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Direct examination of Si atoms spatial distribution and clustering in GaAs thin films with atom probe tomography

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ABSTRACT

In this contribution, we report on the Si atoms spatial distribution via Atom Probe Tomography (APT) in Si-doped GaAs thin films grown by MOCVD. As a result, we clearly identify the presence of Si precipitates occurring with increasing Si content in the layers. Using ToF-SIMS characterizations, we have been able to highlight the increasing evolution of the silicon content in the material as a function of silicon flux while that of the charge carriers studied by Hall effect decreases. Thus, this degradation of the electrical properties was directly linked to the observed clusters by APT.

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Heavily doped n-type GaAs layers offer the possibility to fabricate low resistance ohmic contacts and high speed electronic and optoelectronic devices. Silicon (Si) is a widely used element for doping of gallium arsenide (GaAs). Like other atoms of group IV, Si can either be a donor or an acceptor depending on whether it is incorporated in the Ga or As sites of the host lattice. However, since the covalent radius of Ga (1.26 Å) is larger than that of As (1.18 Å), thus Si atoms tend to occupy Ga sites. Usually p-type conductivity can be obtained by the crystals grown from Ga solution by liquid-phase epitaxy (LPE) [1]. However, due to the compensation effect especially in heavily Si-doped GaAs, the concentration of conducting electrons is lower than the number of introduced silicon dopants [2]. This reduces the doping efficiency and is a subject of great technological interest. The compensation phenomenon in n-type heavily Si-doped GaAs was especially intensively investigated [3–7]. The reasons for this has been disputed and many contradictions in the literature can be found. In previous studies, the electrical deactivation of silicon donors (Si_{Ga}^{+}) was attributed exclusively to silicon acceptors (Si_{As}^{-}), which were forming due to the amphoteric incorporation of Si atoms into the GaAs crystal lattice [8]. This mechanism is known as the "auto-compensation". Afterwards, the analysis of infrared local vibrational mode (LVM) absorption showed that the auto-compensation alone could not explain strong electrical deactivation of Si_{Ga}^{-} donors in heavily Si-doped GaAs epitaxial layers [2]. This was confirmed, some years later, by near-edge and extended X-ray absorption fine structure techniques (NEXAFS and EXAFS) [9,10]. It was established that only about half of the losses of the electrical activity could be explained by auto-compensation and therefore some other compensating center had to be taken into account. A variety of defects participating in the compensation was proposed: Si_{As}-Si_{Ga} dimers [10], Si clusters [3,11] and $Si_{Ga}V_{Ga}$ [2,12,13]. The formation of Si clusters is observed above a certain critical Si concentration where the Coulombic interaction forces between Si_{As} and Si_{Ga} become strong enough to create neutral Si—Si pair and consequently a Si cluster. As a result, all Si atoms added to the crystal, in excess of the critical concentration, precipitate as Si clusters. Thus, the solubility limit of Si in GaAs is governed by screened Coulomb interaction and the free carrier concentration remains unaffected by the Si concentration above a critical limit. The maximum equilibrium free-carrier concentration, obtained in a heavily doped n-type GaAs is typically (4–7) × 10^{18} cm^{-3}, limited by self-compensation of donors [3,14]. Despite all the interest that has been given to the $Si_{Ga}V_{Ga}$ defects, few studies have been interested in the formation of silicon precipitation in heavily doped GaAs layers. Although the first indications of Si precipitation date back to the late 80s early 90s [11,15] using energy-dispersive X-ray analysis (EDXA) and transmission electron microscopy by evidencing the formation of planar defects, no direct observation of these precipitates has been made. In this letter, we attempt to shed light on the spatial distribution of Si atoms in GaAs epitaxial layers by performing 3D Atom Probe Tomography (APT). The latter has emerged as a unique technique that is able to provide information about the chemical composition of elements together with a 3D map indicating the position of each atom from a specimen at the atomic scale. Our overall objective is to monitor the evolution of the spatial distribution of Si atoms as a function of Si content.

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The growths of n-type doped GaAs thin layers were performed in an Applied Materials metalorganic chemical vapor deposition (MOCVD) reactor using hydrogen (H_2) as carrier gas, trimethylgallium (TMGa) as group-III precursor, tertiarybutylarsine (TBAs) as group-V precursor and disilane (Si_2H_6) for the n-type doping. For all the studies, 3-in. GaAs (001) substrates with a miscut angle <0.5° were used. Before the growth, the GaAs substrate was deoxidized by heat treatment for 1 min under As at high temperature (600–700 °C). Subsequently, 200–300 nm thick Si-doped GaAs layers were grown at a temperature range between 600 and 700 °C [16].

APT experiments were performed on a FlexTAP-CAMECA instrument. An amplified ytterbium doped laser operating at a wavelength of 343 nm, with a 450 fs duration, an energy of 1nJ/pulse, and a 100 kHz repetition rate, was used. The tip temperature was maintained around 40 K during analysis. In an APT experiment, the specimens must be needle-shaped having an end-radius below 50 nm. The preparation of such tips was achieved by performing in-situ lift-out followed by successive Ga ion annular milling at 30 keV and a final low energy cleaning at 2 keV using a dual beam FIB-SEM FEI Helios NanoLab 450S. A detailed description of APT technique can be found in Lefebvre-Ulrikson et al. [17]. Hall effect measurements in Van der Pauw configuration were carried out at room temperature to measure the carrier concentration. Photoluminescence (PL) measurements have been performed at room temperature using a 532 nm laser excitation wavelength. The surface morphology change was investigated by Atomic Force Microscopy (AFM) in tapping mode.

Fig. 1(a) shows both the net carrier concentration ($n = N_D^+ - N_A^-$) obtained by Hall effect measurements and Si concentration measured by ToF-SIMS as a function of Si_2H_6 flow rate for different Si-doped GaAs epitaxial layers. The disilane flow rate was varied from 0.13 up to 225 μmol/min. Carrier concentration evolves linearly with respect to the dopant gas flow to a maximum corresponding to 8×10^{18} cm^{-3}. At this stage, carrier concentration saturates and decreases with increasing Si_2H_6 flow rate at high Si-doping. However, as expected, the Si concentration increases proportionally with dopant flow rate. These observations reveal that a fraction of Si dopants does not act as donors in the highly Si-doped region (>8×10^{18} cm^{-3}). This phenomenon results from a well-known compensation mechanism that appears at high doping levels [3,4]. Indeed, in GaAs, silicon is preferentially substituted for gallium as the Si—As bond energy (1.65 eV) is smaller than that of Si—Ga (2.13 eV). However, at high doping levels, Si atoms also occupy the As site (Si_{As}) and act as acceptors. In addition to the appearance of p-type doping (Si_{As}), numerous studies have shown that the decrease in carrier concentration can be also due to the formation of electrically inactive defects such as electrically neutral Si_{As}-Si_{Ga} pair [10], $Si_{Ga}V_{Ga}$ [13] and/or silicon precipitates [11].

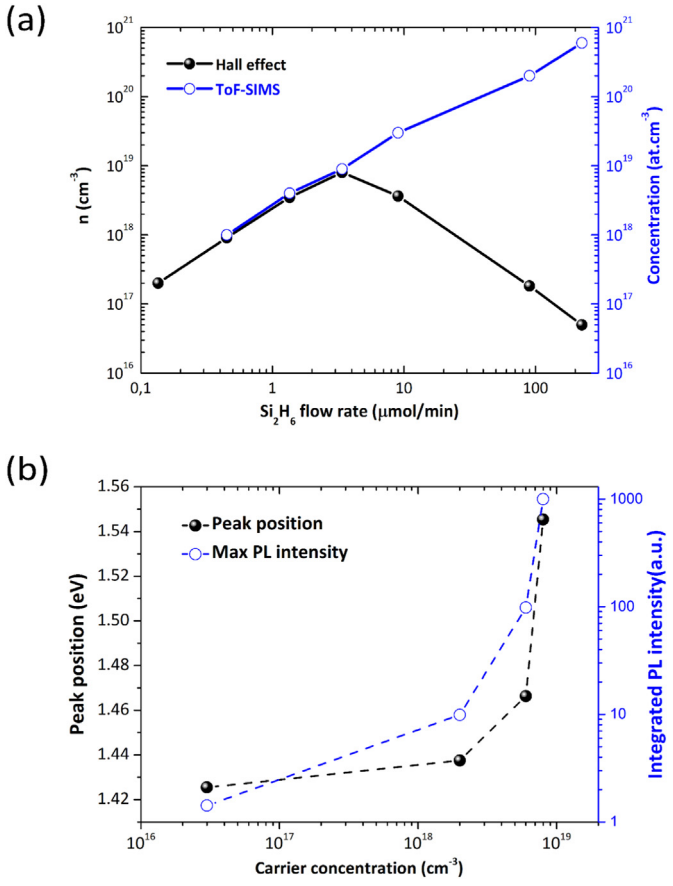

Fig. 1. (a) Net carrier ($n = N_D^+ - N_A^-$) and silicon concentrations as a function of dopant gas flow. The left-hand scale denotes carrier concentration. The right-hand scale denotes silicon concentration by ToF-SIMS measurement. (b) PL peak position (left-hand scale) and integrated PL intensity (right-hand scale) as a function of carrier concentration.

On the other hand, Fig. 1(b) presents the photoluminescence measurements performed at room temperature on the samples. Analysis of the GaAs peak emission position shows that it tends to shift towards high energies as the silicon concentration increases. This process is caused by the filling of the conduction band [15]. In parallel, the PL intensity increases with doping concentration, indicating that non-radiative transitions dominate at low doping density. The relevancy of the recombination centers is reduced at high doping concentrations thus leading to a significant increase in the PL intensity. However, for silicon concentrations >8×10^{18} cm^{-3}, we could not investigate the peak shift because we did not observe any signal. This result is consistent with the work of X. Tang et al. [15]. This absence of signal is correlated with the formation of non-radiative defects in the material due to compensation mechanism.

The surface morphology of Si-doped GaAs layers was studied using AFM (Fig. 2). For low Si content of 8×10^{18} cm^{-3}, the surface exhibits [100] oriented atomic steps as it can be seen from Fig. 2(a). The Root-Mean-Square (RMS) roughness extracted from a 1×1 μm^2 area of the sample is 0.16 nm. As the Si Concentration increases, the RMS increases up to 0.62 nm for [Si] = 2×10^{20} cm^{-3} (Fig. 2(b)) and 9.35 nm for [Si] = 6×10^{20} cm^{-3} (Fig. 2(c)). This indicates that an increase in Si doping concentration deteriorates the crystallinity quality of the films due to Si clustering-induced defects for high doping concentrations. Up to now, no direct proof of the formation of Si precipitates has been given. In this contribution, we aim to highlight their presence by using Atom Probe Tomography.

In order to check the presence or not of the precipitates in our samples, we used APT to explore the spatial distribution of Si atoms in our films. Fig. 3 shows the 3D reconstructions of Si atoms in GaAs for three different concentrations (a) 8×10^{18} cm^{-3}, (b) 2×10^{20} cm^{-3} and (c) 6×10^{20} cm^{-3} as measured by ToF-SIMS. Each violet dot corresponds to one silicon atom in the analyzed volume. The reconstructions show the evolution of the enrichment of the silicon atoms. The distribution of silicon atoms in GaAs seems to be homogeneous for a Si content of 8×10^{18} cm^{-3} (Fig. 3(a)). However, this is clearly not the case for the sample containing 2×10^{20} cm^{-3} (Fig. 3(b)) where 3D reconstruction shows the formation of tiny silicon-rich clusters. And finally, for the third sample containing 6×10^{20} cm^{-3} (Fig. 3(c)), a higher density of silicon-rich clusters is observed. The unique advantage of APT is its 3D capabilities, making possible both the detection and quantification of Si-rich clusters. Here, we have carried out the first nearest neighbor (1NN) statistical technique as described in T. Philippe et al. [18]. In this approach, we can plot atomic distance distribution of Si atoms from APT reconstructed volume. For uniform Si concentration, this distribution is symmetric and close to Poisson's distribution and can be theoretically written according to the Eq. (1):

$$P(r) = 4\pi r^2 Q C_0 \exp\left(\frac{4}{3}\pi Q C_0 r^3\right) \quad (1)$$

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