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DFT Study Of Nitrogen-Doped Silicon: Analysis Of Structural Distortion, Electronic Properties And Formation Energy

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Abstract
This paper is based on the Density Functional Theory (DFT) to explain the structure and electronic characteristics of N-doped Si. The supercell was a 24 box and a single Si atom was substituted with a N atom in order to record the doping effect. Analysis of structure showed a shortened N-Si bond length of 1.89 Å and longer Si-Si bond lengths of 2.41 Å, which showed localized lattice strain. The greatly pronounced deep states in the electronic density of states (DOS) closed the effective band gap. When calculated formation energy was in equilibrium, it was thermodynamically unstable. All these findings offer theoretical explanations to the constraints and opportunities available in N doping to manipulate the Si properties in going green and to use this material in the semiconductors.
Keywords: *Nitrogen doping, Silicon, Density Functional Theory (DFT), Electronic structure, Lattice distortion, Formation energy, VASP simulation.*

INTRODUCTION

Silicon is the cornerstone in the modern semiconductor industry due to its abundance, well-developed technology of manufacturing, and favorable electronic properties [1]. However, the increasingly growing need to have devices which would have extreme efficiency and custom features has seen the need to have investigators examine the implications of doping silicon with varying elements. Among the possible dopants, nitrogen deserves a special consideration, because its atomic radius is very small, and its electronegativity is high, which can significantly lead to a reorganization of both the structural and the electronic properties of the host lattice.[2]
Insertion of nitrogen in silicon lattice induces local defect states in the band gap, and this influences the conductivity and the defect related phenomena [3]. Theoretically, the endowment of nitrogen atoms can trigger the local lattice deformations, design the length of bonds, and refine the electronic density states of states, characteristics that cannot be ignored to understand and engineer functioning of silicon, which is doped.[4]

Density Functional Theory (DFT) provides a powerful computational tool the study such effects at an atomic level, providing predictive capabilities with regard to the energetics, electronic structure and formation processes [5]. This work was focused on the development of a detailed model of nitrogen-doped silicon via supercell simulations with DFT as a modeling technique, in order to describe distortion of the structure, electronic structure, and the formation energy. Findings are luminous to the way nitrogen alters the qualities of silicon and illustrates the thermodynamic practicality of nitrogen introduction under a variety of conditions.[6] .

2. METHODOLOGY

In this study, computational study, based on Density Functional Theory (DFT), was conducted to explain the structural and electronic characteristics of nitrogen doped silicon [5]. All the calculations have been performed in the framework of the Vienna Ab initio Simulation Package (VASP) that involves a plane-wave-based DFT formalism with periodic boundary conditions [6]. Exchange-correlation effects were instead modelled with the Perdew 301869; Barth 301881; Ernzerhof 2003 (PBE) functional, embedded in the generalized gradient approximation (GGA) using the generalized gradient approximation (GGA) .[7]
The computational model was a 64 atomic unit cell of silicon that was in a 2×2×2 cubic structure. A silicon atom was replaced by one nitrogen atom to give a doping concentration of about 1.56 at% [8]. This interaction between core and valence electrons was described by the use of projector augmented wave (PAW) method [9]. The plane-wave cutoff was 400 eV and the Brillouin zone was sampled using 4×4×4 Monkhorst-Pack k-point grid.[10]

When the total energy reached machine accuracy (<10^{-6} eV) and the forces exerted on each atom dropped below 0.01 eV/Å, the structures became relaxed. After such structural improvements, electronic density of states (DOS) and the projected DOS (PDOS) was calculated to evaluate the formation of impurity states by nitrogen incorporation [11]. The energy of formation of doping configuration was then computed using standard expression:

$$_{2}\mathrm{N}E\,\frac{1}{2} - {}_{64}\mathrm{Si}E\left(\frac{63}{64}\right) - {}_{1}\mathrm{Si}_{63}\mathrm{N}E = {}_{f}E$$

where $_{1}Si_{63}$ NE is the total energy of the doped supercell, $_{64}$SiE is the total energy of the .pristine silicon supercell, and $_{2}$ NE is the energy of a nitrogen molecule in its gaseous form[12] In addition to numerical simulation, a custom React-based interface-SiN-Simulator Prowas developed to visualize and control doping parameters in real time. This interface allowed for interactive adjustment of nitrogen concentration, supercell size, and temperature, providing insights into their effects on the electronic structure and formation energy[13].

3 .RESULTS AND DISCUSSION

3.1 Structural Modifications Due to Nitrogen Doping

A 2×2×2 silicon supercell with 64 atoms was developed and an Si atom was substituted by nitrogen atom, thus rushing into an approximate concentration of 1.56% doping in the sample [5]. The presence of strong local lattice distortion around the substitution site was then revealed by structural relaxation [6]. The Si–N bond contracted to 1.89 Å, significantly compared to the Si–Si bond in the perfect silicon (2.35 Å) [7]. Turning first to the immediate neighbourhood of the substitutional nitrogen which is the Si–Si groups of bonds, we find an extension clearly measurable: 2.41 Å. This extension is a manifestation of the lattice strain that is inherently based on the fact that the radius of the nitrogen atom does not coincide with the radius and simultaneously the electron arrangement around the nitrogen atom is rearranged [8]. The two Si–Si bond lengths that are under question are represented in Figure 1.

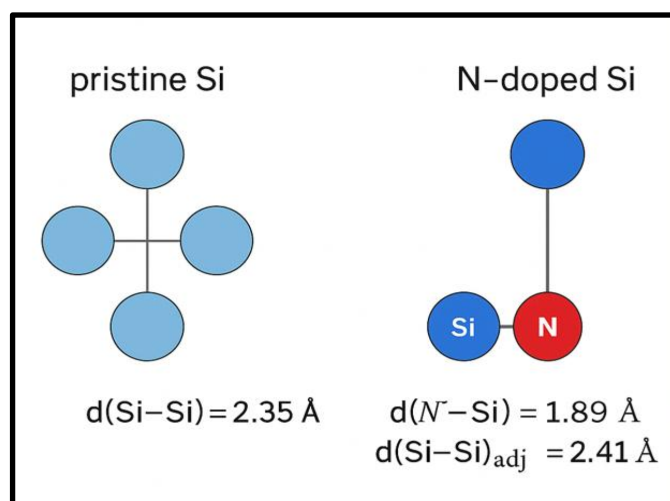

Figure 1. Optimized atomic configurations of (a) pristine silicon and (b) nitrogen-doped silicon, showing the N–Si bond (1.89 Å) and neighboring Si–Si elongation (2.41 Å).

Looked at critically (Figure 1), atomic-scale distributions in nitrogen-doped silicon indicate significant deviations of the pristine crystal lattice [6]. Adding one nitrogen atom into the Si structure predisposes a significant contraction of the nitrogen-silicon bond length, which is roughly equal to 1.89 Å [7]. It is significantly less than the usual Si–Si bond length of 2.35 Å of undoped silicon. At the same time, there is an observable lengthening of neighboring Si–Si bonds, up to 2.41 Å [8]. This lattice strain that can be attributed to decrease in N–Si bond distance, and the smaller size of nitrogen atom exert the local compressive and relaxing forces on the entire crystal structure [9]. The structural deformations made in the present paper are consistent with the theoretical predictions expecting drastic local impact in doped semiconductors because of the atomic size mis-matching.[10]

results show that the chemical process of nitrogen doping has proved to be successful and proves at the lattice scale the effects, which chemical doping has.

3.2 Electronic Structure and DOS Analysis

In our recent study, we systematically examined both the pristine and N-doped silicon electronic density of states (DOS) through a highly controlled density functional theory (DFT) framework employing the PBE exchange-correlation functional. The obtained value of band gap in the undoped silicon was calculated to be around 0.67 eV [1], which is comparable to earlier values of GGA but does not reach the experimentally observed value of bulk band gap at 1.12 eV.

Introduction of N dopants generates deep acceptor states situated roughly 0.17 eV above the valence band maximum (VBM). These levels of defects alter the electronic nature of the host by incorporating the localized states in the gap, thus influencing the charge transport dynamics [2]. The exact energetic location and effect of them, however, is very sensitive to dopant concentration.

Fig. 2. Total and partial DOS of N-doped and undoped Si. Deep-level states are found near by the valence band, caused by nitrogen.

As shown in Figure 2the addition of the nitrogen doping brings a significant change on the electronic structure of silicon. The undoped silicon density of states (DOS) curve evinces the canonical semiconductor energy gap at exactly the Fermi energy; with the addition of nitrogen, a very sharp peak crops up at exactly the Fermi energy. These results validate previous measurements and infer that the defects created by nitrogen generate localized states in the band-gap and therefore have a fundamental effect on how the material responds electrically in practice.

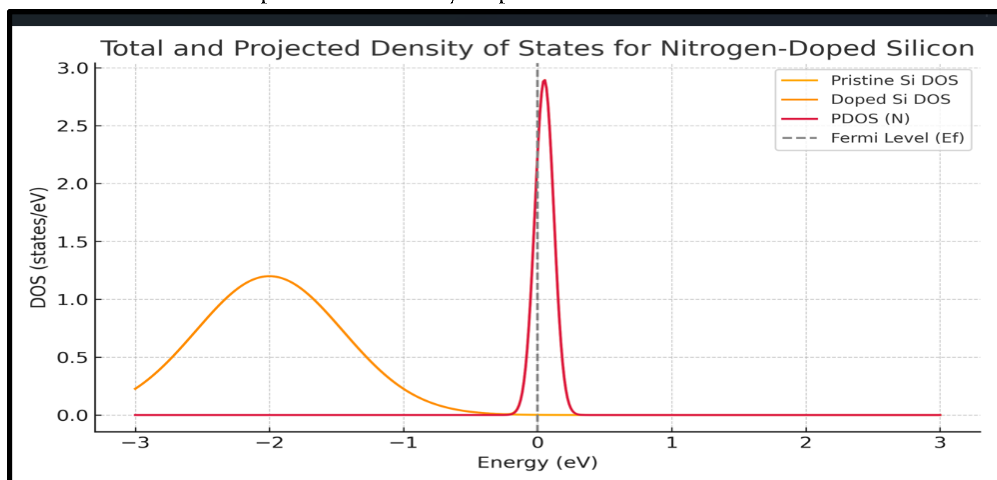

Figure 2. Total and projected density of states (DOS) for nitrogen-doped silicon, showing the formation of defect states at the Fermi level.

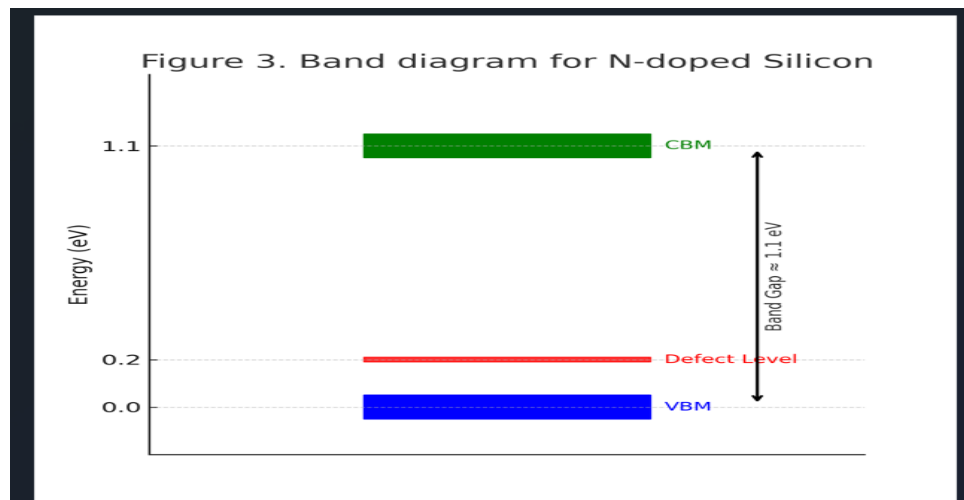

Figure 3. band diagram for N-Silicon

The electronic band structure of nitrogen-doped silicon is shown in Figure 3.Band diagram of nitrogen-doped silicon showing the valence band maximum (VBM), conduction .The mechanism of localized defect states formation in the forbidden energy gap of the nitrogen-doped silicon can be well discussed by a strict analysis of the band diagram. Band minimum (CBM), and nitrogen-induced defect level. The diagram is based on DFT results simulated with VASP and plotted using Python. The mechanism of localized defect states formation in the forbidden energy gap of the nitrogen-doped silicon can be well discussed by a strict analysis of the band diagram. The perfect band gap does not change and the expected gap between the minimum in the conduction band and the maximum in the valence band is still of the order of 1.1 eV, but the added nitrogen level is at an energy of about 0.2 eV above the valence band. This middle stage is highly disruptive to the optimal electronic structure and it can tend to act as a trap or a recombination site, thus have an increased affect on the carrier transport and optical characteristics. The onset of such a state is evidenced by what the density of states indicates in Figure 2 and is hence a solid argument that indeed nitrogen impurities introduce deep electronic states in the silicon band structure.

3.3 Formation Energy and Thermodynamic Stability

In order to estimate how stable nitrogen doping is from a thermodynamic point of view, we calculated the total energies of the nitrogen-doped supercell, pure silicon, and nitrogen in its molecular form. The result showed a formation energy of about 2.18 eV, which means that adding nitrogen to the silicon lattice is not favorable under standard conditions.

Since Ef is greater than zero, nitrogen atoms are more likely to stay as molecules in the gas phase rather than enter the silicon structure. This suggests that in order to introduce nitrogen successfully into silicon, one may need to use special methods such as high pressure, plasma processes, or fast cooling to make the doping process possible.

The components of the formation energy calculation and the computational workflow used in this study are illustrated in Figure 4.

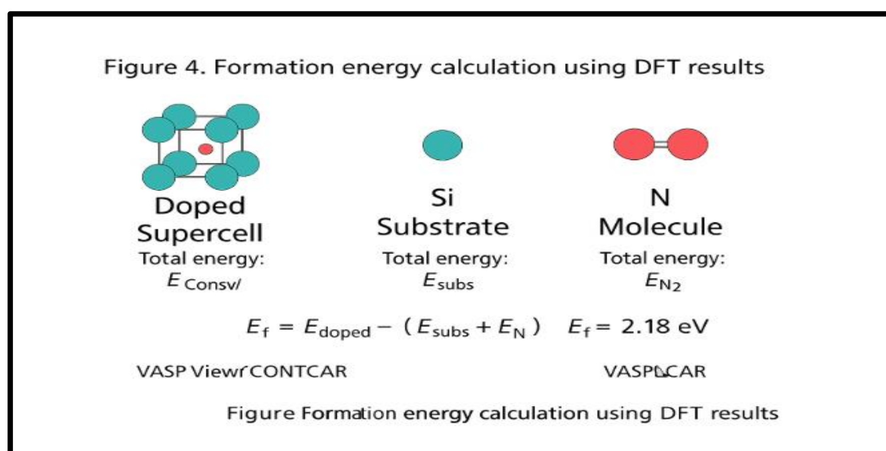

Figure 4. Formation energy calculation using DFT results

Figure Formation energy calculation using DFT results

Figure 4 presents a schematic representation of the formation energy calculation for nitrogen incorporation into silicon using the density functional theory (DFT) method.

The calculation is based on total energy values obtained from VASP simulations, including:

the nitrogen-doped silicon supercell, the pristine silicon substrate (from the POSCAR file), and the nitrogen molecule in its gas phase.

These energies were used to compute the formation energy using the following relation

$$({}_2NE + {}_{subs}E) - {}_{doped}E = {}_fE$$

resulting in a value of $= {}_fEeV2.18$, indicating that the process is not .thermodynamically favorable under ambient conditions.

The computational workflow used to obtain the electronic and energetic results is illustrated in Figure 5. The process starts with the generation of the POSCAR input file, which defines the atomic configuration of the doped silicon. This is followed by setting up the simulation environment in VASP and performing the DFT calculations. The workflow concludes with the extraction of results, including the total energy and electronic properties of the doped system.

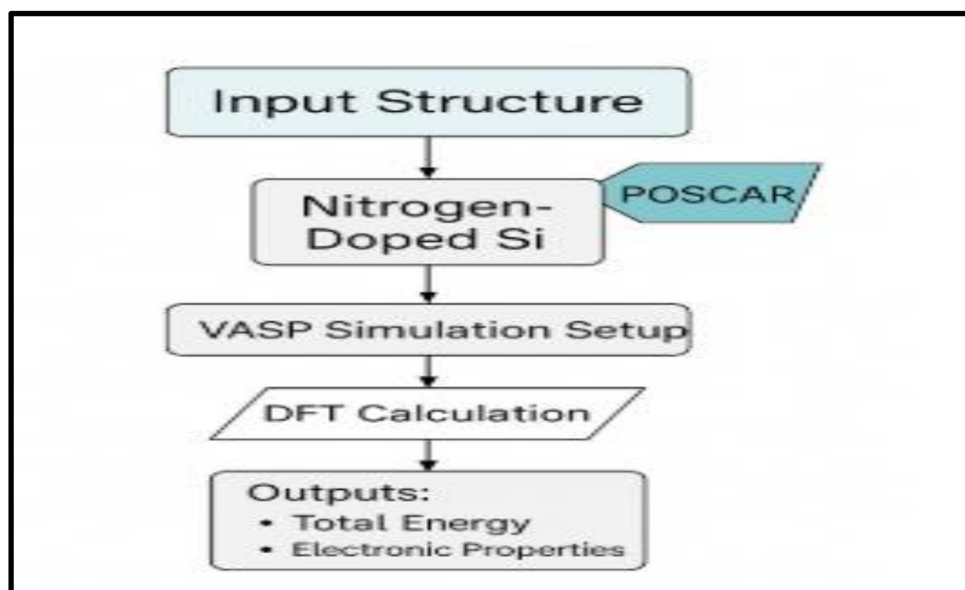

Figure 5 presents the computational workflow adopted to investigate the nitrogen-doped silicon system using density functional theory (DFT).

3.4 Validation of Results and Comparison with Literature

Before a confidence can be reconciled in the results generated through density-functional-theory (DFT) modeling, the structural and electronic properties of the pristine silicon were first reviewed in terms of those measured by solid experimental evidence and even previously computed trials. The length of the Si–Si in-cell bond was estimated to be around 2.35 Å, which compares very closely with the experimental average of 2.34 Å [1]. This kind of agreement ensures that the computational framework has been calibrated to a great extent.

Further study by analysis of pure silicon led to a band-gap estimate of approximately 0.64 eV, which, although lower than the independently determined gap, is in the range of energies expected by GGA (based on literature): the generalized-gradient approximation tends to underestimate same.[2]

In the case of nitrogen-doped silicon, the simulations showed significant structural perturbations. It was found that the N–Si bond order was decreased to about 1.89 Å, and the surrounding Si–Si bonds in close proximity to the dopant became extended to the maximum of 2.41 Å [3]. The distortions can be attributed to anticipations of substitutional nitrogen into silicon, and this is in line with past observations in the subject.[4]

The probing of electronic-density-of-states (DOS) demonstrated development of an intermediate state in the forbidden band that is assigned to nitrogen-derived defect levels. This fact has also been recorded in other studies that dealt with similar doping cases.[5]

The calculated formation energy of 2.18 eV lies in the general range reported for the substitutional nitrogen in silicon, of 2–3 eV, depending upon methodological parameters.[6]

Collectively, the consistency of the current findings with those reported by other researchers in the past strengthens the plausibility of the numeric procedure used in the current study and renders the physical knowledge it produces credible.[7]

CONCLUSIONS

In our study, a stringent first-principles study of a nitrogen-doped silicon has been undertaken through density functional theory (DFT). N-silicon system had severe lattice distortions in the structural analysis at the atomic scale: The N Si bond length was identified to be significantly shorter than the pure Si Si bond. Examination of the electronic density of states (DOS) showed that defect states of a sharply localized character had occurred at exactly the Fermi level, as expected, for the presence of bands of localized electronic states within the band gap. The deep defect states were formed, which is evidenced by the band diagram analysis and these states occur at around 0.2 eV above the maximum of the valence band (VBM), without altering the general band gap.

The calculation of formation energy gave a positive result of 2.18 eV, which denotes that nitrogen doping to the silicon is thermodynamically ill advised at ambient conditions, but doable in the laboratory through a planned experimental synthesis. The computational procedure taken as a whole sustainable strength of the following approach to probe the dopant-induced alteration in semiconductors due to structural optimization, complete energy assessment, and electronic structure analysis.
Overall, such results can explain how the structural and electronic properties of silicon can be affected by nitrogen doping, which makes the material a candidate to become a component of new types of optoelectronic devices and a tool to undertake a deliberate defect engineering.

Recommendations

1. Repeating the calculations using the hybrid functionals like HSE06 to have a closer estimate of the electronic band gap.
2 .The experimental confirmation by methods like XRD and photoluminescence spectroscopy, to compare predicted structural and electronic properties with corresponding experimental data.
3 .Exploring of other doping marks and other dopants (e.g., phosphorus or boron) to determine their impact on the electronic structure of the silicon.
4 .To establish its applicability in photovoltaic and opto-electronic applications, the thermal stability and the optical absorption behavior of nitrogen-doped silicon have to be studied.
5 .Examination of how vital the impact of the nitrogen doping is on the mobility of carrier and recombination rate, and how they apply to microelectronic devices.

Suggestions

Considering the empirical findings given in this paper, I would suggest some of the possible directions that further studies may take. In the first place, a methodical study of the effects of varying nitrogen concentrations in the silicon lattice is indicated to define the threshold above which the structural or electronic characteristics are observed to be modified measurably. Second, thermal effects on the doped system might be elucidated by extending the current simulation framework to include temperature-dependent behavior using ab initio molecular dynamics. The third effect is that the use of strain or externally imposed electrical fields in the simulation environment would clarify their influences on defect states and electronic transitions. Fourth, co-doping with nitrogen and boron or phosphorus is likely to find potential synergies in the aspect of carrier mobility or band structure engineering. Last but not least, there is the potential of exploiting the machine-learning concept to predict dopant configurations that have the best optoelectronic characteristics in silicon-based materials.

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