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Abstract. Germanium nanocrystals were grown on CaF$_2$/Si(111) by molecular beam epitaxy. Specific features of Ge and CaF$_2$ growth have been analysed in this work, using electron diffraction and atomic force microscopy. Well-pronounced Ge quantum dots were observed in case of growth on thick CaF$_2$ buffer.

Introduction

Heteroepitaxial films with Ge islands of small sizes (quantum dots) are very attractive because Ge is a prospective semiconductor for new devices based on quantum effects. Ge quantum dots or structures with 3-D electron confinement have potential applications in advanced electronic and optoelectronic devices, e.g. single electron transistors and multispectral detectors. In optoelectronic applications, germanium nanostructures can successfully compete with traditional A$_{III}$B$_V$ materials [1, 2]. Such structures are also interesting because their growth techniques are compatible with usual silicon microelectronic technology. However, there are some drawbacks of Ge/Si nanostructures. Because silicon has relatively narrow band gap, only shallow quantum wells can be created using this heterocouple. Therefore quantum effects in these heterostructures are important only at low temperatures. Moreover, some of the Ge islands may luminesce at the Si absorption edge. To avoid the above-mentioned problems, the Ge dots studied in the present work were grown on CaF$_2$/Si(111) heteroepitaxial substrates. The previous reports on Ge growth on CaF$_2$ mainly dealt with relatively thick films [3, 4]. In this work, we studied Ge/CaF$_2$ heteroepitaxy starting from the initial stages when average coverage by Ge did not exceed a few monolayers (0.5–1 nm).

1. Experimental technique and pre-growth Si treatment

Ge/CaF$_2$/Si(111) and CaF$_2$/Ge/CaF$_2$/Si(111) heterostructures were grown in a research MBE system at the Institute of Semiconductor Physics, Novosibirsk, Russia. After standard chemical cleaning, the silicon substrates were loaded into the growth chamber and cleaned thermally at 830°C in ultra high vacuum. This procedure allows obtaining atomically clean Si(111) surfaces with a 7 × 7 superstructure. The fluoride and Ge were evaporated from graphite crucibles. Due to molecular mode of CaF$_2$ sublimation, the stoichiometry of the grown layers was kept naturally. The growth rate of CaF$_2$ or Ge layers was about 1 nm/min for a few nanometers films and about 15 nm/min for thick (over 100 nm) films. The CaF$_2$ buffer growth temperature was kept within the 700 to 780°C range. Germanium films were grown at 350°C.
2. **In situ RHEED measurements**

At the first stage, CaF$_2$ buffer layer was grown on clean 7 × 7 Si(111) substrates. The buffer layer thickness was 100–200 nm. The growth modes and crystalline quality of the fluoride layers were monitored in situ using reflection high energy electron diffraction (RHEED). To avoid undesirable influence of electron beam on growth processes its intensity and exposure time were kept as low as possible. One can see a RHEED pattern taken after 200 nm CaF$_2$ growth in Fig. 1(a). The picture demonstrates two-dimensional diffraction typical for a single crystal film with the smooth surface.

![RHEED patterns](image)

**Fig. 1.** RHEED patterns from: (a) CaF$_2$ surface at electron beam azimuth [112]; (b) the same structure after Ge deposition, electron beam azimuth [110].

Ge was grown at the second stage of heteroepitaxy. The substrate temperature was chosen about 350°C because a Ge film has no defects at this temperature [5], and diffusion current is too low to produce large islands [6]. A RHEED pattern does not change at first, but as an average film thickness increases to 11.5 nm, bright spots appear on the streaks in Fig. 1(b). This implies, that the growth proceeds in the Stransky–Krastanov mode. Germanium growth on CaF$_2$ is quite likely to start in the layer-by-layer mode, and then the strain relaxes resulting in coherent islands on the surface. At the final stage, we covered the most of the structures by a thin CaF$_2$ cap layer to protect Ge from oxidation after the growth.

3. **Surface morphology studies by AFM**

The main method of surface morphology studies was an atomic force microscopy (AFM), because of CaF$_2$ radiolysis under electron beam in the electron microscope. The surface morphology measurements have been carried out using a P4-SPM-MDT microscope produced by NT-MDT (Zelenograd, Russia). The samples were studied at the ambient conditions in the tapping mode. The typical radius of the cantilever’s tip produced by Silicon MDT was about 20 nm. The resonance frequency was in the 20–60 or 250–500 kHZ ranges.

Figure 2(a) shows Ge small islands situated on atomically flat CaF$_2$ triangular shape terraces resulting from thermal stress relaxation in thick fluoride layers on Si(111) [7]. The average radius of Ge islands does not exceed 20 nm. This value is close to the expected lateral resolution limited by the sharpness of the AFM tip. The average height of the islands is less than 10 nanometers.

Increasing Ge deposition time, at the same substrate temperature (~350°C), one could obtain more pronounced Ge nanocrystals (Fig. 2(b)). The typical lateral size of Ge islands was about 70 nm and the height was about 30 nm. The average thickness of Ge, that assembles in the islands, is 10 nm.

Summarizing the above, we have demonstrated MBE-growth of Ge nanocrystals on
Fig. 2. AFM images of Ge/CaF$_2$/Si(111) structures having various average thickness of deposited Ge: (a) 1 nm, (b) 10 nm.

CaF$_2$ surface. Their size and density can be controlled by choosing proper growth conditions. Optical and electrophysical characterization of the Ge dots is underway.

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References