Formation of Self Assembled PbTe Quantum Dots in CdTe on Si(111)

F. Felderå,* A. Fogniniå, M. Rahimå, M. Fillå, E. Müllerå and H. Zogga

åThin Film Physics Group, ETH Zurich, Technoparkstr. 1, 8005 Zurich, Switzerland
åElectron Microscopy ETH Zurich (EMEZ), Wolfgang-Pauli-Str. 16, 8093 Zurich, Switzerland

Abstract

We describe the growth and formation of self assembled PbTe quantum dots in a CdTe host on a silicon (111) substrate. Annealing yields different photoluminescence spectra depending on initial PbTe layer thickness, thickness of the CdTe cap layer and annealing temperature. Generally two distinct emission peaks at ~0.3 eV and ~0.45 eV are visible. Model calculations explaining their temperature dependence are performed. The dot size corresponds well with the estimated sizes from electron microscopy images. The quantum dots may be used as absorber within a mid-infrared detector.

Keywords: PbTe, quantum dots, infrared, epitaxial growth, annealing, formation, photoluminescence

1. Introduction

Quantum dot infrared photodetectors (QDIP) have high sensitivity limits due to the long lifetimes of photoexcited carriers. Contrary to quantum well infrared detectors (QWIP), QDIP are sensitive to radiation of all polarizations. Therefore no special light coupling is needed, increasing efficiency and reducing cost. Whole infrared focal plane arrays (IRFPA) using QDIP have already been described with III-V materials [1,2]. The QDIP technology has the potential to replace conventional QWIP and even narrow band semiconductor IRFPA [3]. For a high efficiency, the quantum dots (QD) should have a high aspect ratio, i.e. a large height compared to their width. Additionally, the density of the QD has to be extremely high for good absorption. This is typically not the case for self assembled QD employed in most published work up to date. In resonant cavity enhanced IR-photodetectors however, the necessary density may be lower since here photons entering the cavity are reflected many times between the mirrors until they are absorbed in the detector layer [4].

The narrow gap IV-VI semiconductors are promising candidates for QD detectors. Lead-salts have a very high dielectric constant and a very low Auger recombination rate, which makes them fault tolerant to structural defects [5]. In addition, epitaxial QD with pyramidal shape are formed with such IV-VI narrow gap semiconductors in (111) oriented layers, e.g. PbSe QD in a PbTe(111) host [6,7]. Diffusion leading to truncation of the pyramidal QD is
greatly reduced when alloying the host, e.g. PbSrTe, or covering the QD with a very thin EuTe layer before continuing with IV-VI overgrowth. Photoconductivity in such layers has been demonstrated, too [8].

A different approach is to obtain coherent PbTe or PbSnTe QD in a CdTe host [9,10,11]. PbTe is nearly lattice matched to CdTe, but has a different crystal structure: The structure is rocksalt for PbTe, while CdTe crystalizes in the zinc blende structure. Coherent PbTe precipitates are formed, but intermixing is avoided. The size of the QD are adjusted by the annealing conditions, while the shapes are highly symmetric cubo-octahedral. All these experiments were performed with (100) oriented CdTe layers grown on lattice mismatched GaAs(100).

Here we analyze properties of PbTe QD in a CdTe host layer for (111) orientation. The CdTe(111) layers were grown on Si(111) substrates using a CaF2/BaF2 buffer layer [12]. This is at variance to most other works where different orientations like (001) or (211) and different buffer layers were employed. However, (111) oriented CdTe layers on Si(111) substrates were described with ZnSe buffer layers [13].

2. Experimental

Growth is performed in a two chamber molecular beam epitaxy (MBE) set-up onto 3 inch Si(111) substrates. First a thin (2 nm) CaF2 intermediate layer which is nearly lattice matched to Si, then a BaF2 buffer layer (~200 nm) is deposited. BaF2 is water soluble and thus allows an epitaxial-layer liftoff process. Next the CdTe buffer layer of several μm thickness, which forms the host matrix for the QD, is deposited. The active PbTe layer is then grown at a substrate temperature of 220 °C with different mean thicknesses ranging from 2 nm to >50 nm. As last step, a 10 nm to 1 μm thick CdTe cap layer is grown. RHEED studies are performed in situ on the CdTe layers, as well as during growth of the PbTe layer. After growth, the PbTe layer is converted to QD outside of the MBE chamber by annealing. Various temperatures and durations are used as discussed below. For photoluminescence (PL) measurements, a commercial laser emitting at 1.55 μm with random polarization is used for pumping. The sample is cooled with liquid nitrogen via a temperature controllable heat sink. The spectra are recorded with an InSb-detector connected to a Fourier transform spectrometer. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) is used for structural analysis, and energy dispersive x-ray spectroscopy (EDX) for element identification.

3. RHEED studies

The CdTe RHEED pattern of the first part of the buffer layer before deposition of PbTe shows a symmetry depending on the azimuthal direction of the incident electron beam [14]. As shown in fig. 1 the pattern alternates between mostly streaks and mostly points for every azimuthal increment of 30°. This six-fold symmetry also appears in AFM images of the surface and its Fourier transform. The root mean square roughness of the surface is ~6 nm with peak to valley differences up to 40 nm. Bumps are aligned like pearls on a necklace in the <112>-type
directions. This angular periodicity of the bumps explains the RHEED patterns, while neither the width or length nor the spacing between them needs to be uniform. Depending on azimuth, the majority of incoming electrons is either deflected at the two dimensional top surface of the superimposed elongated hills, thus contributing to the streaks, or passes through the bumps, thus contributing to the points.

The RHEED images during growth of the PbTe layer show a transition from 2D to 3D growth mode. Starting with a streaky image of the CdTe surface in a <112>-type azimuthal direction, the pattern changes after 2 ML of deposited material to mainly points. A deposited thickness of a <9 ML suffices for the RHEED image to show only points now in all azimuthal directions. This indicates a nucleated (3D) PbTe growth. When growing the CdTe cap layer the patterns changes almost instantly, after ~2 ML, back to a 2D/3D surface with bumps along <112>-type directions as described before.

4. Photoluminescence measurements

PL spectra of all samples show one or two emission peaks, depending on the mean thicknesses of the deposited PbTe layer and the cap layer, and on annealing conditions. Fig. 2 shows the PL spectra recorded at 110 K of samples with 10 nm mean thickness of the PbTe layer and a 1 μm thick cap layer, annealed for 1 h at different temperatures. The first peak A at lower energies ~0.31 eV appears for all samples with a cap layer > 50 nm, regardless of PbTe thickness. It does not shift during annealing and is also faintly visible in the unannealed samples. The second peak B at ~0.43 eV appears after a first annealing step for all samples with an originally < 50 nm thin PbTe layer. It shifts towards higher energies with higher annealing temperatures before it vanishes for temperatures above 340 °C. For samples with a PbTe layer thicker 50 nm only the first emission peak appears regardless of annealing time and temperature. For samples with both a thin CdTe cap layer < 10 nm and a thin PbTe layer < 10 nm, only the second peak at higher energies occurs. The thickness of the lower CdTe buffer layer has no observable influence on the PL spectrum.

To investigate the first peak A at ~0.31 eV a sample with a PbTe layer of 8 nm mean thickness embedded 1 μm deep in the CdTe host and annealed at 360 °C for 4 h is chosen. As shown in fig. 3, it is emitting only at the lower energy peak in the PL spectra. With higher measurement temperatures the emission is blue-shifted (the bandgap of PbTe increases with higher temperatures). The noted measurement temperatures are not corrected for heating effects due to pumping. In the high angle annular dark field STEM image of this sample precipitates with a thickness of >30 nm to 50 nm and a length of several hundred nm are visible. As depicted in the insets, their trapezoidal shape results from the intersection of the (100), (010), and (001) facets with the (1-11) viewing plane. Due to the threefold symmetry of the (111) plane, it can be concluded that the precipitates are truncated pyramids. However, the size of these precipitates is too large in order that quantization effects are discernible in the PL. The emission peak rather relates to a shifted bandgap caused by strain, induced from the CdTe host in PbTe due to the lattice mismatch and different thermal expansion coefficients. With the temperature-dependent deformation potential as published in Ref [15], the bandgap energy raises to ~0.29 eV at 100 K whereof ~0.07 eV is strain induced.
To investigate the emerging peak B at ~0.45 eV a sample with an originally 7 nm thick PbTe layer and a cap layer of 10 nm was chosen. After annealing at 320 °C for 4 h, its PL spectra exhibit only the emission peak at higher energies, as seen in fig. 4. With higher measurement temperatures the emission is red-shifted. Also shown is a SEM image of back scattered electrons, revealing information about the material composition on and slightly below the surface due to z-contrast. The tilted view of 55° reduces the contribution of surface roughness on contrast. Brighter spots correspond to higher atomic ordering numbers, indicating PbTe QD beneath the cap layer. By counting contrasts one may estimate an average dot density of ~2 \times 10^{10} \text{ cm}^{-2}. With the initial PbTe layer thickness of 7 nm this yields an average cubic dot size of 32 nm. However, more QD could be below the penetration depth of the SEM, effectively decreasing the estimated dot size due to an increased dot density. The inset shows a cross-section STEM image of QD with a thickness ~10 nm and a length of 10 nm to 20 nm. It is however not known whether a part of it has been removed by the preparation process. According to EDX measurements the surrounding material is composed of Cd and Te, while the dots additionally consist of Pb. With these sizes of the dots quantization effects are expected. The markers in the PL spectra show the calculated emission energies for the longitudinal and oblique (100) to (100) interband transitions for a QD size of 20 nm. A finite rectangular potential was assumed, with 0.135 eV valence band offset [16]. The calculated values reproduce the temperature-dependence of the emission peak very well, owing to the change of effective masses proportional to $E_g(T)$.

From the SEM and STEM images in conjunction with PL measurements a conclusion on the formation of the QD is possible. The deposition of PbTe does not produce individual QD, but a connected nucleated 3D PbTe film of nonuniform thickness. Annealing at a low temperature of any sample with a thin PbTe layer deeply embedded in the CdTe host leads to the formation of QD as well as larger PbTe precipitates. Additional annealing at higher temperatures leads to diffusion of material from the smaller dots towards the larger precipitates. The diffusion leads to a reduced size of the dots, thus a stronger quantization. This is seen as a blue-shift of the emission peak corresponding to QD in figure 2. For annealing temperatures > 340 °C all the remaining PbTe aggregates in the large precipitates, and the QD emission peak disappears. This diffusion behavior is at variance to results obtained with other orientations and host materials: size-controllable PbTe QD in CdTe have been reported on GaAs(100) substrates [11]. In conjunction with the presented results, this indicates a very anisotropic diffusion of the PbTe material into the CdTe host for the (111)-oriented layers. However, for PbTe host layers, truncation of self-assembled PbSe QD with originally pyramidal shape was observed when overgrown again with PbTe [6]. Here the alloying with Eu hinders diffusion. Also, ultrathin EuTe or SrTe intermediate layers have been employed as stabilizing barriers [7]. In this work, for a thin cap layer only small QD and no large precipitates are formed. Since in this case the thickness of the thin cap layer is equal or less than the roughness of the CdTe surface, the final interface to air may act as a boundary for diffusion during annealing.

![STEM image (left) and PL measurements (right) of an annealed sample with a PbTe layer of a mean thickness of originally 8 nm embedded 1μm deep within the CdTe. The large PbTe precipitates are in the shape of truncated pyramids (insets).](image)
5. Conclusion

The growth of self assembled PbTe QD in a CdTe(111) host matrix on Si(111) has been studied. Dot formation during annealing depends heavily on the thickness of the overgrowth layer. For a cap layer of 50 nm or thicker, the PbTe aggregates as large precipitates with the shape of truncated pyramids, as well as smaller QD. With higher annealing temperatures, the PbTe from the dots diffuses and aggregates at the larger precipitates. The reduced dot size is seen as blue-shift of the QD emission peak B, before it completely vanishes. The formation of PbTe QD on Si(111) is quite different from published results on (100)-orientated GaAs and indicates a very anisotropic diffusion. A very thin cap layer with a thickness in the order of the CdTe surface roughness hinders diffusion. Such a sample forms QD with sizes < 20 nm, also seen in photoluminescence measurements.

References