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Germanium on SiC(0001): surface structure and nanocrystals

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Abstract
Germanium nanocrystals as potential candidates for a future optoelectronics in group-IV semiconductors have been grown on SiC(0001). A monoatomic wetting layer is formed in a Stranski-Krastanov growth mode. The surface structure of this wetting layer studied by STM and LEED depends on the SiC surface preparation. 3x3 and 4x4 Ge superstructures are observed by growing on the silicon-rich SiC(0001)-3x3 surface. Surface structures with mainly two-fold periodicity as well as 6x6 are observed after Ge deposition on silicon-deficient SiC(0001)-(?3x?3)-R30° or (6?3x6?3) surfaces. Two-dimensional Ge islands of lateral dimensions between 2 and 4 nm and a density of $3 * 10^{12}$ cm^{-2} are initially formed on the wetting layer to reduce strain. Further deposition results in the growth of nanocrystals of lateral dimensions between 40nm and 150nm and heights between 5 and 30nm. A maximum density of 10^{10} cm^{-2} and minimum size of these nanocrystals has been obtained for low deposition temperature of 470°C and high rate of 1.5nm/min. The epitaxial orientation of the nanocrystals has been determined as (111) and (220) by TEM and XRD.

Introduction
Low-dimensional semiconductor structures are investigated for their interesting properties for electronic and optical applications [1]. Nanometer scale structures are expected to show electron confinement the stronger the smaller the size. Quantum dots confining the electrons in three dimensions can be grown by Stranski-Krastanov growth mode. Due to the strain induced by a different lattice constant of substrate and deposited material, an initially two-dimensional (2D) epitaxial growth changes to 3D island growth on a thin wetting layer. This formation of self-assembled islands reduces the strain and lowers the total energy of the system.
Germanium nanocrystals embedded in a semiconductor matrix are potential candidates for a future optoelectronics in group-IV semiconductors. Although an indirect semiconductor, high intensity luminescence is expected for germanium quantum dots due to carrier confinement. Many investigations have dealt with Ge on Si(001) or Si(111) [e.g., 2-5]. We have grown Ge on SiC(0001) by solid-source MBE. The wide-band gap semiconductor SiC may give the possibility to arrange quantum dots at a p-n junction for electroluminescent devices. A Stranski-Krastanov-like growth mode is observed due to the huge lattice mismatch of some 30% between silicon carbide and germanium. We investigated the surface structure of Ge on differently prepared SiC(0001) by Scanning Tunneling Microscopy (STM) and Low-Energy Electron Diffraction (LEED). The formation of Ge islands by Stranski-Krastanov growth mode is measured in situ by STM and ex situ by Atomic Force Microscopy (AFM), High-Resolution Transmission Electron Microscopy (TEM), and X-ray diffraction (XRD).

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Experimental

The 4H and 6H on-axis and (high miscut) off-axis SiC(0001) surfaces were prepared ex situ either by plasma etching, subsequent oxidation and HF dip or by hydrogen etching and in situ by heating in a Si flux to get definite reconstructions of 3x3, (?3x?3)-R30° or (6?3x6?3) observed by electron diffraction (LEED). Germanium was deposited from effusion cells with evaporation rates of 0.1 to 1.5 nm/min at substrate temperatures of 470 and 550°C. Additionally, several samples were deposited with germanium at room temperature and, subsequently, heated to form nanocrystals.
The surface composition before and after Ge evaporation was measured by X-ray Photoelectron Spectroscopy (XPS). Surface structure and morphology as well as size, geometry, density and distribution of nanocrystals were determined in situ by STM and ex situ by AFM, TEM and XRD.

Results and Discussion

A wetting layer was formed by Ge deposition at substrate temperatures of 470 and 550°C. Depending on Ge coverage and surface preparation, different reconstructions were observed in LEED and STM. Most of the samples showed a 1x1 LEED pattern after more than 2ML Ge deposition. In this temperature range the large lattice mismatch causes a transition from 2D to 3D (islands) growth of Ge on SiC at a coverage near 1 monolayer (ML).
After deposition of Ge on a Si-rich SiC(0001)-3x3 surface, 3x3 and 4x4 hexagonal, trigonal and honeycomb structures have been initially observed by STM depending on the coverage in the submonolayer range, annealing temperature and annealing time (fig.1a). A deposition of more than 2ML of Ge at temperatures of 470°C and rates between 0.5 and 1.5nm/min results in nanocrystals of typical dimensions between 50 and 100nm and a Si-Ge alloying as characterized by TEM and XRD [6].
The evaporation of Ge on SiC(0001)-(?3x?3)-R30° or (6?3x6?3) leads to a wetting layer showing a complex surface structure of mainly two-fold (0.6 nm) periodicity (fig. 1b). Linear „tracks“ which may be formed of dimer rows obviously to reduce stress were observed by STM for a higher Ge coverage near 1 ML. Two-dimensional (2D) Ge islands with a high density of some $3 * 10^{12}$ cm^{-2} and dimensions between 2 and 4 nm are formed on the Ge wetting layer (fig. 2). At step edges of the SiC substrate, two-dimensional Ge islands of up to 50nm lateral dimensions and weak corrugation were observed on top of the first Ge wetting layer (fig. 3). Additionally, small regions of some tens of nm showed a 6x6 surface structure.

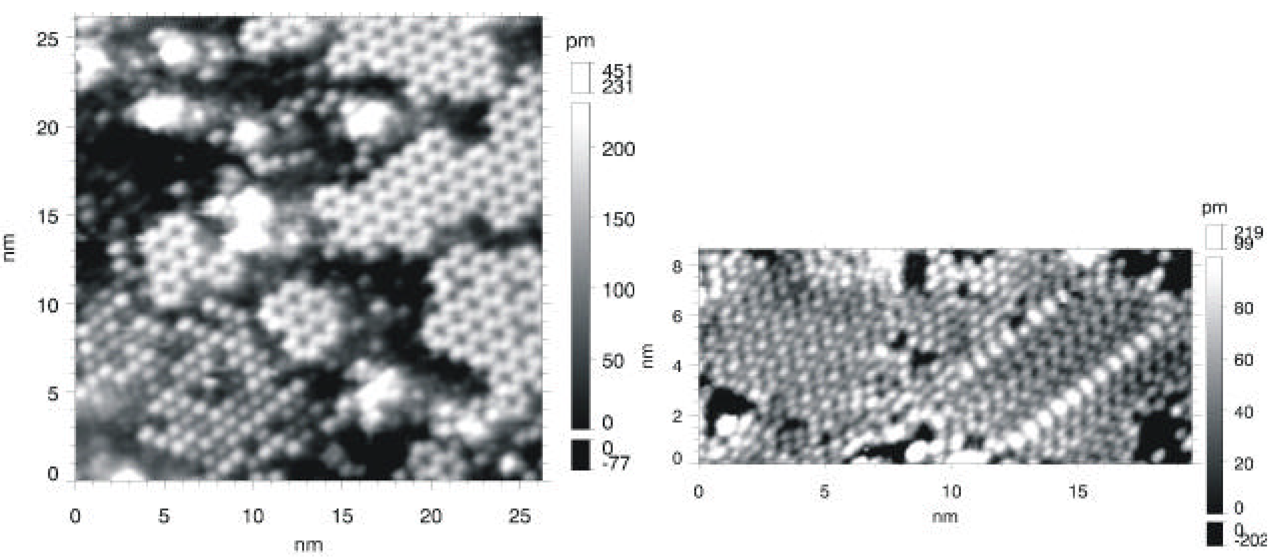

Fig. 1 (a) (b)

STM images of (a) 3x3 and 4x4 reconstructions of Ge on 6H SiC(0001)-3x3 and (b) surface structures observed on 6H SiC-(?3x?3)-R30° showing mainly two-fold periodicity and dimer rows or „tracks“.

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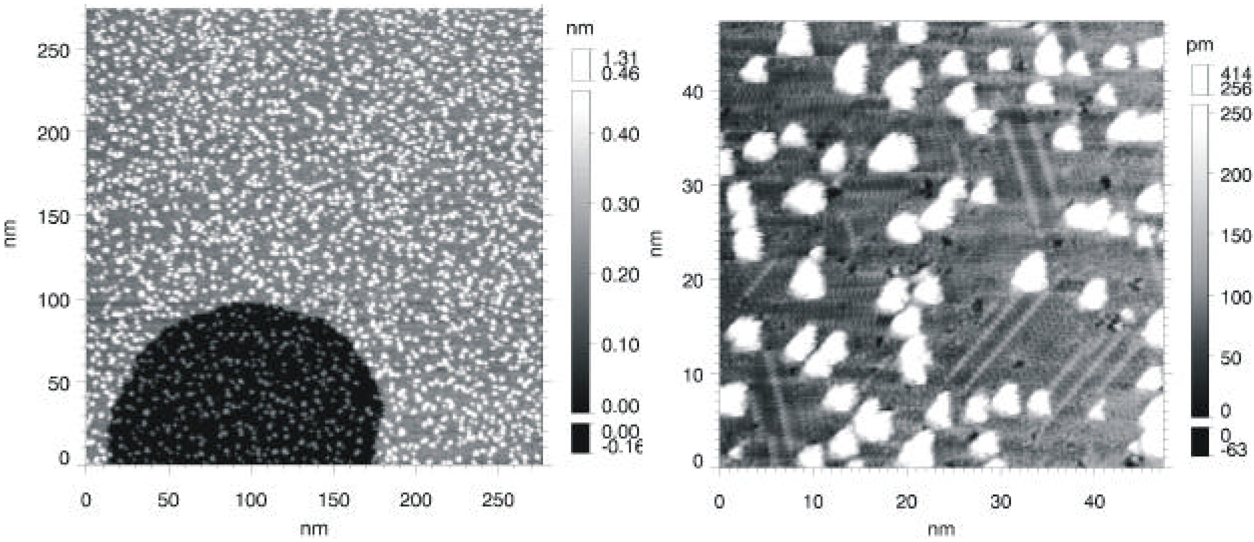

Fig. 2 (a) (b)

STM images of 2D Ge islands grown on 6H SiC(0001)-(?3x?3)-R30° at a deposition rate of 1nm/min at 470°C.

(a) An equal 2D nucleus density is observed on neighboring terraces differing in height of one Si-C layer.

(b) The 2D islands are formed on the Ge wetting layer showing a surface structure with two-fold periodicity and dimer rows.

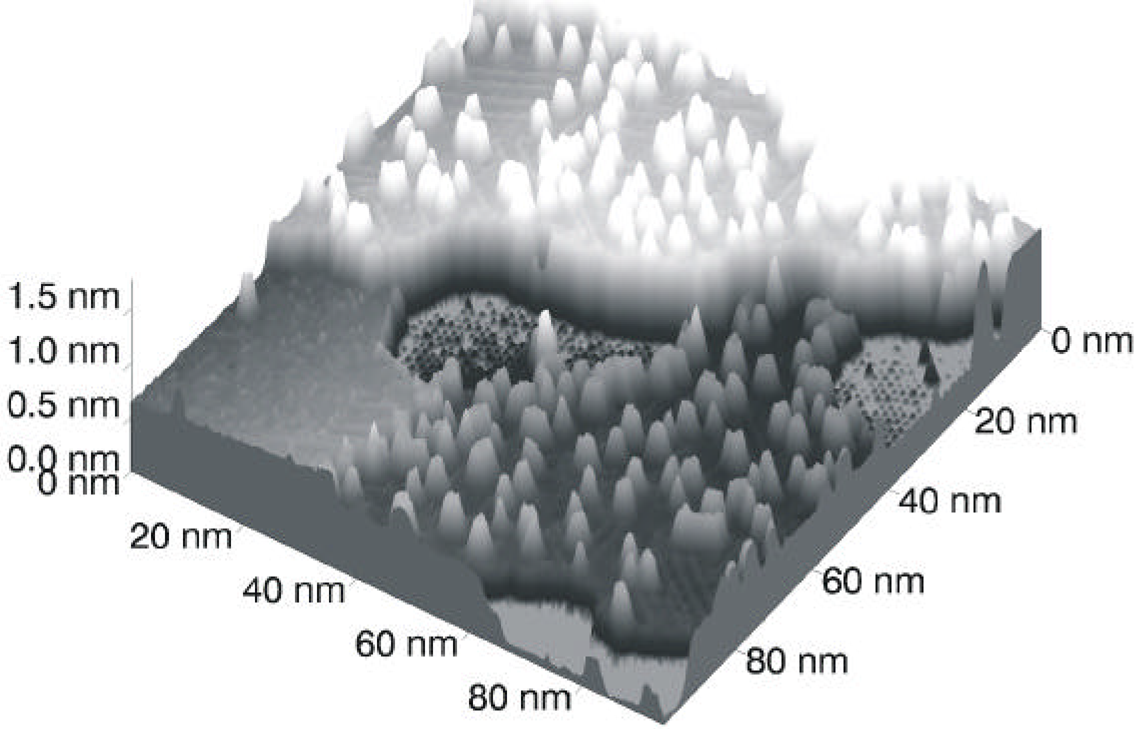

Fig. 3

STM image of approximately 1.5 ML Ge deposited on SiC(0001)-(?3x?3)-R30° showing nanosized 2D Ge islands on a Ge wetting layer. At SiC step edges two-dimensional Ge islands of some 50nm lateral dimensions are observed as well as regions of 6x6 structure.

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At a higher Ge coverage between 2 and 8 ML, 3D nanocrystals with average diameters between 40 and 150 nm and heights between 5 and 30 nm were measured on most of the samples. The epitaxial orientation of the nanocrystals has been determined as (111) and (220) by TEM and XRD [6]. Those films grown at lower temperature (470°C) and high rate show a narrow size distribution of the nanocrystals and a maximum density of 10^{10} cm^{-2} (fig. 4). Depending on growth conditions also much smaller nanocrystals of only 2nm in height and a high density in a bimodal distribution of island sizes were observed by AFM. No difference was found for deposition on on-axis and off-axis substrates as well as on 4H and 6H. Especially, large crystals (200 to 800nm) formed at low evaporation rate and high temperature or by annealing a Ge film grown at room temperature showed a regular shape, like pyramides, with facets or with flat top, whereas, no regular shape was observed by AFM for most of the samples.

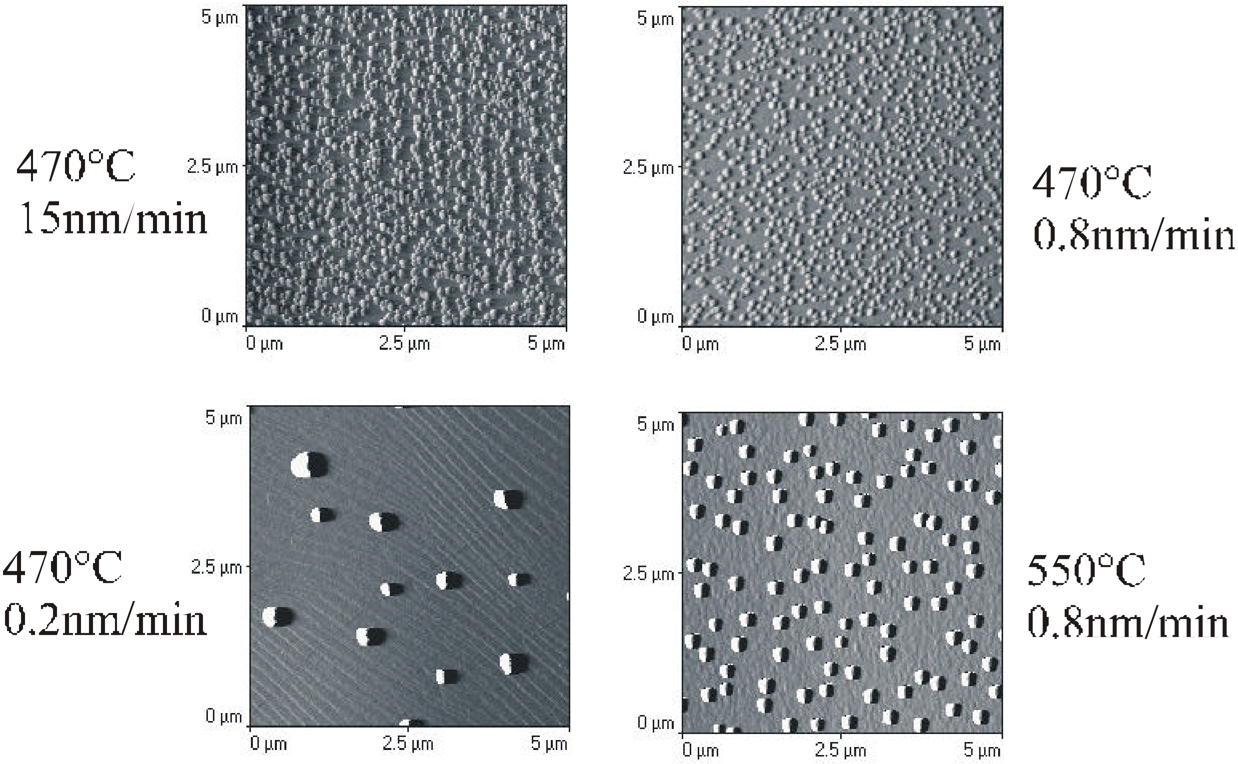

Fig. 4
AFM images of Ge nanocrystals grown on SiC at different deposition rates and temperatures.

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