



# Charge carrier passivating nitrogen–phosphorus defects in crystalline silicon



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## ABSTRACT

In this work, the geometric and electronic structure of the neutral and charged nitrogen–phosphorus defects were for the first time rigorously investigated by density functional theory. The ground state structures were located by screening all possible geometric configurations of the defects. It is shown that the modified self-interstitial nitrogen–phosphorus defect passivate the free carrier states of isolated substitutional phosphorus, known to be an excellent dopant in crystalline silicon. Furthermore, the band gap is shown to be similar in magnitude to bulk silicon, but direct. However, this study indicate that the nitrogen–phosphorus defect is possibly less stable than the self-interstitial nitrogen dimer at high nitrogen defect concentrations. Finally, the vibrational spectra were analyzed by means of linear response theory and phonon calculations. The resulting vibrational spectra yield a peak split of the modified self-interstitial nitrogen mode of 4 THz compared to the isolated self-interstitial nitrogen defect.

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## 1. Introduction

Isolated defects and their complexes in crystalline silicon have been extensively studied in the literature. However, there still exist potentially important defects that are not yet investigated in detail. In particular, studies of defect complexes between dopants in silicon and nitrogen are limited, even though their hydrogen counterpart has been more extensively studied [1–3]. Nitrogen defects, in particular the fast diffusing nitrogen self-interstitial and the nitrogen dimer [4–7] are expected to be largely present during nitridation of silicon wafers (or deposition of silicon–nitride on bulk or thin film silicon) for passivation purposes. Usually, the nitridation or deposition processing is executed after silicon has been doped to a specific carrier concentration and nitrogen creep into the silicon is expected. Nitrogen monomers diffuse fast in silicon and tend to form stable nitrogen dimers [7]. These dimers are currently considered the most stable nitrogen defects [8] in bulk silicon.

Phosphorus is extensively used as an *n*-type dopant in order to create an emitter and its concentrations can approach  $10^{21} \text{ cm}^{-3}$  in the emitter region. Recent studies show that phosphorus is more stable close to a silicon–nitride passivation interface compared to bulk silicon [9]. It is thus expected that the phosphorus concentra-

tion is high precisely in the same region where a significant amount of nitrogen defects will be present. Detailed knowledge of the nitrogen–phosphorus interaction, and in particular their defect complexes is thus a necessity in order to better understand and improve the passivation properties.

This study pursues this path and investigates different configurations of neutral and charged nitrogen–phosphorus defects, (NP), in crystalline silicon. These configurations' electronic and phononic structure are analyzed and compared to their respective references containing isolated N and P defects. The stability of the different charged configurations are investigated, including the stability of the nitrogen–phosphorus relative to the self-interstitial nitrogen dimer defects.

## 2. Computational details

DFT calculations were performed using the Perdew–Burke–Ernzerhof (PBE) [10] exchange–correlation functional, where the projector–augmented–wave (PAW) [11–13] method was employed. All calculations were performed in the framework of the Vienna Ab-initio Simulation Package (VASP) [14,15]. The configurational search was performed with a  $1 \times 1 \times 1$  for relaxation and a  $3 \times 3 \times 3$  *k*-point grid for the total energy calculations, respectively. An energy cutoff of 400 eV was used and the relaxations were terminated when the residual forces were below 0.01 eV/Å. For the final relaxation and total energy calculations, an energy

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cutoff of 500 eV with a  $k$ -point sampling of  $5 \times 5 \times 5$  were found to yield satisfactory convergence. The final relaxations were terminated when the residual forces between the atoms were less than  $10^{-5}$  eV/Å. The resulting structures formed the input for the linear response calculations.

The formation energy of the (NP) defect was calculated using

$$\Delta E = E[\text{Si}_{63}\text{NP}] + E[\text{Si}_{64}] - (E[\text{Si}_{64}\text{N}] + E[\text{Si}_{63}\text{P}]), \quad (1)$$

where  $E[\text{Si}_{63}\text{NP}]$ ,  $E[\text{Si}_{64}]$ ,  $E[\text{Si}_{64}\text{N}]$  and  $E[\text{Si}_{63}\text{P}]$  are the calculated energies for the (NP) defect, the bulk Si, the self-interstitial nitrogen defect and the substitutional phosphorus defect, respectively. All calculations were performed in a silicon supercell containing 64 atoms.

Linear response calculations were performed to generate the necessary force constants and the phonon calculations were executed in Phonopy [16]. Visualizations were performed in VESTA [17].

### 3. Results and discussion

The geometric structure of the nitrogen–phosphorus complexes is unknown and it is, a priori a rather difficult task to map all configurations and how they relate in energy. In order to do this in a consistent manner, a silicon supercell containing one substitutional phosphorus atom was generated. Then nitrogen was introduced in initial configurations surrounding the substitutional phosphorus atom (separated by 0.2 Å in each direction). This configurational search is sufficiently large to cover all relevant input positions. To account for defect charging, the background charges were compensated by  $\pm 1$  electron to yield results for the (NP)<sup>−</sup>, (NP)<sup>0</sup> and (NP)<sup>+</sup> defects. Separate calculations to locate the most energetically stable configurations were performed for each charged state.

The maximum allowed nitrogen–phosphorus distance was 3.38 Å and all input configurations with a Si–N or P–N distance less than 1.5 Å were disregarded in order to reduce the number of input configurations to 2983 excluding symmetry. These input configurations were then relaxed and the total energy was calculated. Due to the fact that numerous input configurations relax into the same structure, it is possible to categorize the formation energies of these structures into different manifolds, where each manifold contain structures with similar geometrical configurations. In order to further refine the search for the most stable configurations the structure with the lowest energy in each manifold was further relaxed using a denser  $k$ -point grid and higher energy cutoff (see computational details). Following the last relaxation step, the resulting structures were investigated for imaginary phonon frequencies. The structures containing such frequencies were discarded as unstable due to the fact that the structure are not in a global minimum on the potential energy surface. Finally, the total

energy where calculated for the remaining structures. The resulting relative energies and structures are listed in Table 1, and Figs. 1 and 2.

Here it is apparent, that for (NP)<sup>+</sup>, the self-interstitial nitrogen–phosphorus is not the configuration with the lowest energy. Instead, a modified self-interstitial nitrogen defect (with a slightly distorted silicon self-interstitial position) is present in all four configurations with phosphorus one and two silicon atoms away. The most stable configuration of the (NP)<sup>+</sup> defect is a distorted self-interstitial nitrogen defect separated from the substitutional phosphorus defect by one silicon atom. This configurations has a low formation energy of  $-0.53$  eV relative to an isolated N<sup>+</sup> and P<sup>0</sup> defect.

The (NP)<sup>0</sup> defect with the lowest energy relaxes into a self-interstitial nitrogen–phosphorus configuration, by compensating the extra electron on the phosphorus and the nitrogen atom. In fact, the formation energies of the (NP)<sup>0</sup> defect is low and significant;  $-0.95$  eV starting from N<sup>0</sup>P<sup>0</sup>,  $-1.28$  eV from N<sup>+</sup>P<sup>−</sup> and  $-0.90$  eV from N<sup>−</sup>P<sup>+</sup>. There is a significant difference in formation energy (0.5 eV) between this configuration and the less stable configuration which separates the self-interstitial nitrogen and phosphorus defect by two silicon atoms. As for (NP)<sup>+</sup>, the self-interstitial defect is not entirely symmetric compared to an isolated self-interstitial nitrogen defect. Phosphorus is instead slightly distorted out of the silicon plane (consult Figs. 1 and 2). A symmetric (NP)<sup>0</sup> defect was located during the search, but contained imaginary frequencies and was thus discarded.

For the (NP)<sup>−</sup> defect, the most stable configuration also has a self-interstitial nitrogen–phosphorus character. This configuration is very similar to the most stable configuration for the (NP)<sup>0</sup> defect. At higher formation energies, there are configurations which separates the isolated nitrogen and phosphorus defect by one and two silicon atoms. Due to the extra electron, there are also two configurations where the nitrogen is only two-coordinated with two silicon atoms, but still separated by one silicon atom from phosphorus. The most stable configurations of (NP)<sup>−</sup> also yield low formation energies at  $-0.85$  and  $-0.99$  eV, assuming the isolated N<sup>−</sup>P<sup>0</sup> and N<sup>0</sup>P<sup>−</sup> reference, respectively.

All configurations possess negative formation energies signifying their stability with respect to the isolated nitrogen and phosphorus defects. It is thus reasonable to expect the (NP) defects to be present over the isolated constituent defects even at elevated processing temperatures. However, it is important to take into account the possible formation of the stable nitrogen dimers.

The formation energy for the self-interstitial nitrogen dimer, (N<sub>2</sub>) was in this study calculated to  $-3.84$  eV in good agreement with previous calculations [8]. Since this is currently considered to be the most stable interstitial nitrogen defect in silicon [8], it is interesting to put the (NP) defect into this perspective. In order to do so, the self-interstitial nitrogen dimer structure was as an input. One (for (N<sub>2</sub>P)) or two (for (N<sub>2</sub>P<sub>2</sub>)) phosphorus atoms were then added along the axis of the nitrogen atoms and normal to this axis. These structures were relaxed and phosphorus settled close to the original silicon positions. The resulting relative energies (with respect to two self-interstitial nitrogen and two substitutional phosphorus atoms) are listed in Table 2. In the most stable configuration, the (N<sub>2</sub>P)<sup>0</sup> defect, phosphorus resides on one of the positions along the nitrogen axis (0.28 eV more stable than the normal configuration). For the (N<sub>2</sub>P<sub>2</sub>)<sup>0</sup> defect, phosphorus preferred to occupy the same positions. Relaxations containing one phosphorus on this axis and one on the normal axis failed to reach a force cutoff below 0.05 eV/Å (the other structures reached 0.001 eV/Å). From Table 2, we see that the energy difference between two (NP) defects and the self-interstitial nitrogen dimer is  $-1.90$  eV. Furthermore, the dimer complex with phosphorus, the (N<sub>2</sub>P)<sup>0</sup> defect is 0.45 eV less stable than the phosphorus free

**Table 1**

Formation energies,  $\Delta E$  at  $E_F = 0$  eV for the final high accuracy relaxation and total energy calculations. The formation energies for different configurations are included up to 0.5 eV above the most stable configuration. Only values complying with charge neutrality during the formation of the (NP) complex has been included.

Initial	Final	$\Delta E$ (eV)				
		1	2	3	4	5
N <sup>0</sup> P <sup>0</sup>	(NP) <sup>0</sup>	−0.95	−0.45	−	−	−
N <sup>+</sup> P <sup>−</sup>	(NP) <sup>0</sup>	−1.28	−0.78	−	−	−
N <sup>−</sup> P <sup>+</sup>	(NP) <sup>0</sup>	−0.90	−0.40	−	−	−
N <sup>+</sup> P <sup>0</sup>	(NP) <sup>+</sup>	−0.53	−0.51	−0.42	−0.30	−
N <sup>0</sup> P <sup>+</sup>	(NP) <sup>+</sup>	−0.30	−0.27	−0.18	−0.06	−
N <sup>−</sup> P <sup>0</sup>	(NP) <sup>−</sup>	−0.85	−0.81	−0.52	−0.49	−0.35
N <sup>0</sup> P <sup>−</sup>	(NP) <sup>−</sup>	−0.99	−0.95	−0.67	−0.63	−0.49

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