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Epitaxy of $In_{0.01}Ga_{0.99}As$ on Ge/offcut Si (001) virtual substrate

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ABSTRACT

$In_{0.01}Ga_{0.99}As$ thin films free of anti-phase domains were grown on 7° offcut Si (001) substrates using Ge as buffer layers. The Ge layers were grown by ultrahigh vacuum chemical vapor deposition using 'low/high temperature' two-step strategy, while the $In_{0.01}Ga_{0.99}As$ layers were grown by metal-organic chemical vapor deposition. The etch-pit counting, cross-section and plane-view transmission electron microscopy, room temperature photoluminescence measurements are performed to study the dependence of $In_{0.01}Ga_{0.99}As$ quality on the thickness of Ge buffer. The threading dislocation density of Ge layer was found to be inversely proportional to the square root of its thickness. The threading dislocation density of $In_{0.01}Ga_{0.99}As$ on 300 nm thick Ge/offcut Si was about 4×10^{8} cm^{-2}. Higher quality $In_{0.01}Ga_{0.99}As$ can be obtained on thicker Ge/offcut Si virtual substrate. We found that the threading dislocations acted as non-radiative recombination centers and deteriorated the luminescence of $In_{0.01}Ga_{0.99}As$ remarkably. Secondary ion mass spectrometry measurement indicated as low as 10^{16} cm^{-3} Ge unintended doping in $In_{0.01}Ga_{0.99}As$.

1. Introduction

During the past decades, a variety of high performance Si-based optoelectronic devices have been fabricated except for electrically pumped light source with high efficiency [1,2]. Fortunately, hybrid integration is a promising technique to fabricate a practical Si-based light source [3,4] by wafer bonding or heterostructure epitaxy. Intel and the University of California at Santa Barbara have demonstrated InP-based laser bonding on Si [4]. Nevertheless, the deposition of GaAs on Si is viewed as a promising strategy to fabricate laser diodes on commercial wafer scale [5,6]. There are five main challenges in the growth of GaAs on Si [7]: (a) the lattice mismatch between GaAs and Si; (b) the suppression of anti-phase domains (APD) on the GaAs side of the interface; (c) the lack of electrical neutrality at the GaAs/Si interface [8]; (d) the cross-doping between GaAs and Ge; (e) the thermal expansion coefficient of GaAs (5.83×10^{-6} k^{-1} at 293 K) is much larger than that of Si (2.92×10^{-6} k^{-1} at 293 K). In order to prevent the formation of APDs and overcome the 3.9% lattice mismatch between GaAs and Si, the growth of GaAs/Ge/$Si_{1-x}Ge_x$/offcut Si is of great interest [5,9]. Although a room temperature strained InGaAs/GaAs quantum well laser on Ge/$Si_{1-x}Ge_x$/offcut Si virtual substrate has been reported [9,10], the 10 μm thick $Si_{1-x}Ge_x$ compositionally graded buffer layer made it difficult to integrate with Si-based complementary metal-oxide-semiconductor integrated circuits. As a result, the deposition of GaAs directly on Ge/offcut Si, which avoids the thick $Si_{1-x}Ge_x$ compositionally graded layer is especially worth studying [11]. Usually the Ge layer directly on Si substrate with R_{rms} (root mean square roughness) of ~1 nm and TDD (threading dislocation density) of ~10^{5} cm^{-2} is grown using the 'low/high temperature' two-step strategy. In the first step, a 30–50 nm thin Ge buffer layer is grown at low temperature of about 300 °C to relieve the misfit stress and maintain a smooth surface using the limited mobility of Ge adatoms at low temperature. In the second step, Ge is grown at higher temperature of about 600 °C to obtained higher crystal quality and growth rate [12,13]. With the aid of high quality Ge film on Si substrate, high quality GaAs film with smooth surface and low TDD can be obtained on Ge/offcut Si virtual substrate, because the surface energy of GaAs is smaller than that of Ge [14,15] and the lattice constant of GaAs (0.56536 nm) is only 0.076% smaller than that of Ge (0.56579 nm). The epitaxy of GaAs/Ge/offcut Si is also widely applied in multi-junction solar cells [11].

In this paper, the growth of $In_{0.01}Ga_{0.99}As$ by metal-organic chemical vapor deposition (MOCVD) on Ge/offcut Si(001) virtual substrate with different Ge thicknesses is reported. The Ge layer was grown by ultrahigh vacuum chemical vapor deposition (UHVCVD) using the 'low/high temperature' two-step strategy [16]. The dependence of $In_{0.01}Ga_{0.99}As$ quality on Ge thickness, which is very important in the design of Si-based lasers and multi-junction solar cells, was studied by etch-pit counting, plane-view transmission electron microscopy (TEM), cross-section TEM, and room temperature photoluminescence (RT PL) measurements. The atomic force microscope (AFM) and cross-section TEM measurements were carried on to

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investigate the suppression of APDs in $In_{0.01}Ga_{0.99}As$. The unintended Ge doping in the $In_{0.01}Ga_{0.99}As$ films was studied by secondary ion mass spectrometry (SIMS) measurements. The problem of lack of electrical neutrality at the $In_{0.01}Ga_{0.99}As$/Ge interface will not be covered in this paper.

2. Experiments

The 2-inch n^- Si (001) substrate with resistance of 3–5 Ωcm was 7° offcut towards the [110] direction, as measured by X-ray diffraction. The substrate was cleaned using an improved RCA wet-chemical cleaning recipe, i.e., using H_2O_2:H_2SO_4 = 1:4, H_2O_2:NH_4OH:H_2O = 2:1:5, HF (hydrofluoric acid): H_2O = 1:10, H_2O_2:HCl:H_2O = 7:1:2 solutions sequentially to clean the substrate. Before growing in the cold wall UHVCVD system, the offcut Si substrate was degassed at 300 °C in the pretreatment chamber and then deoxidized in the growth chamber by heating to 930 °C for 5 min. The base pressure of the UHVCVD system was about 1×10^{-7} Pa. Then a 60 nm Ge film was grown on the offcut Si substrate at 260 °C using pure GeH_4 with a flow of 8 sccm. To achieve a higher crystalline quality and growth rate, the heater temperature was then elevated to 550 °C in the following Ge epitaxy process to obtain a thick Ge layer. For comparison, three samples were grown with total Ge thicknesses of 300 nm, 550 nm and 1020 nm. Then the Ge/offcut Si virtual substrates were transferred into the MOCVD system. The virtual substrates were heated up to 740 °C to remove the oxide layer. Finally, the 1500 nm $In_{0.01}Ga_{0.99}As$ layer with 3×10^{18} cm^{-3} Si-doping on 300 nm, 550 nm and 1020 nm thick Ge/offcut virtual substrates were grown in an AXITRON 2400 system. The Si-doped $In_{0.01}Ga_{0.99}As$ layer was grown at 658 °C with growth rate of 1.1 nm/s.

Before and after the temperature elevation from 260 °C to 550 °C of Ge growth, the strain and surface morphology of the 60 nm Ge layer grown at 260 °C were studied by Raman spectroscopy (JY HR800) and AFM measurements (Seiko Instruments, nanonavi Esweep S-II in contact mode). AFM images were acquired using Silicon Nitride tip (OMCL-TR400PSA-1, Olympus). During the Raman measurements, the samples were emitted by 488 nm Ar^+ laser with an intensity of 1 mW. The surface morphology and TDD of Ge films were studied by AFM and etch-pit counting. The solution of 250 ml CH_3COOH mixed with 80 ml HNO_3 (68 wt.%), 9 ml HF (40 wt.%), and 100 mg I_2 kept at 30 °C was used as the etchant for the etch-pit counting [17]. The etching rate was estimated to be ~1.5 nm/s and the top 100 nm of the Ge layers were etched off. During the etching, the samples of Ge films on Si were continually agitated in order to obtain a uniform etching rate over the Ge surface.

After the growth of $In_{0.01}Ga_{0.99}As$ films, the etch-pit countings were performed for the 1500 nm $In_{0.01}Ga_{0.99}As$ layers on Ge/offcut Si. The etchant was the solution of 80 ml H_2O mixed with 8 ml HF (40 wt.%), 300 mg $AgNO_3$, and 2 g CrO_3 kept at 30 °C which has been reported by Abrahams and Buiocchi [18]. The etching rate was estimated to be ~300 nm/min and the top 600 nm of the $In_{0.01}Ga_{0.99}As$ layers were etched off. During the etching the samples were continually agitated, in order to prevent the deposition of green powder-like Cr_2O_3 on the $In_{0.01}Ga_{0.99}As$ surface. The cross-section TEM, plane-view TEM (Tecnai G2F20S-Twin, 200 kV), AFM and RT PL measurements (JY HR800) were also performed to evaluate the quality of the $In_{0.01}Ga_{0.99}As$ layers. During the TEM measurements, the energy-dispersive X-ray spectrum (EDS) was also measured using TEAM™ EDS system for TEM-X-ray Microanalysis (EDAX incorporation). A 488 nm laser spot with power of 0.01 mW and with ~50 μm radius was used during the RT PL measurements. Besides, the RT PL measurements over the whole 2-inch wafer were also performed. The SIMS measurements (Quad SIMS, PHI 6600) were performed to study the Ge diffusion in the $In_{0.01}Ga_{0.99}As$ layer. Cs beam was used during SIMS measurements.

3. Results and discussions

3.1. Growth of Ge film on offcut Si (001) substrate

The growth of Ge on Si is a typical example of Stranski–Krastanow growth [19]. Due to the 4.0% lattice mismatch, when the thickness of Ge layer is beyond the critical thickness (about 4 monolayers) [20], the growth mode tends to switch from 2D (two-dimensional) growth to island growth, thus resulting in a wavy surface and high density of dislocations. However, this transition can be avoided because of the limited mobility of Ge adatoms on the Si surface at an appropriately low temperature [21]. As a result, the rough surface caused by the 3D Ge islands can be prevented at this temperature. With the Ge layer growing to be thicker under these conditions, the strain caused by the Ge/Si lattice mismatch was further relaxed. Finally, a high quality Ge layer with smooth surface can be obtained.

The 60 nm Ge layer grown at 260 °C is under 0.3% compressive strain as measured by Raman scattering spectroscopy. As can be seen in Fig. 1(a), the 60 nm thick Ge layer has smooth surface with R_{rms} over the area of 3 μm × 3 μm of 1.70 nm. The surface morphology of the 60 nm Ge layer after the temperature elevation from 260 °C to 550 °C is shown in Fig. 1(b). As can be seen, the 60 nm Ge layer is thermally stable at 550 °C. After the temperature elevation, the surface becomes smoother with R_{rms} = 1.32 nm. The reason may be that the Ge atoms can migrate in Frank-van der Merwe mode at higher temperature because of the low Ge surface energy and low compressive strain of 0.3%. Thus the 60 nm Ge layer grown at 260 °C is suitable for the following Ge deposition at 550 °C.

3.2. TDD of the Ge layer and the $In_{0.01}Ga_{0.99}As$ layer

The R_{rms} over the area of 10 μm × 10 μm of the 300 nm, 550 nm and 1020 nm thick Ge/offcut Si virtual substrates are 1.73 nm, 1.28 nm and 1.67 nm, respectively, measured by AFM (the AFM images are not shown here). Because most of the strain in the Ge layer is relaxed, there is no significant difference between the surface morphologies of the samples. For the sake of quantitative evaluation of the quality of the Ge layers, the etch-pit countings were performed. The TDDs under 100 nm of the vicinal surface of the 300 nm, 550 nm and 1020 nm thick Ge films are 1.8×10^5 cm^{-2}, 1.2×10^5 cm^{-2} and 8.4×10^4 cm^{-2}, respectively, as obtained by counting the etch-pits in typical 500 μm × 500 μm optical microscope images of the etched samples, as shown in Fig. 2.a–c. The TDD is approximately inversely proportional to the square root of h_{Ge}. The thickness dependence of TDD on h_{Ge} in our experiments agrees with the theoretical results of some research groups: TDD$\propto h_{Ge}^{-n}$ (n = 0.5 in our work, n = 1 in [22] and n = 2 in [23]). The difference of n is unknown.

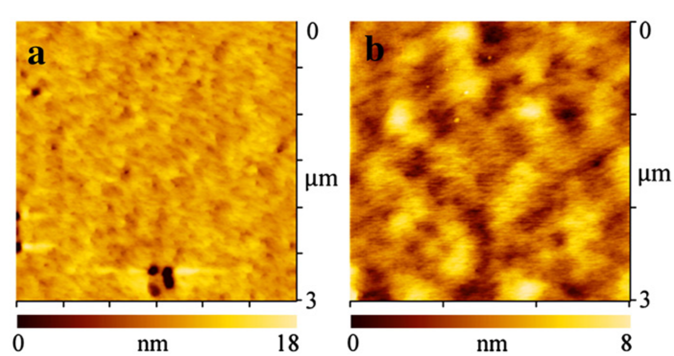

Fig. 1. The AFM images of the 60 nm Ge film grown at 260 °C (a) before and (b) after the temperature elevated to 550 °C. The R_{rms} over the area of 3 μm × 3 μm is 1.70 nm and 1.32 nm respectively.