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On the manifestation of phosphorus-vacancy complexes in epitaxial Si:P films

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In situ doped epitaxial Si:P films with P concentrations >1 x 10^{21} atoms/cm^3 are suitable for source-drain stressors of n-FinFETs. These films combine the advantages of high conductivity derived from the high P doping with the creation of tensile strain in the Si channel. It has been suggested that the tensile strain developed in the Si:P films is due to the presence of local Si_3P_4 clusters, which however do not contribute to the electrical conductivity. During laser annealing, the Si_3P_4 clusters are expected to disperse resulting in an increased conductivity while the strain reduces slightly. However, the existence of Si_3P_4 is not proven. Based on first-principles simulations, we demonstrate that the formation of vacancy centered Si_3P_4 clusters, in the form of four P atoms bonded to a Si vacancy, is thermodynamically favorable at such high P concentrations. We suggest that during post epi-growth annealing, a fraction of the P atoms from these clusters are activated, while the remaining part goes into interstitial sites, thereby reducing strain. We corroborate our conjecture experimentally using positron annihilation spectroscopy, electron spin resonance, and Rutherford backscattering ion channeling studies. © 2016 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4942605]
around these, giving rise to an E center (dopant bound to a vacancy defect forming a deep level in the bandgap). These vacancy centers disappear after annealing concurrent with an improvement in the conductivity. With the temperature/time budget of our anneals (1200 °C/0.5 ms with 2 pulses), not all of the P atoms complexed with vacancies are substitutionally dissolved, as demonstrated by the ESR measurements. Moreover, it appears that, based on the increased channeling yield from RBS measurements, a fraction of the undissolved P atoms goes into interstitial positions. This displacement of P atoms to interstitial sites also explains the loss of strain for the annealed layers as measured by HR-XRD.6

Details on the epitaxial growth of Si:P are described in Ref. 6. For the growth conditions used, a maximum P concentration of 4.6% can be obtained, while retaining a fully strained epitaxial film. For concentrations beyond 4.6%, the roughness of the epitaxial layers increases and the film undergoes an epitaxial breakdown. Hence, we restrict our study on the local clustering phenomena for P to a maximum P concentration of 4.6%. The ab-initio simulations were carried out using the quantum espresso9 package combined with Vanderbilt pseudopotentials. A 340 eV kinetic energy cut off and gamma k point mesh sampling were used, combined with Perdew–Burke–Ernzerhof (PBE)10 exchange correlational function. The model used consists of a 216 atoms silicon unit cell in which two P atoms (labelled as P1 and P2) were randomly placed at different radial distances from each other. The atomic positions of the structure were then relaxed, and the resulting total energy was calculated for the different configurations. The change in total energy with respect to the reference energy, corresponding to different configurations is extracted and shown in Fig. 1(a).

As evident from Fig. 1(a), the concomitant presence of two P atoms in their immediate vicinity leads to an increase in the total energy. When the P atoms occupy positions farther and farther apart, the total energy of the system decreases. The kink computed for a radial distance at 5.9 Å is attributed to a specific configuration where two P atoms lie in parallel planes that leads to a maximum stress transfer.11 As the system considered is confined to 216 atoms, the maximum distance to which the second P atom (P2) can be positioned from the first one (P1) without interfering with the imposed periodic boundary conditions, is 12 Å, and the total energy of the system at 12 Å is defined as the reference minimum energy. Whenever the difference in total energy between the considered configurations and the reference one (P2 located at 12 Å from P1) is lower or equal to the thermal energy at 300 K, i.e., 0.026 eV, we determine the configuration to be stable. It is found that, when P atoms are located at least 6.6 Å from each other, the difference in energy becomes close to the thermal energy, suggesting that this configuration is possible at room temperature. This suggests that energetic considerations favor the distributions with P atoms separated at least 4 atomic sites (or more) from each other. Similar trends have been found when performing the simulations for different P doping concentrations (≤4.6%). The P atoms always favor to stay as far away as possible from each other. In view of their similarity, we restrict the remaining discussion to layers with the 4.6% P doping concentration.

It must be noted that unlike Si:C,12 which has a distinct energy minimum for a 3nn distribution of C atoms,13 there is no such minimum energy position for the distribution of P atoms. Although P atoms give rise to tensile stress, when they are present in an ionized form, the coulombic repulsion prevents any sort of nearest neighbor arrangement. Thus, in the as grown samples and in the absence of defects/vacancies, P does not like to have another P atom as a close nearest neighbor.

The situation becomes different if a vacancy is inserted in the system. Indeed for the combination of a single P atom with a vacancy, the total energy of the system decreases when the distance between the P atom and the vacancy is reduced. This affinity of P towards vacancies is similar to the one noted previously by Ganchenkova et al.13 The formation enthalpy of a PnV complex with n = 1 is positive and equals to 3.4 eV, and it decreases as the number of P atoms (n) increases. Consequently, the formation enthalpy of the P3V complex, where the vacancy is surrounded on all sides by a P atom, is found to be negative (−0.31 eV), indicating that its formation is a spontaneous process from a thermodynamic perspective. (A similar behavior for the formation of P3V complex is also reported by Chen et al.,14 in their studies on gettering.) The question arises whether two such PnV clusters can co-exist next to each other forming a divacancy configuration. The enthalpy of formation for two such configurations, where the two P3V clusters are located as 3nn (Fig. 1(b)), has indeed negative energetic values (−0.2 eV and −0.6 eV) indicating their stability. Hence, our finding suggests that, from an energetic perspective, P3V clusters could be present as both monovacancies and divacancies in the Si:P lattice.

The density functional theory (DFT) results obtained on the P distribution and P-V complexes distribution within the silicon matrix are corroborated by PAS measurements to understand the nature of the vacancies that are formed in the Si:P layers. For a detailed description on Positron annihilation spectroscopy, the reader is referred to Refs. 15 and 16.

We used Doppler broadening (DOBS) and Coincidence Doppler Broadening Spectroscopy (CDOBS) to study the vacancy defects in the Si:P-layers. For DOBS, we used a
variable positron implantation energy for depth profiling. In order to improve the sensitivity for the layer, the surface oxide was removed by etching the samples in HF acid prior to the measurements.\textsuperscript{17,18}

Fig. 2 shows the CDOBS ratio curves for the 4.6% P sample (as-grown, annealed) together with the results for an E-center (P-V) and a divacancy in silicon. An $e^+$-trap-free silicon sample was used as a reference for normalization. The S and W parameters\textsuperscript{15,16} were first measured as a function of positron implantation energy (DOBS) and the corresponding W(S) plot for the 4.6% Si:P layer is shown in the inset. The arrows in the inset indicate the direction of increasing positron implantation energy (1, 2 indicating the lowest implantation energy). The circled points are characteristic for the dominant defects and correspond to the maximum S parameter observed in the layers. The $e^+$-diffusion length in the as-grown layers is very short owing to P-V complexes formed by the high P concentration. A sharp turning point from the surface-Si:P-layer-line to the Si:P-layer-bulk line confirms this and therefore suggests that the $e^+$-trapping is in saturation or close to saturation in the respective layers.

The CDOBS measurements were carried out at an implantation energy of 1.3 keV that yields a narrow implantation profile with a mean $e^+$-implantation depth in the middle of the Si:P layer. The Si:P 4.6% samples fall in between the P-V and V$_2$\textsuperscript{19,20} with the characteristic momentum peak at 1.2 a.u. being slightly higher in the annealed sample and closer to the P-V center. Previous studies\textsuperscript{21} indicate that adding more P atoms to a vacancy in Si decreases the intensity at high momenta and hence also the W parameter (inset in Fig. 2).

Hence, this suggests that the dominating defect in the as-grown layers is most likely a monovacancy decorated with several P atoms. However, divacancy-sized complexes also cannot be ruled out. Annealing reduces the concentration of the vacancy defects, indicated by a reduction in the S parameter of the layer and the increase in intensity at high momenta in the CDOBS spectrum.

The exact mechanism responsible for the reduction in vacancies, resulting from the post-epi annealing process is not understood. Here, we will restrict ourselves to the qualitative interpretation of the increase in conductivity and the loss in strain reported for the annealed Si:P films.

To assess the atomic nature of occurring point defects, the location (site properties) and the distribution of P atoms, K-band ($\sim$20.4 GHz) ESR has been carried out at 4.3 K. (for details, see Ref.\textsuperscript{22}). For the annealed Si:P film (Fig. 3), the only signal observed from the sample itself is a weak doublet, of splitting $a = 42.0 \pm 0.4$ G and centered at $g = 1.99866$. It is the well-known doublet stemming from unpaired electrons at P atoms that have taken the substitutional doping sites in c-Si. The doublet splitting arises from the hyperfine interaction of the localized unpaired electron wave function with the nuclear spin ($I = \frac{1}{2}$) of the $^{31}$P isotope (100% natural abundance) nuclei. The as-grown films were excessively lossy,\textsuperscript{23} so no reliable ESR data could be attained. The doublet, of low intensity, indicates that a small portion of the P atoms has taken the dopant-active position as a result of the annealing. The reduced intensity of the doublet compared to the reference marker at $g = 2.00229$ clearly points out that the number of activated P atoms constitutes a fraction (50%) of the total P atoms after anneal. The ESR finding is also in line with the observation that 50% of the dopant atoms are activated by laser anneal as noted by Rosseel et al.\textsuperscript{6} This poses a fundamental question regarding the location of the remaining fraction of the P atoms complexed to vacancies.

We propose that after annealing, the remaining of the P atoms attached to the mono and divacancies have reached the interstitial sites, leading to a reduction in the vacancy defects. This proposal is supported by the increase in the RBS channeling yield for the annealed Si:P films. The channeling yield for the as-grown 4.6% Si:P films is measured to be 7.9%, while it rises to 17.6% after laser annealing, which is almost a factor of 2 higher than for the as-grown films, suggesting a...
Yosuke Shimura would like to thank FWO for granting him a pilot line, the logic program of imec, and to all core partners for their support on XRD and RSM measurements, to our plexes in the Si:P films.

As a summary, we have investigated the structure and lattice position of P atoms when incorporated in highly P-doped films used for S/D stressor applications in n-FinFET devices. The as-grown and annealed Si:P films were studied using first-principles calculations complemented with PAS, ESR, and RBS measurements. From the DFT studies, we inferred that the formation of isolated $P_4V$ and $P_3V$ clusters in a third nearest neighbor configuration is likely to occur, thanks to their negative enthalpies of formation. With PAS, we clearly observe the signatures of monovacancies, whereas the structure of divacancies with P decoration has precluded us from observing them, even if they had manifested. Upon laser annealing, the concentration of vacancies reduces. This reduction suggests that $P_4V$ complexes can be broken up by the annealing process. As a result, a fraction of the P atoms complexed to $P_0V$ moves to substitutional sites (as inferred from ESR measurements), whereas the remaining fraction of the P atoms either moves to interstitial sites or takes a relaxed atomic position from the substitutional sites, as evidenced from the channeling yield of RBS measurements and from the loss of strain measured by HR-XRD. Thus, the conductivity increases, and the reduction in strain is explained by the formation of interstitials from different $P_nV$ complexes in the Si:P films.

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23Note: Similar to Si:P, another material that exerts tensile strain is Si:C. Even though both Si:P and Si:C exhibit tensile strain at a macroscopic level, their local atomic arrangements do not show any similarities.


45Note: Lossy nature of the as grown Si:P films is currently believed to be a result of numerous $P_4V$ complexes. Further ESR studies have been planned to investigate this effect.