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Tensile strain in arsenic heavily doped Si

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In this paper we highlight the existence of tensile stress in heavily arsenic-doped epitaxial silicon (Si:As) prepared by low pressure chemical vapor deposition. Despite the large size of As atoms compared to Si ones, we demonstrate with x-ray diffraction and convergent electron beam diffraction that the heavily doped epitaxial layers show a tetragonal lattice with a reduced out of plane parameter. Using positron annihilation spectroscopy, we highlight the formation of arsenic-vacancies defects during the growth. We show that the tensile strain is related to this type of defects involving inactive As atoms and not to the As active concentration. © 2007 American Institute of Physics. [DOI: 10.1063/1.2816251]

I. INTRODUCTION

In industry, silicon and silicon alloys epitaxy has been intensively used to improve the performances of heterojunction bipolar transistors (HBT) and is now widely spread in many applications such as metal-oxide-semiconductors transistors (TMOS) or microelectromechanical systems. Epitaxy has recently focused interest to realize stress engineering. As an example SiGe (Ref. 1) and SiC (Ref. 2) are commonly used to tune the Si lattice constant and create compressive or tensile stress in surrounding layers. At the same time, heavily doped films have also been extensively developed. They find their interest in reducing sheet resistance and thus increase devices electrical performances, such as the cutoff frequency of HBT or the access resistance of raised source and drain TMOS. An elegant way to obtain such layers is to use low pressure chemical vapor deposition (CVD) allowing in situ doping. This method permits one to avoid, among other things, implantation damages and allows low thermal budgets, but also permits one to precisely control the dopant level and abrupt profile. In this paper we are interested in the strain created by the presence of high As concentration in in situ doped Si and we show that its origin belongs to the inactive dopant concentration.

II. EXPERIMENTAL

The *in situ* doped films are grown in a 200 mm single wafer rapid thermal CVD industrial tool (HTF-Centura from Applied Materials) over monocrystalline (100) silicon wafers (lightly *p*-type doped) who undergo a high temperature prebake to ensure good epitaxial growth. During the deposition, temperature is monitored via an optical pyrometer. The films are grown from high purity silane (SiH₄) and hydrogendiluted arsine (AsH₃). Hydrogen is also used as a carrier gas during deposition. The total pressure and SiH₄ flow are maintained constant, whereas the AsH₃ flow is unsettled and varies from 30 to 300 sccm to tune the dopant level. The As is well known to segregate during epitaxial growth.³ This phenomenon is linked to the high affinity between *n*-type dopants and Si surface and leads to important growth rate reduction and high surface concentration⁴ which limits the incorporation. As the incorporation is surface coverage dependent, to increase the doping level the temperature is settled between 570 and 675 °C where the coverage is maximum.⁵

The main technique used to characterize our epilayer is x-ray diffraction (XRD). It is employed to check the layer lattice parameter, layer thicknesses, and crystalline quality. This last criterion is subjective as it consists in the comparison between measured and theoretical spectra. The diagrams are acquired around the Si (400) peak. Considering the case of quasiperfect epitaxial layers, deposited over the Si substrate, with no defect and no relaxation, if the lattice parameter is different from the Si substrate one, the film is stressed in the plane and the lattice becomes tetragonal as a compensation (the vertical lattice parameter c differs from the growth plane parameters a and b). This is typically the case for SiGe epitaxial films that demonstrate a larger c parameter, the epifilm is compressed by the substrate. A smaller angle diffraction peak, positioned on the left-hand side of the bulk Si peak, will be seen on the XRD diagram. The opposite example is the SiC layers where the C reduces the Si lattice parameter. The layer is therefore tensely strained in the plane and the XRD pattern exhibits a larger angle peak due to the reduced c parameter. XRD is very sensitive to the epilayer lattice parameter and can be used to estimate the deformation of the film.

Calibrated x-rays fluorescence (XRF) permits the determination of the total amount of As incorporated in the film (As chemical dose) and has a lower detection limit of about 1.6×10^{14} cm⁻². Combining the XRF dose and the XRD thickness we are able to determine the As chemical (total)

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FIG. 1. XRD patterns for bulk silicon and undoped epitaxial Si layer (${\sim}100$ nm).

concentration ([As]). The film sheet resistances and resistivities (ρ) are determined with a standard four point probe measurement. ρ is also measured together with carrier mobility (μ) and carrier concentration ([n]) via Hall effect measurements. The measurements are carried out with a semiautomated workbench in the van der Pauw configuration.⁶ The temperature is set to 300 K and the magnetic field to 8 kG. The films are cut in 6×6 mm² samples and ohmic contacts are realized via wire bonding. Different currents are applied, ranging from 25 to 200 μ A, and slopes of voltage versus current curves are used to determine ρ and Hall coefficient (R_H) and thus calculate μ and [n].

III. RESULTS AND DISCUSSION

Primarily, to dissociate the effects of the deposition process from the effects of the dopant on the epilayer strain, we compare together in Fig. 1 the bulk Si wafer and the undoped Si film XRD patterns for the 100 nm layer. Note that the XRD diagrams are vertically shifted for easier observation and this representation will be applied for all XRD diagrams. We observe that the undoped layer does not exhibit a special XRD pattern, bulk Si and undoped Si patterns are identical. This demonstrates that the present process conditions do not induce significant strain of the epilayer. Figure 2 illustrates the evolution of the XRD pattern when increasing the dopant concentration for 100 nm layers and Table I summarizes [n]and ρ , determined from Hall measurements, and [As] of these three epilayers. We can note that the $([n], \mu)$ couples are close to standard values from Masetti.⁷ The low-doping level film exhibits a pattern similar to the bulk Si one, show-



FIG. 2. Evolution of Si:As XRD patterns for different As concentrations (\sim 100 nm).

ing that no strain is detected. For the medium-doped layer the Si peak is clearly enlarged on the large scattering angle side (positive angle on the relative angle scale). When the dopant concentration is increased more, for the highly doped film, the pattern exhibits a clear satellite peak. This deformation of the XRD pattern on the large scattering angle side is the sign of a smaller vertical lattice parameter and therefore of a biaxial tensile strain in the plane. The evolution of the peak position with the doping level illustrates clearly that the strain is induced by As and is strongly linked to its concentration. Moreover, referring to Table I, both lowly and highly doped films have equivalent ρ , μ , and [n] values but differ in the total dopant concentration. The "low" doping level layer presents 2×10^{20} cm⁻³ of inactive dopant and no strain is observed by XRD. The highly doped film has ten times more inactive dopant $(1.8 \times 10^{21} \text{ cm}^{-3})$ and demonstrates a clear deformation in the vertical plane [from Eq. (1), $\Delta d =$ -0.36%]. We can therefore conclude that only the electrically inactive atoms play an important role in the appearance of the strain.

Assuming a uniform elastic biaxial strain in the layer, the displacement of the satellite peak from the substrate peak $(\Delta \theta)$ associated to the Bragg's law permits one to calculate the fractional change in the (400) interplanar spacing which is equal to the vertical deformation (named Δd). Assuming that $a_{Si}\Delta\theta \ll 2\lambda$, it becomes

$$\frac{c_{\rm Si:As}^{\rm strained} - c_{\rm Si}}{c_{\rm Si}} = \Delta d = \frac{\Delta d_{400}}{d_{400}} = \frac{a_{\rm Si}\Delta\theta}{2\lambda},\tag{1}$$

with $c_{Si:As}^{strained}$ as the lattice parameter of the strained epilayer and c_{Si} as the lattice parameter of the Si substrate. Figure 3

TABLE I. Evolution of film properties for different doping levels.

Doping	Т (°С)	$ ho$ (m Ω cm)	$\mu (cm^2 V^{-1} s^{-1})$	[n] (cm ⁻³)	[As] (cm ⁻³)	[Inactive As] (cm ⁻³)	Δd (%)
Low	630	0.77	46	1.8×10^{20}	3.8×10^{20}	2.0×10^{20}	0
Med	630	0.66	36	2.6×10^{20}	9.3×10^{20}	6.7×10^{20}	-0.138
High	600	0.78	48	1.7×10^{20}	1.9×10^{21}	1.8×10^{21}	-0.356



FIG. 3. Si:As vertical deformation Δd calculated from the XRD peak shift as a function of inactive As concentration.

shows the evolution of the vertical deformation (as the vertical lattice parameter is reduced Δd is negative) as a function of electrically inactive As concentration ([inactive As]). The inactive As concentration is deduced from the XRF total concentration and Hall carrier concentration, both reported in Table II. We can see that up to about 2×10^{20} cm⁻³ of inactive As atoms ([As] $\approx 6 \times 10^{20}$ cm⁻³) no deformation of the XRD pattern and then no strain is detected. Over this limit the strain in the layer is found to rise up very rapidly to $\Delta d = -0.52\%$. The reduction of the layer lattice parameter is also confirmed by the use of a XRD model, with the corresponding Δd deformation, to fit the measured diagrams. As it can be seen from Fig. 4, comparing together the heavily doped sample data and the model ([As]= 4.5×10^{21} cm⁻³), the large scattering angle satellite peak is well fitted by the model. And this remains true for all Δd obtained in the range.

The existence of the tensile strain in the layers is confirmed by convergent electron beam diffraction (CBED) (Ref. 8) on a medium doped Si:As sample ([As]=8.5 $\times 10^{20}$ cm⁻³—sample named "med" in Table I and Fig. 2). Figure 5 shows side by side the CBED patterns for bulk Si and the medium doped layer. Even if small, we can see the differences in the lines positions. Theoretical calculation on the lines position of the doped sample permits one to determine the film properties. We confirm the reduction of the vertical lattice parameter and obtain a *c* of 0.5422 nm instead of 0.5431 nm for Si, which gives a deformation Δd = -0.17%. The values obtained from XRD and CBED are in good agreement (see Fig. 3).

In the case of a layer biaxially strained by the (100) Si substrate, the material lattice parameter $a_{\text{Si:As}}^{\text{bulk}}$, i.e., the lattice parameter that the layer would have if not constrained (as-



FIG. 4. Heavily doped sample measured and simulated XRD diagrams (~ 100 nm).

suming tetrahedral symmetry), can be obtained by correcting Δd [previously determined from Eq. (1)], from the Poisson expansion⁵

$$\frac{\Delta a}{a} = \frac{\Delta d_{400}}{d_{400}} \frac{c_{11}}{c_{11} + 2c_{12}} = \frac{a_{\text{Si:As}}^{\text{bulk}} - a_{\text{Si}}}{a_{\text{Si}}},\tag{2}$$

with the elastic constant for Si,

$$\frac{c_{11}}{c_{11} + 2c_{12}} = 0.56. \tag{3}$$

From Fig. 6, representing the evolution $a_{Si:As}$ as a function of the inactive As concentration, we can see that the lattice is reduced down to 0.5415 nm for the heavier doped sample, which corresponds to a 0.29% reduction of the lattice parameter compared to undoped Si.

This type of tensile strain has already been observed in implanted and annealed Si.9 Cargill and co-workers attributed the observed strain to the increased population of conduction band states which reduces Si-Si bond length. According to our results, we show that the strain is rather related to the appearance of a high concentration of electrically inactive As atoms. It has been reported from experimental evidence and theoretical results that heavily doped materials exhibit vacancy-impurity complexes or inactive impurity clusters.¹⁰⁻¹³ Vacancies complexes are easily detected using positron annihilation spectroscopy (PAS).¹⁴ Figure 7 shows the Doppler broadening momentum parameters S and W as a function of [As] from our episamples. Previous studies on highly *n*-type Si (Refs. 15 and 16) have shown that a decrease in the S parameter and an increase in the W parameter is a clear indication of an increase in the average number of As atoms per monovacancy. When S/S_B is below

TABLE II. Epilayers dopant concentration and corresponding carrier concentration.

[As] (cm ⁻³) [n] (cm ⁻³)	$6.0 imes 10^{18}$	2.6×10^{20}	3.8×10^{20}	6.2×10^{20}	9.3×10^{20}	1.9×10^{21}	4.5×10^{21}
	6.0×10^{18}	1.1×10^{20}	1.8×10^{20}	2.3×10^{20}	2.6×10^{20}	1.7×10^{20}	1.5×10^{20}



FIG. 5. CBED patterns of bulk Si and medium doped Si:As.

unity most monovacancies are bound in V-As₃ complexes. The measurements show that the average As-decoration per monovacancy increases with the dopant concentration up to 5×10^{20} cm⁻³. When the As concentration is further increased the *S* parameter also starts to increase and the *W* parameter decreases. We interpret this as a consequence of the formation of larger vacancy complexes, i.e., the number of As atoms per vacancy decreases when complexes such as V_2 -As₅ start to form, and as a consequence of the change in the layer lattice parameter which modifies the momentum distribution. Details of the PAS experiments will be published elsewhere.

It has been previously observed¹⁶ that during high temperatures annealing [800 or 900 °C in furnace, or 900 °C rapid thermal annealing (RTA)] the V-As complexes that are present in the as-grown samples ([As]>10²⁰ cm⁻³) breakup and recombine, leaving less vacancy complexes after the annealing. However, their concentrations are still very high after heat treatment, indicating that the recombination processes at these very high doping levels are quite efficient. This is basically the whole point of doing RTA or spike, i.e., the breakup of deactivating V-As₃ (and/or V₂-As₅) complexes and fast cooling down trying to avoid the recombination of vacancies with dopants. We performed Hall measurements after 1080 °C spike anneal (standard activation annealing in complementary MOS technologies). The extractions of ρ and [*n*] are done with thicknesses corrected from



FIG. 7. Evolution of S/S_B and W/W_B parameters from PAS as a function of dopant concentration.

dopant diffusion and As profiles are obtained with secondary ion mass spectroscopy measurements. We obtain the same carrier concentration and Hall mobility for both as-deposited and annealed samples. This annealing had no effects on the XRD pattern too, from the Fig. 8, presenting together XRD pattern of as-deposited and annealed medium-doped samples, we can see that the satellite peak shift is constant, so the strain is still present. Therefore, these results demonstrate that the defects present in the film are very stable comforting the hypothesis of the presence of vacancy-type defects.

Transmission electron microscopy (TEM) observations (Fig. 9) show the existence of three-dimensional extended defects in very low concentrations, the fast Fourier transform (FFT) of the defect gives a signature of a stacking fault of Si (111) planes. In addition to their low density, this type of defect usually reduces the stress in the layer therefore we can assume it does not contribute extensively to the global lattice parameter reduction observe with DRX.

We postulate therefore that the presence of high concentration of these vacancy-type point or extended defects, like impurities clusters, is responsible for the lattice parameter



FIG. 6. Evolution of the lattice parameter calculated from the XRD peak shift as a function of inactive As concentration.



FIG. 8. Evolution of the medium doped Si:As XRD pattern for as-deposited and spike annealed layers.



Fig. 9

FIG. 9. High-resolution TEM image and FFT of the epitaxial Si-As doped layer showing a crystal defect.

reduction (despite the large amount of As atoms) and thus for the lattice deformation. In addition, the trapping of the As atoms in these defects explain the difference between carrier and total concentration.

The main application of such layers is the high performances HBT emitter, as it requests heavy doping and is not very sensitive to defects (polysilicon emitters are commonly used). For MOS technologies, the heavily doped layers are certainly not suitable due to high defect concentration and reduced electrical properties.

IV. CONCLUSION

Combining XRD and CBED we have been able to highlight the existence of tensile strain in As-heavily doped Si epilayers. We report a vertical deformation of the Si:As lattice parameter up to -0.63%. We show that this strain is linked to the inactive As atoms involved in complexes or clusters and the use of PAS exhibits that precursors of these defects are vacancy related defects. These complexes, that trap a large number of dopant atoms, are assumed to be responsible of the appearance of voids in the lattice and therefore of its contraction. The electrical properties are affected by these defects who trap the As atoms and strongly reduced the carrier concentration.

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