

In situ analysis of epitaxial Calcium fluoride thin films grown on Silicon

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Heteroepitaxial growth of dielectrics films on Si substrates is of considerable interest in the formation of SOI-structures and 3d-integrated circuits for microelectronic applications. CaF_2 crystallizes in the cubic fluorite crystal structure, which is closely related to the diamond structure of Si. In the course of the present work, CaF_2 epitaxial films were grown on Si(111) substrates by means of MBE. It was evaporated from a Knudsen-type cell by use of a graphite crucible, while the growth temperature was held at 700 °C. The Si substrates were chemically cleaned, and the final volatile oxide was desorbed in situ by heating to 900 °C, proven by AES. RHEED has been used to monitor the film growth in situ, and RBS to study the epitaxial quality. Usually good crystallographic properties are achieved under optimum growth conditions, with values of $\chi_{\min} < 5\%$.

Keywords:

1. Introduction

The high cost effectiveness of actually practiced silicon material technologies places severe demands on any silicon-MBE (Molecular Beam Epitaxy) process step [1]. A number of substrate preparation methods have proven adequate for research purposes [2]. It has been known for some time, that a perfectly clean silicon surface has a strong affinity, particularly for carbon, and that SiC is easily formed, but its bonds are extremely hard to break [3].

The creation of a passivating surface oxide layer rather than a clean silicon surface at the end of an *ex situ* preparation process avoids its formation on the way to the growth chamber. The volatility of the silicon oxide is enhanced, and consequently the protection layer can be removed at temperatures below 800 °C, when a thin non-stoichiometric oxide is grown [4]. With the objective of achieving three-dimensional integrated devices structures, the epitaxial salts CaF_2 , BaF_2 and SrF_2 have been investigated intensively since their original MBE synthesis some years ago [5, 8]. Besides the technological advantage of their evaporating as stoichiometric molecules, of higher importance is that these materials are closely lattice match single crystalline silicon. The so-called CaF_2 -lattice structure is basically identical to that of silicon with the implementation of four lattice sites.

2. Film Growth and Analysis

The CaF_2 films were grown in a custom-built MBE system equipped with RHEED (Reflection High Energy Electron Diffraction) and AES (Auger Electron Spectroscopy) [9]. The silicon substrates were commercially obtained n-type wafers oriented to within 0.5° and polished on one side. Each substrate was chemo-mechanically

polished, etched, passivated with a de-ionized water rinse and immediately loaded into the MBE system. Final cleaning was accomplished by heating at 900 °C to desorb the passivating SiO_2 layer for 15 minutes in ultra-high vacuum.

AES spectra (Fig. 1) show no evidence of either carbon or oxygen contamination to an estimated detection sensitivity of $\leq 1\%$ of a monolayer for the standard single-pass cylindrical mirror analyzer used [10]. The CaF_2 epilayers were grown on the clean Si(111) substrates by molecular evaporation from a CaF_2 compound source, which was operated at 900 °C yielding a growth rate of 1 Å/min at a substrate temperature of 700 °C.

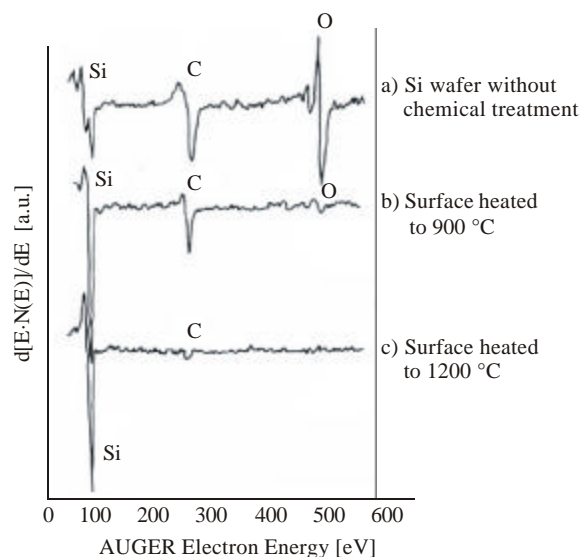


Figure 1. AES spectra of silicon surface showing three steps of characterization. (a) as-received wafer, (b) after thermal annealing at 900 °C, where SiO_2 desorbs, and (c) annealing at 1200 °C, where SiC is dissociated.

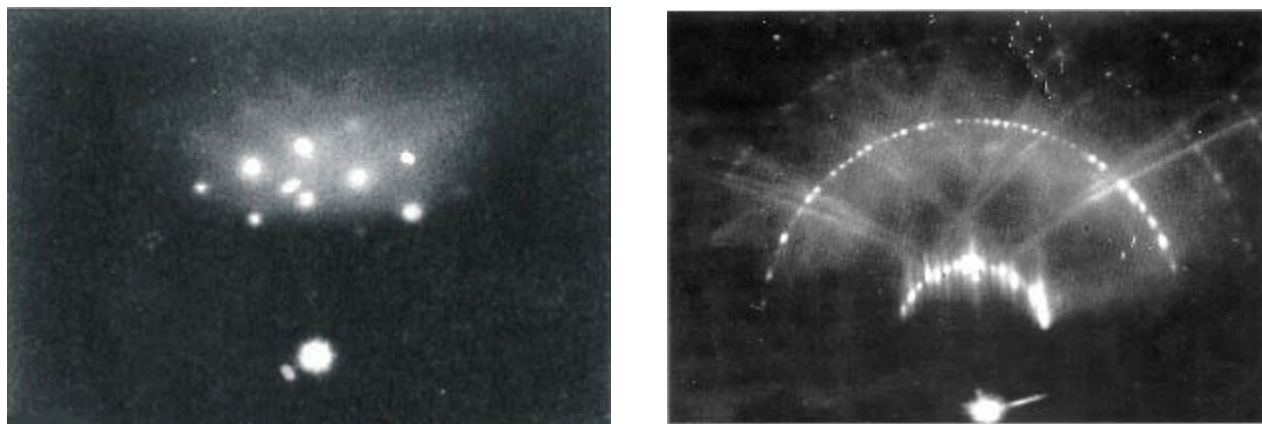


Figure 2. (a) RHEED pattern obtained from “as received” silicon surface; (b) the same as in (a), but after *ex situ* preparation and a thermal *in situ* annealing, azimuth $\langle 110 \rangle$. The 7×7 reconstruction appears as prove of a chemically clean and geometrically perfect silicon surface.

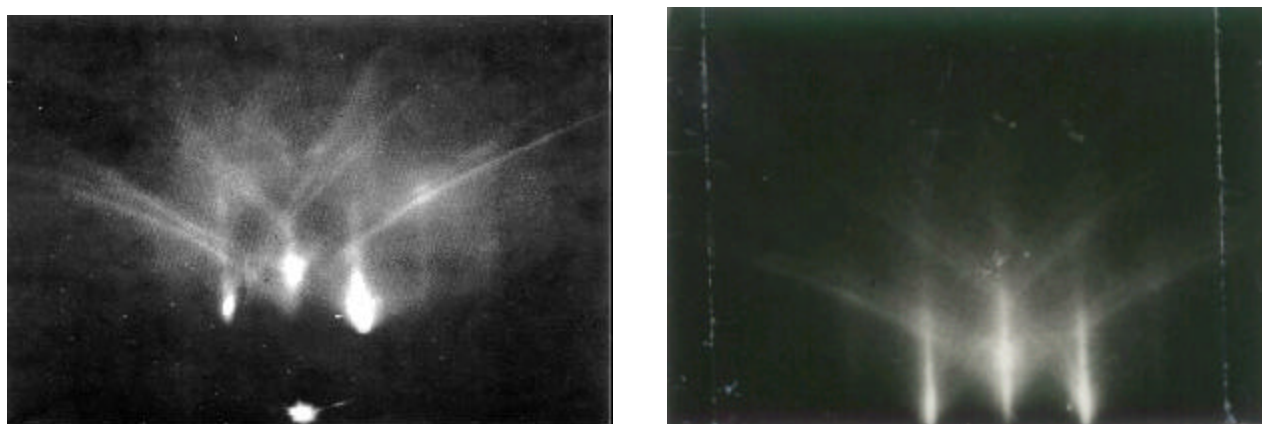


Figure 3. (a) initial RHEED pattern after 30 seconds of CaF_2 evaporation; (b) After an evaporation time of 2 minutes, the RHEED pattern of CaF_2 is well established.

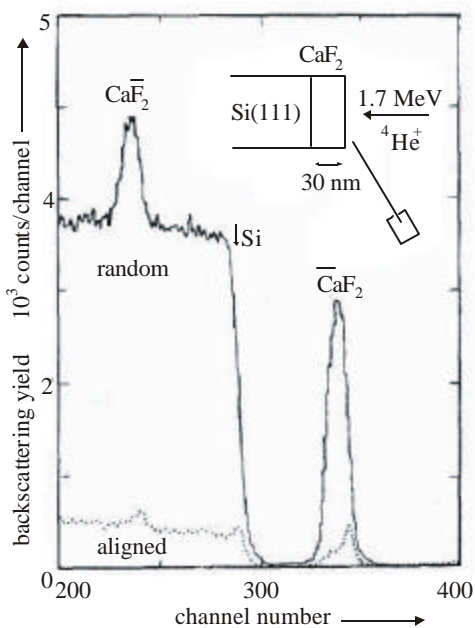


Figure 4. RBS and channeling yield of $^4\text{He}^+$ -ions in the heterosystem CaF_2 on $\text{Si}(111)$. The film thickness is beyond its critical value of about 12 nm for this structure.

Figs. 2a and 2b show the RHEED pattern obtained from the Si(111) substrate prior to growth, and after the final desorption. The RHEED electron beam of 20 keV is at grazing incidence along an in-plane $\langle 110 \rangle$ axis for the (111) surface. The rather spotty appearance of the RHEED pattern for the untreated wafer indicates a rough surface, which converts into a high quality RHEED (7x7) surface reconstruction state after the annealing step. A RHEED streak pattern for the (111) CaF₂ surface grows out of a transition step immediately after the shutter of the CaF₂ Knudsen cell was removed.

The RHEED pattern shown in Figs. 3a and 3b display immediate single crystal growth of CaF₂, indicating atomic order smoothness of the surface [11]. For details of this powerful *in situ* analytic tool and the interpretation of RHEED-pattern see [10, 11]. RBS (Rutherford Back Scattering and channeling) spectrometry was applied in order to probe the chemical composition of the thin films, using 1.7 MeV He⁺-ions. The beam diameter was 1 mm, and the measuring dose 10 μ C, which corresponds to a very low exposure dose of 6 x 10¹⁵ cm⁻². The RBS-spectrum is shown in Fig. 4. The yield of backscattered particles is proportional to the scattering cross section of atoms, so the composition depth profile can be found from knowledge of energy loss and cross section of the interfering atoms. The heavier Ca-atom compared to Si and F bounces back the He⁺-ions with higher remaining energy.

Conclusions

The initial surface preparation of the Si wafer surface is highly important for an epitaxial growth of a CaF₂ thin film. RHEED is a very adequate method for monitoring the static surface prior to CaF₂ evaporation, as well as the dynamic CaF₂ surface during the growth process. Once finished the heterostructure, RBS is the method of choice for evaluating the epitaxial quality. Good crystallographic properties with Rutherford backscattering minimum channeling yields of about or better than ~ 5 % are obtained, which proves the optimum technological operation of the growth process.

Acknowledgement

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