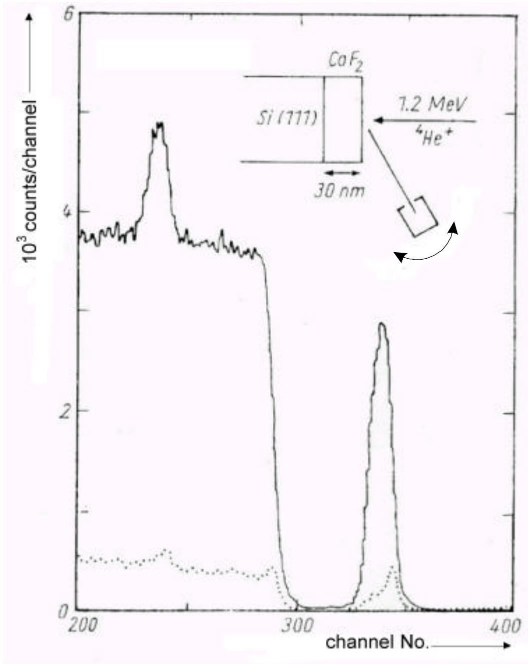

Fig. 1: Typical RBS- plot of the epitaxial system shown as insert.χ_{min}- values as quality measure, drawn from the ratio between random and aligned orientations, are usually better than 5 %.

Figure 3 gives the results obtained at incidence near to <110>Si (a) and <114>Si (b). As can be seen, the minimum yield of back scattered ions for the Si signals is localized at an angle of 35.26° corresponding to the theoretical value between the <111> and <110> direction in a cubic crystal structure. However, the minimum signal of CaF_2 is shifted for about +0.32° in such a manner that the angle between the <111> direction and <110> or <114> direction of CaF_2 is greater than the theoretical value.

This means especially that the point group (crystal class) of the deposit is really not cubic but rhombohedral. The symmetry of the strained CaF_2 layer is decreased with respect to the bulk material ($\bar{3}$m instead of m$\bar{3}$m). Further, from figure 3 it is seen that the back From this diagram a χ_{min}- value of about 5% was obtained demonstrating the high crystalline quality of the grown Further ion channeling experiments in a scanning mode were carried out. Here the incident ion beam was varied in direction near the <110> and <114> crystallographic epitaxial film.scattering yield minimum for Si is lower in the left part than that for CaF_2; in the right part the situation is opposite.

This means that the <110> deposit directions are nearly parallel to the <114> substrate direction. The yield differences are caused by channels of different size in <110> and <114> directions in a cubic crystal structure. Therefore, the deposit crystallites have an orientation with respect to the substrate which corresponds to a twinning $T_{<111>}$ where <111> means the substrate normale. Figure 4 shows a typical plane view TEM picture for the investigated CaF_2 epitaxial layer on {111} silicon.

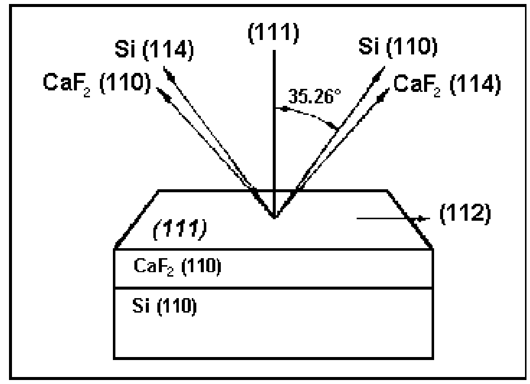

Fig. 2: Geometrical arrangement of the sample and directions as mentioned in the text.

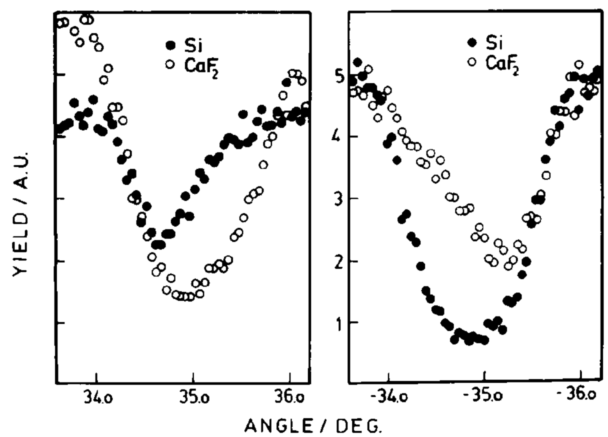

Fig. 3: RBS yield for Silicon (full circles) and CaF_2 (bare circles) around the <110>Si (a) and <114>Si- directions (see fig. 2).

The Moiré fringes visible in this electron micrograph are caused by different lattice constants of the substrate and the deposit, respectively. The distance between the Moiré fringes varies from 15 to 25 nm suggesting that the misfit in the investigated epitaxial system is inhomogeneous. An analysis of the micrograph provides for an actual misfit value in this epitaxial system of about 0.8 to 1.2 %.

4. Discussion

The existence of tensile strain in the Si/CaF_2 -heterosystem is concluded from the misalignment by about +0.32° of the <110> CaF_2 direction (see figure 2 and 3). This measurement proves that a pseudomorphic growth did not happen.

The lattice constant of CaF_2 is larger by 0.6% at room temperature relative to that of Si. Consequently, compressive strain should be expected. An explanation for the existing tensile strain in the CaF_2 film can be drawn from the fact that the thermal expansion coefficient of Si is by far smaller than that of CaF_2.

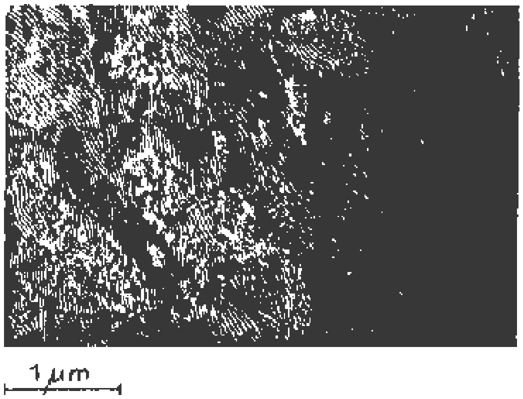

Fig. 4: TEM micrograph with Moiré pattern, caused by the different lattice constants between deposit and substrate.

At 700 °C, corresponding to the growth temperature, the actual lattice misfit between both epitaxial partners is not 0.6 % (room temperature), but 2.1 %. For such a large misfit, the critical film thickness (for pseudomorphic growth) is quite small, at least smaller than the grown film thickness in this study.

After the CaF_2-layer passes over the critical film thickness, the epi-layer will relax and form a series of misfit dislocations in and close to the interface.

The following growth does not depend anymore on the Si-substrate, but the bulk CaF_2 properties will prevail based on the own cubic fluorite structure. During the cooling process after growth a mechanical planar stress in the CaF_2 layer of tensile type occurs due again to the difference of thermal expansion coefficients, providing for the measured (unexpected) data, which yield a real misfit value of about 1 % at room temperature.

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