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A density functional theory study of the C_iN and the C_iNO_i complexes in silicon

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Abstract

Nitrogen (N) is an important impurity in silicon (Si), which associates with impurities as well as with other defects to form defect complexes. The knowledge of the properties and behavior of defects structures containing carbon (C), N and oxygen (O) are important for the Si–based electronic technology. Here we employ density functional theory (DFT) calculations to investigate the association of nitrogen with carbon and oxygen defects to form the C_iN and C_iNO_i defects. We provide evidence of the formation of these defects and additionally details of their structure, their density of states (DOS) and Bader charges. Therefore, C_iN and C_iNO_i defects are now well characterized.

Introduction

Si is the mainstream material for the electronic and microelectronic industry. One way to improve the quality of Si and control its properties is through the introduction of various impurities in the crystal lattice. O is the main impurity in Si and it is unintentionally incorporated in the lattice from the silica crucible during the Czochralski method crystal growth. During processing at elevated temperatures, diffusing O atoms begin to aggregate and form oxide precipitates.[1,2] These defects act as intrinsic gettering sites for metallic contaminants which have detrimental role to Si quality. Thus, the presence of precipitates enhances[3] the device yields. On the other hand, O precipitates and extended defects (dislocations and stacking faults) act as recombination centers affecting the lifetime of charge carriers leading to the reduction of the efficiency of solar cells.[4,5] Thus, the presence of precipitates is not desirable for the case of photovoltaic as it increases recombination of carriers. Additionally, oxide precipitates can influence[6-8] the mechanical properties of Si wafers.

C is the second major impurity in Si, also unintentionally added in the lattice during crystal growth.[9] Importantly, C affects the formation of oxide precipitates. The C behavior on the precipitation process depends on its concentration, the attained precipitate size in the course of the thermal treatment and the temperature of the treatment.[10-12] Obviously, since C affects the O precipitation process it can also affect the mechanical properties of Si wafers.[13,14] Notably, C reacts with O leading to the formation[15,16] of a number of C-O related complexes which can introduce electrical levels in the gap, affecting the electrical properties of the material.

N is another main impurity in Si.[17] Three are the crucial properties of N that play a significant role for the fabrication of Si- based electronic devices. Firstly, N enhances[1,2,18] oxygen precipitation thus improving the gettering ability of Cz-Si. Secondly, N increases[19,20] the mechanical strength of the material by pinning dislocations. Notably, the mechanical properties of Cz-Si wafers dictate fundamental limits on the fabrication of devices. Thirdly, N impends[16,21] the formation of voids, which are undesirable in the surface of Si wafers where microelectronic devices are fabricated[13], by decreasing the concentration of vacancies.

It is important therefore to find ways for improving the manufacturing yield, device performance and the reliability of Si for certain applications. A promising strategy to improve the quality of the material is the so-called "impurity engineering" technique which is based on the introduction of harmless impurities in the crystal lattice.[16,22] It has been found that intentional doping of Cz-Si with suitable concentrations of N and C could improve the internal gettering ability of the material, could eliminate void defects by high temperature anneals, and enhance its mechanical strength.[16,23] Thus, impurities as N and C which are electrically neutral are deliberately doped in Cz-Si, for certain applications. These impurities tend to interact with defects present in the crystal and form various complexes. In this way, they change the dynamic and the evolution of defects and finally influence the mechanical, electrical and optical properties of the material. It has been found that defect interaction linked with C in the course of O precipitation process are significantly affected[24] by the co-existence of N. Furthermore, it has been found that the diffusion of N in ion-implanted samples is affected[25] by the presence of C and O due to the formation of slowly diffusing N-related complexes. It has also been reported that the combination of N and C could be used to reduce the size of microdefects in Cz-Si and control their growth.[26] The addition of C in N-implanted Si has led to the suppression of the intensities of absorption bands in the frequency range of 750-950 cm^{-1}, indicating interactions between the defects.[27,28]In particular, C suppresses the formation of N-O complexes.[29]

Evidently, interactions between impurities or/and between impurities and defects are very important issues related with material processing. In general, they lead to the formation of complexes which introduce levels in the gap. These stimulate investigations to study the properties and behavior of them. In our case it is worth stated that little amount of research has been done on defects in Si crystals containing O, C, and N.

In this work we mainly focus on the C_iN and C_iNO_i complexes in Si. Regarding N-C pairs, Dormen *et al.*[30-35] have systematically studied these defects using Photoluminescence (PL) spectroscopy. They have reported five PL no-phonon transitions in the spectra of C and N implanted Si. These are: N_1= 745.6 meV, N_2= 758.0 meV,N_3= 761.5 meV, N_4= 757.4 meV and N_5= 772,4 meV, each one with different formation temperatures.[32] The close proximity of the lines positions in the spectra

is a strong indication of having similar electronic levels in the forbidden gap and a similar electronic structure of the corresponding defects.[32,33] All five N lines incorporate C and N in their structure. In addition, N_3, N_4 and N_5 configurations may incorporate O atoms which are loosely bound to the N_1 defect.[31] N_1 is the primary and more stable defect of the group. In the course of the implantation process single C atoms are expected to form as well as vacancies and self-interstitials.[32] The self-interstitials promptly interact with C substitutional C_s atoms ejected them at interstitial sites, C_i. These C_i species are very mobile at room temperatures and can be trapped by N atoms to form[32] the N_1 center.

Based on PL studies performed under uniaxial stress and from the Zeeman splitting and the angular dependence of the energy shift of the N_1 line, a model was developed for its N-C structure.[30,33-35] According to this model, the N-C defect involves a N atom distorted out of the substitutional site along [111] in an almost planar Si_3N configuration and a C_i atom, which is inserted into the N-Si bond along the [111] axis, popped out from the bond-centered position in one of the three equivalent (100) planes.[32,33,35]

Regarding the C-N-O complexes the reported experimental results are poor and mainly complement the picture of the C-N pair research. Their existence is gathered in the course of research to investigate and understand the spectra in N and C - implanted Cz-Si.[29,33,34] The study and the analysis of the results indicates the presence of O in the N_3, N_4 and N_5 structures[33] as it was mentioned above. Importantly, two infrared absorption lines labeled as NX_1 and NX_2 have been reported.[36] The lines were considered as local modes of aggregates of C and N or of C, N and O impurities. A signal at 588 cm^{-1} named as X line of the CO complex lead the suggestion that the NX_1 and NX_2 bands in the spectra may be due to a CO complex which is disturbed by an N atom located in the vicinity. It remains to be verified. In the present study we employed DFT calculations to investigate the structure and electronic properties of C_iN and C_iNO_i defects in Si.

2. Methodology

Calculations were performed using the plane wave DFT simulation code VASP (Vienna Ab initio Simulation Package).[37] Simulation cell consisted of 250 Si atoms. A plane-wave basis set with a cut-off energy of 500 eV and a 2×2×2 Monkhorst-Pack[38] k-point mesh were used to relax the structures with the aid of a conjugate gradient algorithm.[39] The force tolerence was set to 0.001 eV/Å. Bader charge anylysis[40] was carried out to calculate the charges on the defects and their nearest neighbour Si atoms. We have used numerous calculations (about 1000 calculations for each defect cluster set up by the DIMS tool[41]) until the lowest energy configuration was attained. This method has been used in recent studies of related systems.[42,43]

3. Results and discussion

The relaxed structure of C_iN defect shows that N forms a distorted trigonal planar configuration with nearest neighbour Si atoms (see Figure 1a) as confirmed by the Si-N-Si bond angles (see Table 1). The shorter Si-N bond distances as compared to Si-Si bond distance (2.37 Å) in pristine Si bulk is due to the higher electronegativity of N (3.04) than that of Si (1.90) (see Table 1).[44] This is further confirmed by the high negative Bader charge (−3.21) accumalated on the N leaving the nearest neighbour Si atoms positive (see Figure 1b). One of the Si in the NSi_3 unit exhibits a high positive Bader charge of +2.25. This is due to the highly electronegative carbon (2.55)[44] atom directly attached to that Si. The interstitial C is tetrahedrally coordinated with four nearest neighbour Si atoms. The tetrdhedral unit is not symmetrical as evidenced by the unequal Si-C-Si bond angles (see Table 1). The electronegativity difference between the C and Si is again reflected in the shorter Si-C bond distances. The negative Bader charges on the both N and C are further supported by the charge density plot of the defective structure (see Figure 1c).

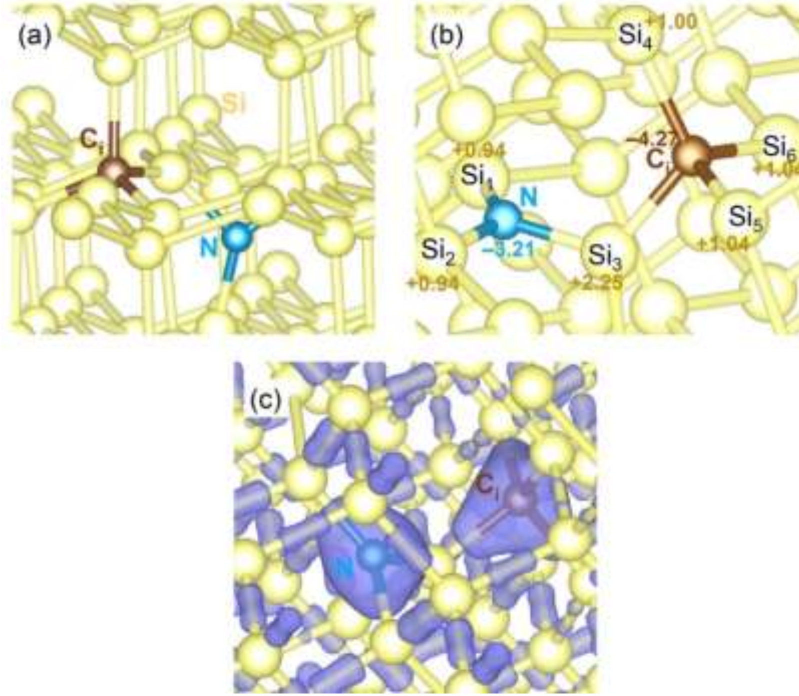

Figure 1. (a)Relaxed structure of an interstitial C (Ci) in the presence of N-doped Si, (b) Bader charges on the impurity atoms (C and N) and their nearest neighbour Si atoms and (c) charge density plot showing the electron distribution around the impurity atoms.

Table 1. Selected bond distances and bond angles in the relaxed configuration of C_iN defect of Silicon.

Bond type	Bond distance (Å)	Angle type	Bond angle (°)
Si_3-C	1.92	Si_3-C-Si_4	114.4
Si_4-C	2.02	Si_3-C-Si_6	93.3
Si_5-C	2.00	Si_4-C-Si_5	111.9
Si_6-C	1.98	Si_4-C-Si_6	112.0
Si_1-N	1.79	Si_5-C-Si_6	114.0
Si_2-N	1.80	Si_1-N-Si_2	136.5
Si_3-N	1.74	Si_1-N-Si_3	121.6
		Si_2-N-Si_3	101.3
		C-Si_3-N	116.6

The introduction of a C_iN defect in Si reduces the band gap slightly (see Figures 2a & 2b). Additional peaks appear near the Fermi energy level and belong to the *p* states of C and N (see Figures 2c & 2d). The band decomposed charge density plot generated for the states near the Fermi level confirms this (see Figure 2e).

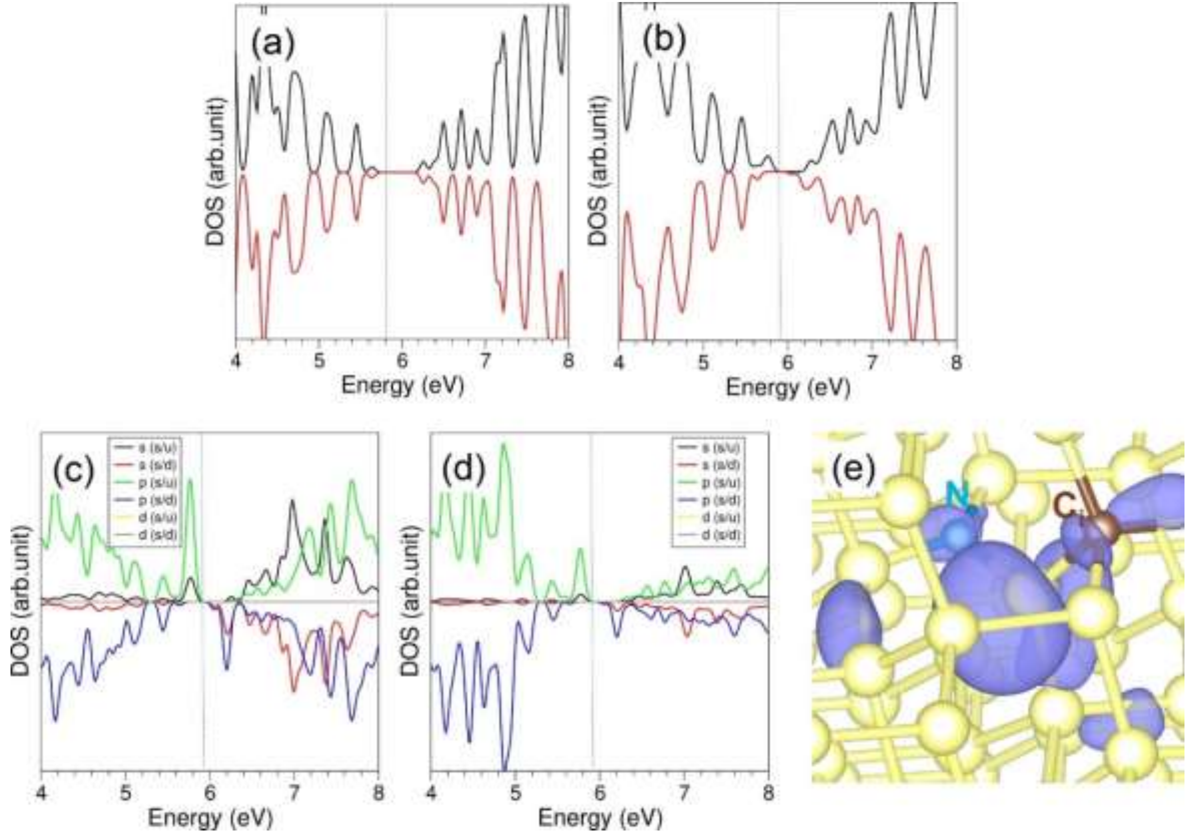

Figure 2. Total DOS plots of (a) bulk Si and (b) Si supercell consisting of Ci and N, atomic DOS plots of (c) C and (d) N and (e) band-decomposed charge density associated with the states near the Fermi energy level.

Next we considered the incorporation of a single oxygen atom in the pre-existing C_iN defect in Si. The relaxed structure is shown in Figure 3a. The trigonal planar and tetrahedral coordination are not altered for N and C respectively, although small changes in the bond distances, bond angles and Bader charges are noted (see Figure 3b and Table 2). While the Bader charge on the C is almost unaffected, there is a small increase in the Bader charge on a Si (Si_2) in the trigonal planar unit. This is because of the higher electronegative (3.44)[44] interstitial oxygen forming a bond with Si_2. The Si-O bond distances are shorter than the Si-N bond distances reselected by the higher electronegativity of O than that of N. The Bader charge on the O is –2.09 again due to its higher electronegativity. The interstitial oxygen forms a non-linear configuration. This is partly due to the two lone pairs on the O repulsing

each other heavily. Charge density plots confirm the presence of negative Bader charges on the C, N and O.

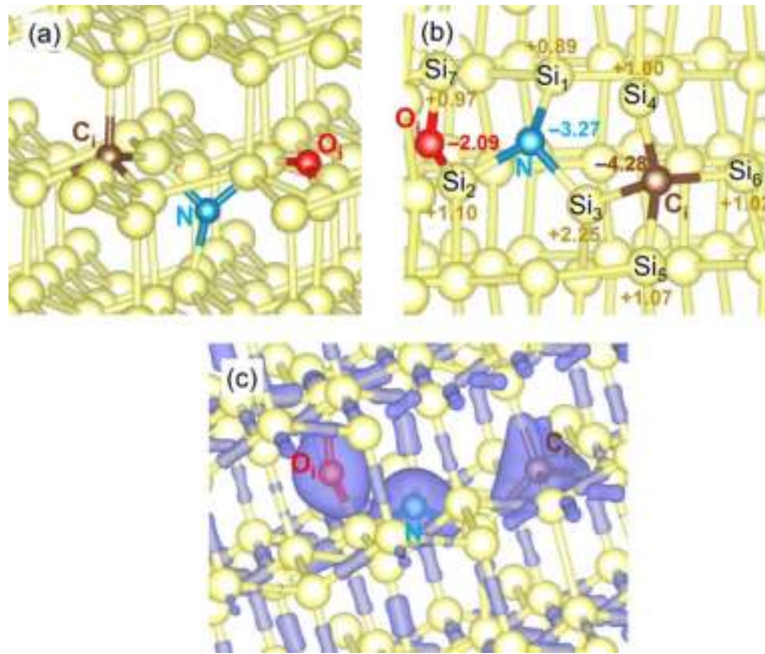

Figure 3. (a)Relaxed structure of C_iNO_i defect (b) Bader charges on the impurity atoms (C, N and O) and their nearest neighbour Si atoms and (c) charge density plot showing the electron distribution around the impurity atoms.

Table 2. Selected bond distances and bond angles in the relaxed configuration of C_iNO_i defect of Silicon.

Bond type	Bond distance (Å)	Angle type	Bond angle (°)
Si_3-C	1.91	Si_3-C-Si_4	115.7
Si_4-C	2.03	Si_3-C-Si_5	92.4
Si_5-C	2.00	Si_4-C-Si_5	112.6
Si_6-C	1.99	Si_4-C-Si_6	112.0
Si_1-N	1.79	Si_5-C-Si_6	113.7
Si_2-N	1.78	Si_1-N-Si_2	140.1
Si_3-N	1.75	Si_1-N-Si_3	121.9
Si_2-O	1.63	Si_2-N-Si_3	95.7
Si_3-O	1.65	C-Si_3-N	117.6
		Si_2-O-Si_7	141.3

The strong interaction of defects with Si is evidenced by the appearance of *p* states of C, N and O near the Fermi level (see Figures 4 a-d). The

band gap is slightly reduced by the defects. The band decomposed charge density plot generated for the states near the Fermi energy confirms the presence of the p states of all three defects (see Figure 4e).

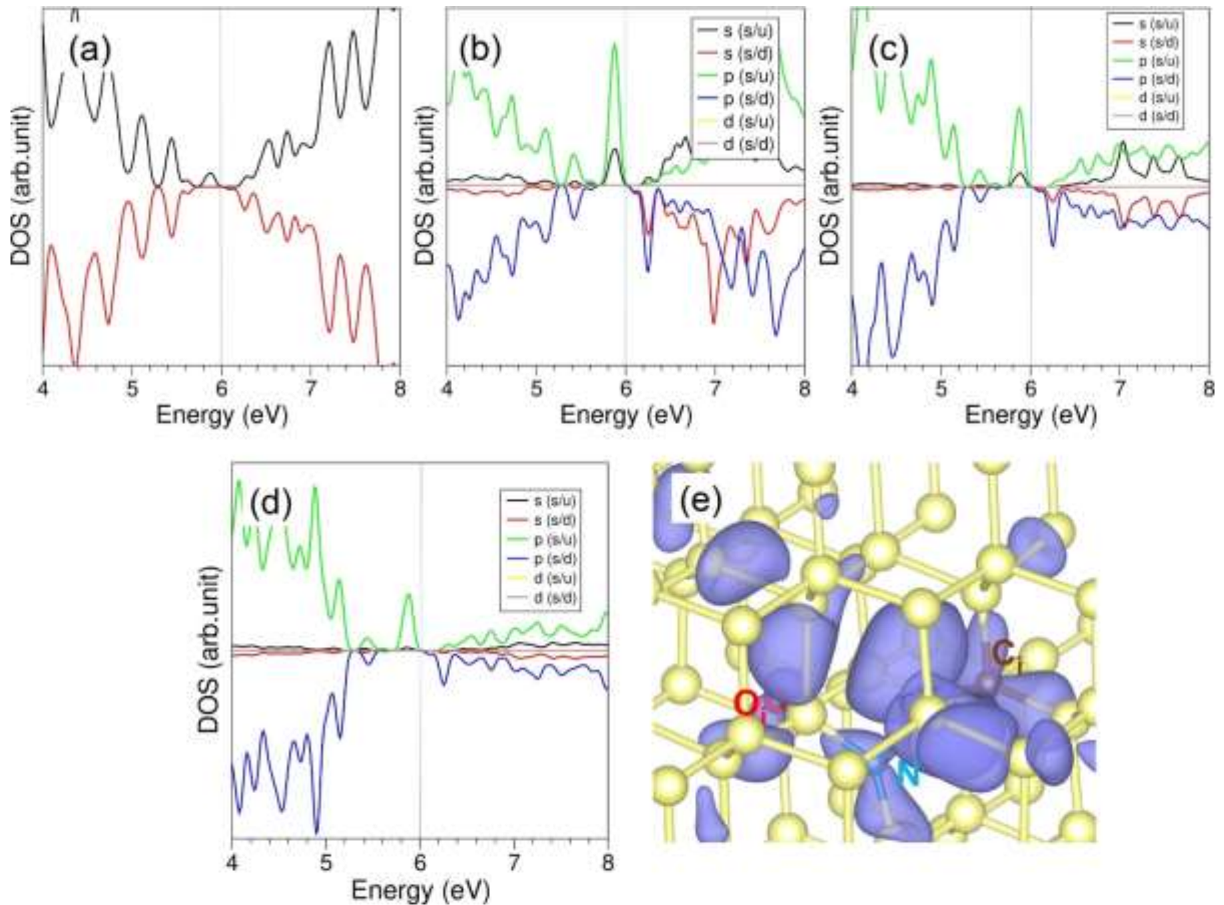

Figure 4. Total DOS plots of (a) Si supercell consisting of C_i, O_i and N, atomic DOS plots of (b) C (c) N and (d)) O and band-decomposed charge density associated with the states near the Fermi energy level.

The present study is consistent with previous experimental work[30-35] supporting the formation of C_iN and C_iNO_i defects. Although we focused on the structure and electronic properties of these defects, future work should also consider the kinetics that are necessary to form C_iN and C_iNO_i. Kinetics would be important to form considerable concentrations of these defects. These concentrations will in turn be dependent upon the initial concentration of carbon, oxygen and nitrogen and will be influenced by non-equilibrium conditions (i.e. irradiation or implantation).[45,46] We have to note that kinetic studies may benefit from the cBΩ thermodynamical model[47,48] that has been recently applied to Si

and related materials.[49-51] The present study is a paradigm that can be used in conjunction with previous studies to study related defects and cluster formation in semiconducting systems.[52-55]

4. Conclusions

The increased potential of N to influence the quality of Si wafers surfaced the issue to investigate the properties N and C and of N, C and O defects in Si. In the present contribution we employed DFT calculations to investigate the structural and electronic properties of C_iN and C_iNO_i. The present results can be employed as a basis for future experimental studies on these and possibly more extended related clusters that might exist. Another fruitful pathway for future investigation will be the study of kinetics in these systems.

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