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MOVPE technology and characterisation of silicon $\delta$-doped GaAs and Al$_x$Ga$_{1-x}$As

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Abstract

This work presents the investigation of MOVPE growth of silicon $\delta$-doped GaAs and Al$_x$Ga$_{1-x}$As epilayers and different methods used for their characterisation. The influence of the growth temperature, SiH$_4$ flow rate and Al$_x$Ga$_{1-x}$As composition on $\delta$-doping characteristics is discussed. Properties of the Si $\delta$-doped structures were examined using capacitance-voltage (C-V) measurements, photoreflectance spectroscopy, micro-photoluminescence, micro-Raman and photocurrent spectroscopies. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: MOVPE technology; $\delta$-doping; C-V profiling; PR spectroscopy; $\mu$-RS; $\mu$-PL; PC spectroscopy

1. Introduction

$\delta$-doping is a novel doping method which spatially confines the dopant atoms to one or a few atomic layers. This type of incorporation of dopant atoms into crystalline structure of semiconductor material modifies its electronic structure by bending the conduction or valence band edges to form a V-shaped potential well. The electrons (or holes) confined in this potential well are regarded as a two-dimensional electron or hole gas. $\delta$-doping is very attractive for application in advanced semiconductor devices, such as HEMTs, HBTs, resonant tunnelling diodes, quantum well infrared photodetectors, homo- and hetero-nipi doped superlattices, modulators. Most of the $\delta$-doped epitaxial structures are deposited by molecular beam epitaxy (MBE) due to the low growth temperatures. On the other hand, MBE growth of $\delta$-doped structures above 600 °C results in large dopant profile broadening caused by the Fermi-level pinning-induced segregation [1,2]. This effect is not observed in $\delta$-doped layers grown by MOVPE, although the growth temperatures are usually between 650 °C and 750 °C, what is explained by hydrogen surface passivation [1–3]. This work presents results of $\delta$-doping of GaAs and Al$_x$Ga$_{1-x}$As structures grown by MOVPE and discusses different methods used for their characterisation.

2. Experimental details

The following epitaxial test structures (type A, type B) were grown by MOVPE on semi-insulated or n-$\delta$-doped GaAs substrates using an atmospheric pressure AIX200 R&D Aixtron reactor:

A. Si $\delta$-doped GaAs sample consisted of a 900-nm of GaAs buffer layer followed by Si $\delta$-layer and a 150–160-nm GaAs cap layer; and

B. Si $\delta$-doped Al$_x$Ga$_{1-x}$As (or AlAs) sample consisted of a 250-nm GaAs buffer layer followed by a 200-nm undoped Al$_x$Ga$_{1-x}$As (or AlAs) in the middle of which the Si $\delta$-layer was placed and a 32±45-nm GaAs oxide protection layer.

The TMGa, TMAI, AsH$_3$ and SiH$_4$ (20 ppm in H$_2$) were used as the growth and dopant precursors. High purity H$_2$ was employed as a carrier gas. The substrate temperature ($T_s$) was in the range of 670÷760 °C for $\delta$-doped GaAs and 760 °C for $\delta$-doped Al$_x$Ga$_{1-x}$As ($x=0.29, 0.34, 0.35, 0.46, 0.6$) and $\delta$-doped AlAs samples. The SiH$_4$ flow rate was changed from 10 to 100 ml/min. A basic $\delta$-doping procedure ‘purge-doping-
purge' was applied [1,2,4]. The obtained structures were examined by C–V measurements using a mercury probe and a HP 4192A impedance analyser (5 Hz to 13 MHz). Also photoreflectance, micro-photoluminescence, micro-Raman and photocurrent spectroscopies were applied.

3. Results and discussion

3.1. Influence of the growth temperature and SiH₄ flow rate on the sheet electron density and the width of C–V profiles of Si δ-doped GaAs epilayers. Results of C–V measurements

The influence of the growth temperature and SiH₄ flow rate on the properties of Si δ-doped GaAs epilayers was investigated. The main method used for determination of the electron concentration and broadening of the dopant distribution in the obtained structures was C–V measurement done at frequencies below 100 kHz. The C–V profiles, presented in Fig. 1, were measured for Si δ-doped GaAs epilayers (type A) grown at 670 °C, 700 °C, 730 °C and 760 °C (samples X107, X115, X116 and X117, respectively). The SiH₄ flow rate was 100 ml/min for all the samples. The best results were obtained for the Si δ-doped GaAs grown at 670 °C (sample X107, Fig. 1a).

For this layer no diffusion broadening of the profile was observed. The width of the C–V profile, FWHM_C–V = 5.5 nm (determined by applying Gaussian approximation) is comparable to the spatial extent of the ground-state wave function $z_0 \approx 5.5$ nm, calculated from the following equation [1,2,5]:

$$z_0 = 2 \sqrt[3]{\frac{\sqrt{2}}{5} \left( \frac{4}{9} \frac{e^2 \hbar^2}{\varepsilon^2 n_{3d} m^*} \right)^{1/3}}$$

(1)

where, $\varepsilon$ is the semiconductor permittivity, $e$ is the elementary charge, $n_{3d}$ is the sheet electron density, $m^*$ is the electron effective mass. Fig. 2 shows the dependence of the sheet electron density and the C–V profile widths of Si δ-doped GaAs (type A) on the SiH₄ flow rate. The growth temperature was 670 °C, SiH₄ flow rate was changed from 10 to 100 ml/min. The values of $z_0$, calculated from Eq. (1) for sheet electron concentrations above $10^{12}$ cm⁻², are also included.

For high values of SiH₄ flow rate (>40 ml/min) saturation of the electron density is observed. It can be explained by establishment of the equilibrium between adsorption and desorption process of the active Si species, autocompensation caused by incorporation of Si atoms into As sites and/or formation of Si clusters [2]. The values of FWHM_C–V are in a good agreement with the calculated values of $z_0$. The C–V profile widths obtained for Si δ-doped AlAs and Al₀.₃₅Ga₀.₆₅As were broad (FWHM_C–V = 12.4 and 29.6 nm, respectively) due to the influence of thermal diffusion at high growth temperature (760 °C) which was required for improving the material quality.

3.2. Photoreflectance spectroscopy

Photoreflectance spectroscopy (PR) was applied to the investigation of Si δ-doped epilayers. The experi-
mental set-up for these measurements has been described previously [6]. The PR spectrum of Si δ-doped GaAs (type A) is presented in Fig. 3. A lot of distinguished Franz–Keldysh oscillations (FKOs) above the band gap energy are seen, demonstrating the existence of a strong uniform electric field in the very high quality epitaxial layer. The observation of FKO and application of fast Fourier transform (FFT) allowed to determine the internal electric field $F$ and the potential barrier height $V_B$ between the surface and the δ-doped region [7].

The following values were obtained for the investigated Si δ-doped epilayers:

$F = 53 \text{kV/cm}, V_B = 0.74 \text{V}$ for GaAs (type A, $T_g = 670 ^\circ\text{C}, V_{\text{SiH}_4} = 100 \text{ ml/min}$); and $F = 68 \text{kV/cm}, V_B = 0.94 \text{V}$ for Al_{0.35}Ga_{0.65}As and $F = 110 \text{kV/cm}, V_B = 1.57 \text{V}$ for AlAs (type B, $T_B = 760 ^\circ\text{C}, V_{\text{SiH}_4} = 100 \text{ ml/min}$).

3.3. Micro-photoluminescence and micro-Raman spectroscopy

Micro-photoluminescence (μPL) and micro-Raman spectroscopy (μRS) were used for determination of a δ-layer position and its spreading in Si δ-doped GaAs structures. A beam of He–Ne laser ($\lambda = 632.8 \text{nm}$) was scanned at room temperature along the bevelled structure, and change of PL (at $\lambda = 870 \text{nm}$) and the ratio of intensities of transversal optical phonon (TO) and longitudinal optical phonon (LO) was detected. The diameter of the spot was 1 ± 2 μm and 10 μm for RS and PL, respectively. The bevels were prepared by chemical etching [8], the bevel angle was approximately $6 \times 10^{-5} \text{rad}$. Fig. 4a presents dependence of PL along the bevelled Si δ-doped GaAs structure (sample X105). The presence of δ-layer makes the PL signal to increase between 135 nm (point U) and 160 nm (point L) below the surface. This is a spreading of the Si dopant. Position of the middle point of δ-layer (145 nm from surface, point D) corresponds to an inflex point of the dependence. Based on the obtained characteristic we could determine a dimension of a δ-layer, much like as in the case of FWHM$_{C-V}$ in C–V profiling. The half width of a δ-layer (HWD) is defined as a distance between point D on the bevel and the point, where PL intensity decreases to 10% of the intensity in point D. The PL intensity in the buffer layer (point L) is defined as zero. The estimated value of HWD for sample X105 is 9 nm. This sample was also examined by Raman spectroscopy (Fig. 4b). The change of TO/LO ratio on the bevelled structure is similar to the PL dependence in the bevel length range 3–3.5 mm, where δ-layer is located. In this case, the same procedure (as for the PL measurements) of determination of HWD was applied and the identical value of 9 nm was obtained. The position and spreading of the δ-layer, determined by RS and PL for sample X105, are in good coincidence with the values obtained for this structure by the C–V measurements ($n_{\text{max}}$ placed 157 nm from the surface, FWHM$_{C-V}$ = 8.6 nm).

3.4. Photocurrent spectroscopy

Photocurrent (PC) measurements were realised on Au–Schottky contacts by illumination from the surface side. The Schottky contacts were evaporated through the metal mask. The diameter of the circular Schottky contacts and distance between them was 830 and 185 μm, respectively. The ohmic contacts were prepared before Schottky contacts deposition on one side of the sample. Photocurrent spectroscopy of δ-doped samples...
Fig. 3. The PR spectrum (a) and its fast Fourier transform (b) for the Si δ-doped GaAs.

Fig. 4. Change of PL intensity (a) and of TO/LO ratio (b) on the bevelled structure X105.

Fig. 5. Photocurrent vs. energy for: (a) Si δ-doped GaAs for different Schottky contact bias; and (b) Si δ-doped Al,Ga, As with different Al content.
is influenced by the electrical field introduced by a δ-doped layer resulting in oscillation of the PC signal above the band gap energy and by the interface on GaAs substrate side (peak at 1.37 eV). The PC spectrum of Si δ-doped GaAs (sample X105) is shown in Fig. 5a. The minimum of oscillations at 1.5 eV, corresponding to δ-layer, shifts the position under bias voltage due to the change of the electric field inside the structure. In the case of the PC measurements of homogeneous n-doped GaAs Schottky diodes, only the shift of the low energy edge under bias voltage was observed.

The PC spectra of the Si δ-doped Al₅₀Ga₁₋₅₀As epilayers with different Al content are shown in Fig. 5b (type B structure; x = 0.29, 0.34, 0.46, 0.6 for sample AX143, AX148, AX149 and AX152, respectively). The presented spectra show AlₓGa₁₋ₓAs absorption edge and GaAs absorption in the GaAs interface layer. The oscillations of the PC signal above the band gap energy are not so pronounced as in the case of Si δ-doped GaAs (Fig. 5a).

4. Conclusions

MOVPE technology and characterisation of the fabricated Si δ-doped GaAs and AlₓGa₁₋ₓAs are described. The best results were obtained for Si δ-doped GaAs structures grown at 670 °C, what was confirmed by C–V, PR and PC measurements. These layers have the narrowest C–V profiles (FWHM_C–V~5.5 nm), comparable to the calculated spatial extent of the ground-state wave function z₀. They exhibit also the best PR spectra and distinct oscillations of the photocurrent above the band gap energy. The C–V profiles obtained for Si δ-doped AlₓGa₁₋ₓAs and AlAs are broader caused probably by the thermal diffusion at high growth temperature (760 °C). The calculated values (based on PR spectra) of the potential barrier heights Vₜ for Si δ-doped GaAs, Al₀₂₅Ga₀₇₅As and AlAs suggest that the Fermi level is pinned at the middle of the band gap of the investigated epilayers, what is in good agreement with previous reports [9]. Micro-Raman spectroscopy and micro-photoluminescence were successfully used for determination of δ-layer position and its spreading in Si δ-doped AlₓGa₁₋ₓAs/GaAs structures. The obtained results are in good coincidence with C–V measurements. The presented investigations are important for optimisation of MOVPE technology of advanced semiconductor devices utilising Si δ-doped AlₓGa₁₋ₓAs/GaAs heterostructures as the active regions. The study helped to evaluate suitable characterisation methods such as C–V and PR measurements, allowing fast, precise and non-destructive examination of δ-doped device structures.

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