Incorporation of InAs nanostructures in a silicon matrix: growth, structure and optical properties

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Abstract

MBE growth and properties of InAs nanoscale islands formed on silicon are reported. Islands capped with Si emit a photoluminescence band in the 1.3 μm region. Upon annealing at increased substrate temperature, extensive interdiffusion leads to the formation of an InAs solid solution in the Si cap layer. Additionally, InAs-enriched regions with extensions of ~ 6 nm, exhibiting two kinds of ordering, are observed. The ordering of InAs molecules occurs, respectively, in (101) and (101) planes inclined to (110) and (110) planes parallel to the [001] growth direction. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Self-organisation effects at semiconductor surfaces during molecular beam epitaxy (MBE) have attracted strong interest during the past decade. The greatest attention was given to the quantum dots (QDs) in III/V–III/V (e.g. InAs–GaAs) [1,2], II/VI–II/VI (e.g. CdSe–ZnSe) [3] or IV–IV (Si–Ge) [4] materials systems. The Si–Ge system stimulated many efforts because silicon remains a key material of the microelectronic industry. For optoelectronic applications, silicon is not well suited because of its indirect bandgap nature. Attempts to improve the situation using SiGe–Si QDs did not led to significant progress, as these nanostructures provide indirect band alignment both in k- and in real space. In order to increase the luminescence efficiency of silicon-based structures, we propose to insert direct bandgap InAs QDs in a Si matrix using MBE growth [5]. We emphasise that this approach is different from the growth utilising InAs QDs on thick GaAs buffers [6]. Small coherent InAs islands additionally offer a possibility to overcome the problems of strong lattice mismatch and formation of antiphase domains inherent for the growth of thick III–V epilayers (e.g. GaAs) on Si.

In this paper, we report on the MBE growth and properties of the InAs nanoscale islands formed on silicon. We have found that, under certain growth conditions, InAs/Si heteroepitaxial growth proceeds via Stranski–Krastanow or Volmer–Weber growth modes depending on the growth parameters leading to the formation of nanoscale islands. The lateral size depends critically on the growth conditions and is in the range 5–80 nm (uncapped islands). Independently of the growth mode used for the deposition of InAs nanoscale islands, they emit in the range of 1.3 μm. Extensive diffusion of InAs in a Si cap layer when the Si/InAsSi heterostructure is subjected to high-temperature annealing leads to the formation of an InAs solid solution and ordered regions with a high InAs concentration (and therefore smaller bandgap) and a size of ~ 6 nm.
2. Experiment

The growth experiments were carried out using EP1203 (Russia) or Riber Supra (France) MBE machines on Si(100) substrates. A calibration of the growth rate, III–V flux ratio, and monitoring of the surface morphology during growth was performed using a specially designed registration and analysis system [7] based on reflection high-energy electron diffraction (RHEED). The Si(100) surface preparation was made in a way similar to that described in Ref. [8]. Thermal desorption of silicon native oxide was performed in the growth chamber at substrate temperature of 830–870°C during 15 min. After that, well resolved (2×1) or mixed (1×2) and (2×1) surface reconstructions typical for cleaved Si(100) surface were observed. Then, the substrate temperature was smoothly decreased to the desired value \( T_s \) and the InAs deposition was initiated in a conventional MBE mode. The InAs deposition rate was typically 0.1 monolayers (ML) per second. After the deposition of the desired average thickness of InAs had been completed, the sample was rapidly quenched to room temperature and removed from the growth chamber for scanning tunnelling microscopy (STM) study. Samples selected for STM studies were covered with silicon vacuum oil immediately after exposure to atmosphere, a procedure used previously for our studies of InAs QDs on GaAs surfaces [9]. Transmission electron microscopy (TEM) images were taken using Philips CM20T and JEOL JEM-4000 EX operating at 200 and 400 kV, respectively. The commercial software package ‘MACTEMPAS’ was used for computer simulations of high-resolution TEM (HRTEM) images [10]. For photoluminescence (PL) experiments, the 514.5 nm line of an Ar⁺ laser was used as the excitation source and a Ge photodiode as the detector. The excitation density was 5–100 W cm⁻². For TEM and PL study, after InAs deposition, a 10–20 nm Si cap layer was grown at \( T_s \), followed by a 10 min annealing procedure at 650–700°C. Then, 30–50 nm Si was grown at the same temperature, with optional subsequent 10 min annealing at 750–850°C in order to smooth the resulting surface. Conventional solid Si effusion cell was used for silicon deposition with the growth rate 1 nm min⁻¹.

3. Results and discussion

We have found that the growth mechanism of InAs/Si(100) depends on the substrate temperature and on the As$_4$/In flux ratio (usually, they are in the ranges 250–450°C and 2–12, respectively). Following the data presented in Ref. [11], the 2D–3D transition can occur in the thickness range of 0.7–4.0 ML InAs deposited. Using both RHEED and STM techniques, we observed two different growth modes for the InAs/Si heteroepi-
taxial growth. The Volmer–Weber growth mechanism could be realised in the temperature range \( T_s = 300–400°C \). Here, InAs nanoscale islands are formed on the bare Si substrate (meaning the critical thickness of deposited InAs, \( d_{\text{crit}} \), at which the nano-islands start to appear, is below 1 ML). For lower and higher \( T_s \) (250–300 and 400–450°C), we observed the Stranski–Krastanow growth mechanism with \( d_{\text{crit}} \) exceeding 1.0 ML and the formation of InAs nanoscale islands occurring on the top of the wetting layer. These results are in agreement with the 2D–3D transition intervals observed by the other groups [12–14]. As measured by STM, the lateral size of the uncapped islands is in the range 5–80 nm.

The samples with InAs quantum dots capped with a 30–50 nm Si layer show a luminescence band in the 1.3 \( \mu \)m range independently of either Stranski–Krastanow or Volmer–Weber growth mode. The PL exhibited a pronounced blue shift with increasing excitation density and decayed with a time constant of \( \sim 400 \) ns [15].

Fig. 1 compares low-temperature PL spectra of the 4.8 and 1.6 ML InAs samples deposited in different growth modes (Stranski–Krastanow for 4.8 ML and

[Image: Fig. 1. PL data for the InAs nanostructures imbedded in the Si matrix: (a) InAs grown via Volmer–Weber, and (b) InAs grown via Stranski–Krastanow growth modes.]
Volmer–Weber for 1.6 ML). These spectra reveal TOphonon assisted exciton emission of the Si substrate at 
\( \sim 1.11 \) eV. The broad emission band in the 0.9–1.05 eV range was observed for both InAs deposition thickness. This was not observed when measuring samples with InAs insertions smaller than the critical thickness or a bare Si substrate, suggesting its origin to be associated with the InAs nano-islands embedded in the Si matrix. However, the size of these insertions evaluated from the TEM measurements do not exceed several nanometres [15], which is definitely not enough for charge localisation and quantum confinement.

In order to clarify the composition of the Si/InAs/Si heterostructure, high-resolution TEM studies were performed. Typical cross-section and plan-view images of the investigated structure are shown in Fig. 2a,b, respectively. The plan-view image shows the good structural quality of the sample with a relatively low density of structural defects marked A in Fig. 2b. These defects (A) are located at the InAs/Si interface and do not penetrate into the Si cap layer. The nature of the contrast features B in Fig. 1a is discussed later.

The average InAs concentration in the Si cap layer can be estimated from selected area diffraction (SAD) taken at once from the substrate and cap layer in a cross-sectional sample, as shown in Fig. 2a. Such SAD patterns reveal a splitting of reflections in the [001] direction perpendicular to the layer surface (Fig. 2c). This splitting is attributed to a tetragonal distortion of the Si cap layer due to the formation of an InAs solid solution. The magnitude of the observed splitting of the reflection (206) measured in SAD corresponds to a tetragonal distortion \( \Delta = \Delta g/|g_{(206)}| = \Delta a/a_{\text{Si}} = 0.007 \). The volume of the distorted unit cell is \( V = a_{\text{Si}}(1 + \Delta a/a_{\text{Si}})^{1/3} \). It follows that average cubic unit cell parameter of the solid solution \( a_{ss} \) is given by:

\[
a_{ss} = V^{1/3} = a_{\text{Si}}(1 + \Delta a/a_{\text{Si}})^{1/3} \tag{1}
\]

Taking \( a_{ss} \) as to be linearly dependent on the InAs concentration in the Si matrix, it follows that:

\[
C_{\text{InAs}} = (a_{ss} - a_{\text{Si}})/(a_{\text{InAs}} - a_{\text{Si}}) \tag{2}
\]

where \( C_{\text{InAs}} \) is the concentration of InAs in the Si cap layer, and \( a_{\text{Si}} \) and \( A_{\text{InAs}} \) are the unit cell parameters of Si and InAs, respectively.

Substitution of \( \Delta a/a_{\text{Si}} = 0.007 \) into Eqs. (1) and (2) gives \( C_{\text{InAs}} = 0.004 \). Thus, the averaged composition of the cap layer can be written as \( \text{Si}_{0.996}\text{InAs}_{0.004} \).

To clarify the type of ordering of InAs insertions in a Si matrix, HRTEM images were taken (Fig. 3a). The dark regions marked by B in Fig. 2a reveal a doubling of periodicity of \{002\} lattice planes in the [110] or [102] directions (Fig. 3a). This leads to appearance of diffuse maxima situated halfway between \((220)\) matrix reflections in the Fourier transformed image (see insert in Fig. 3a). This result can be interpreted as a partial ordering of InAs in Si. A possible model of such an ordering is shown in Fig. 3b, where InAs occupies every other atomic (101) plane inclined 45° to the surface. Let us define the two-dimensional ordering as \((na \times mb)\), where \( n \) and \( m \) are integers and \( a \) and \( b \) are periodicities in two perpendicular directions without ordering. In our case, these directions are (101) and (101), and \( a = b = a_{ss}/\sqrt{2} = 0.192 \) nm. This gives \( (2a \times 1a) \). A HREM image (Fig. 3c) simulated on the basis of this structural model show that the darker rows...
correspond to InAs atomic rows. The contrast calculated for an ideal ordering is in qualitative agreement with the experimental image. The size of \((2\alpha \times 1\alpha)\) coherent ordered regions \((\geq 6\text{ nm})\) is about two times larger than the size of coherent InAs clusters formed at the InAs/Si interface described in a previous paper [16]. Most likely, the size is limited by the misfit parameter, which in turn depends on the local composition. The misfit parameters of fully ordered \((2\alpha \times 1\alpha)\) and \((3\alpha \times 1\alpha)\) structures in Si should be approximately \(e/2 \approx 5\) and \(e/3 \approx 3\%\), respectively. Since the size of the inclusions are approximately inversely proportional to the misfit parameter \(d \sim e^{-1/3}\), the size of the \((2\alpha \times 1\alpha)\) and \((3\alpha \times 1\alpha)\) ordered regions should be, respectively, 2.5 and 4 times larger than the size of pure InAs clusters \((< 3\text{ nm}, e = 10.6\%\)). The experimental results are in a good agreement with this estimation.

Thus, the Si cap layer subjected for the high-temperature annealing procedure is actually a Si–InAs solid solution with \((2 \times 1)\) and \((3 \times 1)\) ordered InAs-rich regions. The ordered regions with a high InAs concentration (and therefore smaller bandgap) and a size of \(\sim 6\text{ nm}\) can provide sufficient carrier localisation to explain the observed 1.3 \(\mu\)m emission. The incorporation of InAs molecules into the Si is expected to shift the relative positions of the conduction and valence bands leading to a quantum structure.

In conclusion, we have demonstrated that InAs/Si(100) heteroepitaxial growth could proceed via Stranski–Krastanow or Volmer–Weber growth modes depending on the MBE growth parameters. The critical thickness at which three-dimensional InAs nano-islands start to appear at the Si(100) surface varies within the range of 0.7–4.0 ML (substrate temperature, 350–430°C; As/In flux ratio, 2–12). Their size depends critically on the growth conditions and is between 5 and 80 nm (uncapped islands). Optical properties of the InAs nanoscale islands capped with Si and subjected to the high-temperature annealing reveal a luminescence band in the 1.3 \(\mu\)m region dependent on the growth mode used for InAs deposition. The origin of this bandgap could be the formation of a Si–InAs solid solution with \((2 \times 1)\) and \((3 \times 1)\) ordered InAs-rich regions Si cap layer. The ordered regions with a high InAs concentration (and therefore smaller bandgap) and a size of \(\sim 6\text{ nm}\) can provide sufficient carrier localisation to explain the observed 1.3 \(\mu\)m emission. The InAs/Si heteroepitaxial system seems to be promising for Si-based optoelectronic applications; in particular, for short distance fiber optics and integration of microelectronics and optical parts at the same silicon wafer.

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