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Effect of germanium substrate loss and nitrogen on dopant diffusion in germanium

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Recent experimental studies demonstrate a significant germanium (Ge) substrate loss and consequently dopant loss even during low temperature annealing. Additionally, for phosphorous (P) implanted Ge the capping layer material affects P diffusion. Silicon nitride (Si_3N_4) capping is more efficient compared to silicon dioxide (SiO_2) capping, but an accumulation of P is observed at the Ge/ Si_3N_4 interface. In the present study, the recent experimental evidence is evaluated and with the use of electronic structure simulations the formation of relevant defects is investigated. It is predicted that the formation of clusters containing nitrogen (N) and vacancies (V) can be related to the observed accumulation of P atoms near the Ge/ Si_3N_4 interface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3086664]

Ge re-emerged as a substrate material for microelectronic applications due to its higher mobility of holes and electrons, similarity to silicon (Si), smaller band gap and increased dopant solubility.^{1–5} This led to a number of studies investigating the properties and the diffusion of impurities in Ge.^{1–5} Under intrinsic doping conditions the diffusion of *n*-type dopants (such as P) is limited, whereas under extrinsic doping conditions significant concentration dependent diffusion is observed (see Refs. 5–7 and references therein).

Previous studies determined that under low temperature annealing (e.g., even at temperatures more than 400 K below the melting temperature of Ge in a conventional resistance-heated furnace with N_2 flow) uncapped Ge samples exhibit significant Ge substrate loss and consequently dopant loss.^{6,8–11} Ioannou *et al.*¹¹ attributed this phenomenon to a thermally activated process obeying an Arrhenius law with an activation energy of 2.03 eV, however, they did not provide a physical explanation of its origin.

Pelieva and Martynenko¹² obtained a value of 3.46 ± 0.26 eV for the activation energy for the evaporation of Ge in a graphite furnace at the temperature range of 1700–1900 K using the method of Smets¹³ (see also Ref. 14). This value is in excellent agreement with the heat of sublimation of Ge at 1700 K.¹² Substrate sublimation must be excluded as a possible cause of substrate loss in the recent experimental studies^{6,8–11} because of the higher temperatures and activation energy required for the phenomenon to occur.

In previous experimental diffusion studies, in which the Ge samples were protected inside closed glass ampoules, no substrate loss was observed.^{5,15} Notably in these studies^{5,15} the annealing temperatures and times were significantly higher (for example 1193 K for 72 000 s) compared to the studies^{6,10,11} using the uncapped samples (up to 848 K for 1800 s). It is therefore the nature of the annealing methodology that leads to the Ge substrate loss.

Concentrations of oxygen (O) have been detected in Czochralski-grown Ge and it is usually introduced when H_2O vapor or oxygen gas is present in the growth atmosphere.¹⁶ Kaiser and Thurmond¹⁷ determined a solubility of O in Ge of the order of 10^{18} cm^{-3} . Oh and Campbell⁹ investigated Ge substrate loss on ion-implanted samples using x-ray photoelectron spectroscopy. It was determined that the native oxide GeO_2 contains only small amounts of GeO_{2-x} .⁹ Under annealing, using a rapid thermal processor with a N_2 purge at atmospheric pressure, the native oxide decomposes thereby producing GeO .⁹ The thermal desorption of the volatile Ge oxides and the successive reoxidation of the Ge substrate results in a significant Ge substrate loss.⁹

By capping the samples with silicon SiO_2 or with Si_3N_4 , it was determined that the dopant loss was reduced.^{6,10,11} It is of interest that in these studies^{6,10,11} a significant accumulation of P was observed at the Ge/ Si_3N_4 interface. This accumulation of P was attributed to the denser Si_3N_4 (compared to SiO_2) that does not allow P to out diffuse. It has been previously established that N is strongly bound in interstitial pairs in Ge (see Ref. 18 and references therein). These resemble N_2 molecules that have high dissociation energy and can enter in the tetrahedral interstice of Ge.¹⁹ A possible route for N to enter the Ge substrate is via the Si_3N_4 capping layer. In the previous experimental studies sputtered Si_3N_4 was used, however, its quality needs to be assessed carefully.^{6,10,11} This is because in recent studies on nitride materials it has been established that a large change in N deficient stoichiometry leads only to a very limited change in the lattice parameter of the nitride.²⁰ The N deficiency was correlated with the formation of N vacancies in the nitride.²⁰ In turn this could lead to an injection of N atoms in Ge. The principle aim of this study is to investigate the effect of N in Ge and its interaction with V and dopant atoms.

Electronic structure calculations using the plane wave density functional theory (DFT) code CASTEP (Refs. 21 and 22) were used to investigate the association of N with V and dopant atoms in Ge. Exchange and correlation interactions are described using the generalized gradient approximation

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TABLE I. Binding energies (eV) for N_nV_m clusters in Ge.

Defect cluster	E_b
NN	-1.39
NV	-1.05
NVV	-1.82
VNV	-0.81
VNN	-1.22
NVN	-2.20

corrected density functional of Perdew *et al.*²³ combined with ultrasoft pseudopotentials.²⁴ The cutoff of the plane wave basis set is 350 eV in conjunction with a $2 \times 2 \times 2$ Monkhorst-Pack²⁵ k -point grid and a supercell consisting of 64 atomic sites adequately describe Ge. The efficacy of the DFT approach used has been established by comparing the results with experiments.^{26–29}

To quantify the attraction between N and V or dopant atoms that can form a defect cluster, it is necessary to calculate binding energies, E_b , that are defined by

$$E_b = E_{\text{defect cluster}} - (\sum E_{\text{isolated defects}}), \quad (1)$$

where $E_{\text{defect cluster}}$ is the energy of the unit cell that incorporates the defect cluster and $E_{\text{isolated defects}}$ are the energies of the cell containing the various components of the cluster (for example, a single N atom). A negative binding energy implies that the defect cluster is stable with respect to its constituent point defect components.

In the present study, it is predicted that N substitutional atoms form strongly bound N_nV_m clusters (see Table I for binding energies and Fig. 1 for the different configurations). For example the NV pair is more bound by -0.53 eV compared to the PV pair, which is bound by -0.52 eV.³⁰ It is evident from Table I that the formation of larger clusters

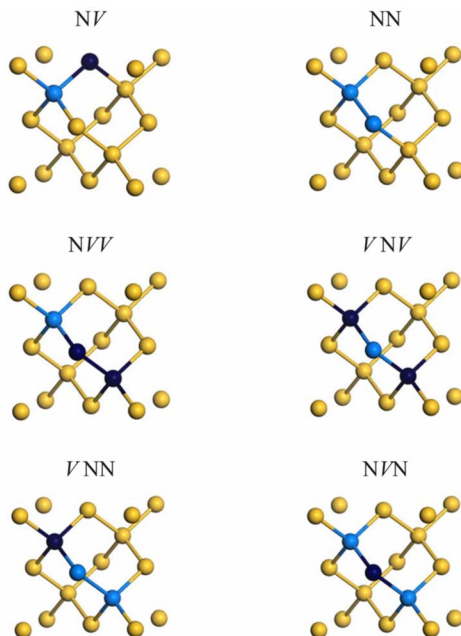


FIG. 1. (Color online) The most bound N_nV_m clusters considered in a unit cell of Ge. Yellow and blue spheres represent Ge and N atoms, respectively, whereas black spheres represent the V.

TABLE II. Binding energies (eV) for dopant-nitrogen and dopant-dopant (Refs. 10, 26, and 33) pairs in Ge.

Dopant-nitrogen	E_b	Dopant-dopant	E_b
PN	-0.65	PP	0.28
AsN	-0.67	AsAs	0.17
SbN	-0.57	SbSb	0.10

containing multiple N atoms (for example NVN, see Fig. 1) or multiple V (for example NVV, see Fig. 1) is energetically favorable. The preference of V for N can have an impact on P diffusion that is predominately V-mediated in Ge.^{4,5} This is because V would preferentially associate with existing N atoms leaving immobile P atoms near the Ge/Si₃N₄ interface. This could explain the almost two orders of magnitude higher concentration observed near the Ge/Si₃N₄ interface ($\sim 10^{21}$ cm⁻³, see Fig. 4 in Refs. 6, 10, and 11) compared to the solid solubility of P in Ge ($\sim 2 \times 10^{19}$ cm⁻³, see Ref. 31). Similar high concentrations of P atoms significantly above the equilibrium solid solubility were observed by Satta *et al.*³² These were determined to be P precipitates and consequently the constituent P atoms electrically inactive.³² Another possibility would be the formation of P_nV_m clusters at the high P-concentration regions.³³ In recent studies^{10,26,33} it was predicted that the PP, AsAs, and SbSb interactions are repulsive (see Table II) when the dopants are at first nearest neighbor sites (analogous to the NN configuration in Fig. 1). Conversely, the NN pairs are strongly bound by -1.39 eV (see Table I). All dopant-nitrogen (PN, AsN, and SbN) pairs considered are bound by a significant binding energy (around -0.6 eV, see Table II). This in turn could mean that if the dopants diffuse toward a region with a significant N concentration they would associate with them. To quantify, however, the effect of N on the diffusion of dopants in Ge will require detailed experimental studies.

It is anticipated that the prediction of P diffusion taking into account a simultaneous Ge substrate loss (and the subsequent dopant loss) is not straightforward. In a recent study,¹¹ an Arrhenius law describing the (100) Ge substrate loss rate was coupled with a process simulator using a concentration-dependent P diffusion model. However, for the experimental conditions considered by Ioannou *et al.*¹¹ (P implanted with an energy of 50 or 150 keV with a dose of 5×10^{13} cm⁻²), it had been previously established⁶ (using Si₃N₄ capped P-implanted Ge samples that retain most of the dose) that P diffusion is very limited. Consequently, the simulations of Ioannou *et al.*¹¹ describe the loss of the Ge substrate with the P profile being in practice almost stationary. Therefore, the proposed model should be validated for a wider range of conditions especially those in which there is significant concentration-dependent P diffusion (including Fig. 4 of Ref. 11).

To conclude Ge substrate loss is a phenomenon that is strongly dependent on the annealing methodology. It is predicted that N forms stable clusters with V and dopant atoms. These clusters can affect the properties of the dopant atoms that are mediated via V. Further investigations are required to

quantify the effect of the capping layer and N on the dopant diffusion.

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