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Density functional theory study of the $V_mN_2O_n$ (m,n = 1, 2) complexes in silicon

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Abstract

Nitrogen is an important impurity in Czochralski grown silicon (Cz-Si) as it enhances oxygen precipitation, through the formation of vacancy-nitrogen-oxygen clusters and in particular the $V_mN_2O_n$ complexes. Here we employ density functional theory to predict the structure of $V_mN_2O_n$ (m, n=1, 2). We report that the lowest energy $V_mN_2O_n$ (m, n=1, 2) defects are very strongly bound. These results are consistent, and support previously reported theoretical and experimental conclusions that $V_mN_2O_n$ structures could form.

1. Introduction

Si has been the semiconductor of choice for the microelectronic industry for over 70 years. The materials properties and in particular the conductivity of Si are dramatically affected by the presence of impurities and defects. These can be intentionally (for example via implantation) or unintentionally introduced in the Si lattice during crystal growth (for example oxygen and carbon in Cz-Si) and processing. Nitrogen (N) in its gaseous form is used as an inert atmosphere during thermal processing and this in turn results in its incorporation in the Si lattice.[1-4]

The presence of N in Si impacts its properties and behavior. Firstly, N interacts with intrinsic defects (i.e. vacancies (V) and self-interstitials (Si_I)), and with impurities such as C and O.[5-8] These in turn affect the reactions taking place during crystal growth and material processing (i.e. thermal treatments and N implantation).[5-8] During crystal growth N reacts with vacancies[5-8] forming complexes such as VN_2 and V_2N_2 leading to the suppression of the formation of voids. The control of voids is important since their presence can cause the failure of gate oxide integrity (GOI) of metal-oxide- semiconductors (MOS) devices[9]. It also reacts with (Si_I)s leading to the formation of $N_2(Si_I)$ clusters.[10] In essence, the presence of N and its reactions with intrinsic defects leads to the reduction of point defect aggregates during microelectronic device treatments.[11] The formation of these aggregates have generally negative effects in device performance. N also reacts with C and a number of photoluminescence lines related with N-C pairs have been reported[12] in nitrogen implanted Si. Furthermore, N reacts very efficiently with O forming nitrogen-oxygen complexes.[13-17]

Secondly, N in Si affects oxygen aggregation process. During crystal growth, oxygen precipitates are formed as a result of thermal processes and N enhances their formation[18-23]. Since these precipitates act as intrinsic gettering centers for deleterious metal contaminants, their increase contributes in the device yield enhancing its quality and credibility. Importantly, N increases the density and size of oxygen precipitates and the concentration of N in the samples determines the nucleation temperature of grown-in oxygen precipitates.[24] These precipitates are hard to annihilate during rapid thermal annealing which is used in the course of device processing, and therefore their presence improves the internal gettering ability of the Si wafers.[23,25,26] These findings have led the community to investigate and understand the reactions processes that nitrogen participates, the complexes that form during the thermal treatments and the mechanisms that enhance the oxygen precipitation process. Complexes containing N, V and O impurities, have been proposed to explain the enhancing effect of N to the formation of O precipitates[26,27]. It is therefore important to investigate the defect processes that lead to the formation of these complexes.

As we mentioned above, N in the form of N_2 reacts with vacancies to VN_2 and V_2N_2 defects. The latter is very stable[6]. N_2V_2 can exist at the temperatures of void formation[5,6] around 1050°C. There are two reaction paths that N_2V_2 is formed[28,29]

$$N_2 + V \rightarrow VN_2,\ VN_2 + V \rightarrow N_2V_2 \ (1)$$

$$N_2 + V_2 \rightarrow N_2V_2 \ (2)$$

Notably, it has been found that attaching more than two vacancies to the N pair is energetically unfavorable.[26,27] Thus N_2V_2 center does not act as a trapping site for vacancies. In contrast to the vacancies, N_2V_2 strongly capture O atoms leading to the formation, in the first place, to the N_2V_2O complex.[30,31] In a second stage more O atoms could be attached in the initial N_2V_2 leading to larger structures[30,32]. Additionally, theoretical calculations have shown the ability of N_2V_2 to act preferentially[28] as nucleation site for oxygen precipitation resulting in grown-in nuclei. In other words, the initially formed N_2V_2 centers capture O atoms to act as heterogeneous nuclei [13,26] for oxygen precipitates at higher temperatures. Theoretical calculations have reach to the conclusion that such stable $N_2V_2O_n$ complexes would act as nucleation sites for oxygen precipitates.[30,33] Afterwards, these complexes enhance the nucleation of oxygen precipitates by increasing the nuclei density.[34]

Given the crucial role of oxygen precipitates in Si wafer technology and the experimental and theoretical findings about the role of (N-V-O) complexes in the enhancing formation of oxygen precipitates it easily understood the importance of N-doped Si wafers for integrated circuits industry.

In the present study, we have employed comprehensive density functional theory (DFT) calculations to investigate the structure and energetics of the $V_mN_2O_n$ (m, n=1, 2) complexes.

2. Methodology

2.1. DFT Calculations

The plane wave DFT code Cambridge Serial Total Energy Package (CASTEP) was used for all the calculations.[35] The exchange and correlation interactions were considered using the corrected density functional of Perdew, Burke, and Ernzerhof (PBE),[36] in the framework of the generalized gradient approximation (GGA) and with ultrasoft pseudopotentials.[37] The supercell contained 250 atomic sites (5 × 5 × 5 supercell) and all the calculations were performed under constant pressure conditions. The plane wave basis set cut-off was set at 350 eV in conjunction with and a 2 × 2 × 2 Monkhorst-Pack (MP)[38] k-point grid. About 1000 calculations were performed for each defect cluster until the lowest energy configuration was reached. To set the calculations the DIMS tool was employed.[39] The efficacy of the present methodological approach has been demonstrated in recent studies of related systems.[40,41]

2.2. Binding Energies

As a criterion for stability between all the possible configurations we computed we considered the minimization of binding energies (i.e. the more negative binding energy corresponds to the more stable configuration). The binding energies are a measure of the energy gain for the point defects to cluster as opposed to their isolated state. As an example, the binding energy to form a VN_2O defect in Si is:

$$E_b[VN_2OSi_{M-3})] = E[VN_2OSi_{M-3})] - E[VSi_{M-1}] - 2E[NSi_{M-1}] - E[OSi_M] + 3E[Si_M] \qquad (3)$$

where $E[VN_2OSi_{M-3})]$ is the energy of an M lattice site supercell that contains a vacant site, two nitrogen substitutional atoms, and an oxygen interstitial atom; $E[VSi_{M-1}]$ is the energy of an M lattice site supercell that contains M-1 Si atoms; $E[NSi_{M-1}]$ is the energy of a supercell containing a N substitutional atom and M-1 Si atoms; $E[OSi_M]$ is the energy of a supercell containing an oxygen interstitial atom and M Si atoms; $E[Si_M]$ is the energy of the M Si atom supercell. The information that can be derived from the binding energy is whether a defect cluster is energetically prevalent with respect to its constituent point defect components being at isolated sites.

3. Results and discussion

Extensive DFT calculations were employed to calculate the lowest energy $V_mN_2O_n$ (m, n=1, 2) complexes. To explore all possible geometries thew constituent defects were placed in all the available sites in the supercell (around 4000 calculations).

Considering first the simplest complex of the family VN_2O it is in essence a VO (or A-centre) that attracts N atoms. It has been experimentally and theoretically determined that the A-centre is highly bound (around -1.5 eV).[42,43] Having formed the VO the next step was to add the two N substitutionals to the crystal to form the VN_2O defect (refer to Figure 1). The binding energy of this defect is -6.79 eV so it is highly bound. This high binding energy is due to the association of the V to the oxygen interstitial but also to the N substitutional. The oxygen interstitial resides 1.70 Å away from the nearest Si atoms (i.e. Si_1 and Si_2 in Figure 1) and the angle of Si_1-O_i-Si_2 is 137.51° (refer to Figure 1).

When a second vacancy is added to form the V_2N_2O defect (refer to Figure 2) the binding energy is even more significant (-8.15 eV). As it can be observed from Figure 2 the second vacancy resides in a nearest neighbour site with respect to the first vacancy effectively forming a divacancy with the defect complex. The significant binding energy gain by this configuration is to be expected as the divacancy reduces the number of dangling bonds by 2 (two isolated vacancies in the diamond lattice result to 8 dangling bonds, whereas in a divacancy there are 6 dangling bonds) and dangling bonds in the lattice cost energy.[44] The oxygen interstitial resides further away from the nearest Si atoms (i.e. d_1 = 1.94 Å and d_2 = 1.90 Å in Figure 2) as compared to the equivalent structure in the VN_2O defect and the angle of Si_3-O_i-Si_4 is now lower (118.35°).

Thereafter, we formed the VN_2O_2 defect by adding an oxygen interstitial to VN_2O (refer to Figure 3). This defect has a binding energy of -7.82 eV so it is more bound than VN_2O by more than -1 eV. Part of this defect resembles the VO_2 defect which is an important defect in Si.[43,45]

Considering the silicon-oxygen distances and angles these are more similar to the VN_2O defect. In particular, d_1 = 1.66 Å, d_2 = 1.68 Å, d_3 = 1.63 Å, d_4 = 1.66 Å, Si_1-O_{i1}-Si_2 is 138.06° and Si_1-O_{i2}-Si_3 is 141.78° (refer to Figure 3).

Finally, we considered the $V_2N_2O_2$ defect which has a binding energy of -9.35 eV (refer to Figure 4). Now the distances and angles are: d_1 = 1.69 Å, d_2 = 1.67 Å, d_3 = 1.63 Å, d_4 = 1.66 Å, Si_3-O_{i1}-Si_4 is 136.02° and Si_3-O_{i2}-Si_5 is 144.33° (refer to Figure 4). Observing Figures 1-4 the common theme is the N atoms reside at very similar positions, whereas the V resides close to the oxygen interstitial effectively forming an A-centre configuration. When there are two vacancies these form a divacancy configuration to reduce the dangling bonds.

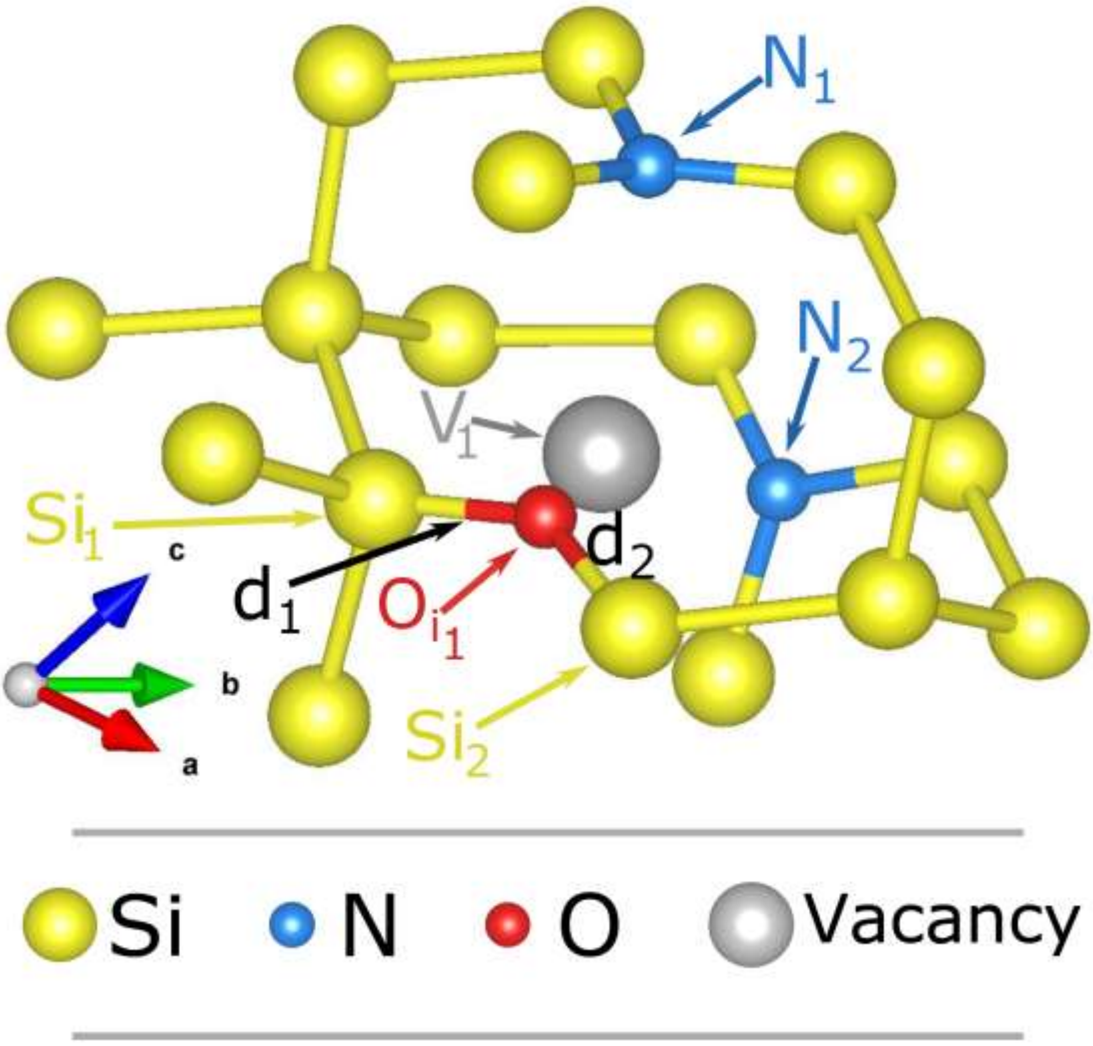

Figure 1. Schematic representation of the energetically favourable VN_2O defect.

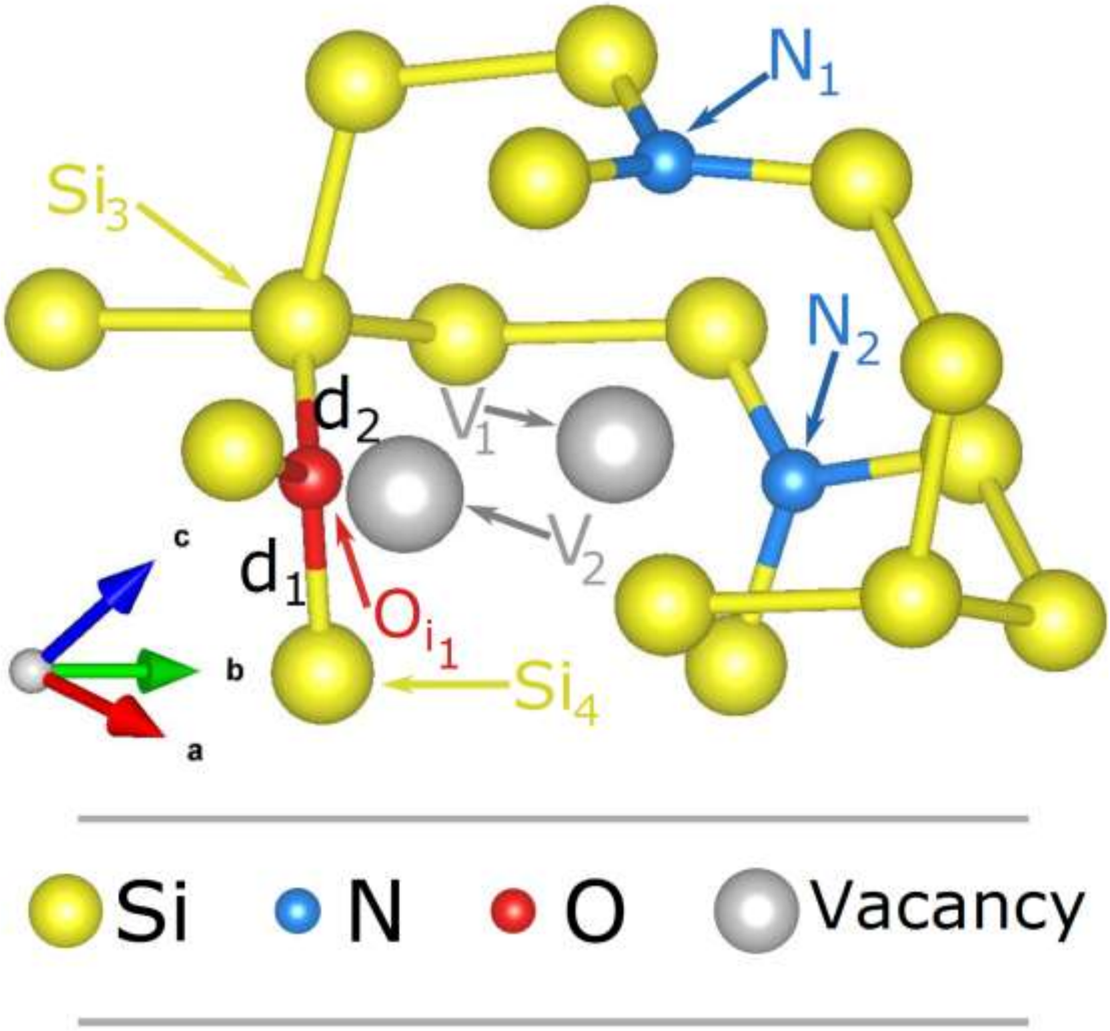

Figure 2. Schematic representation of the energetically favourable V_2N_2O defect.

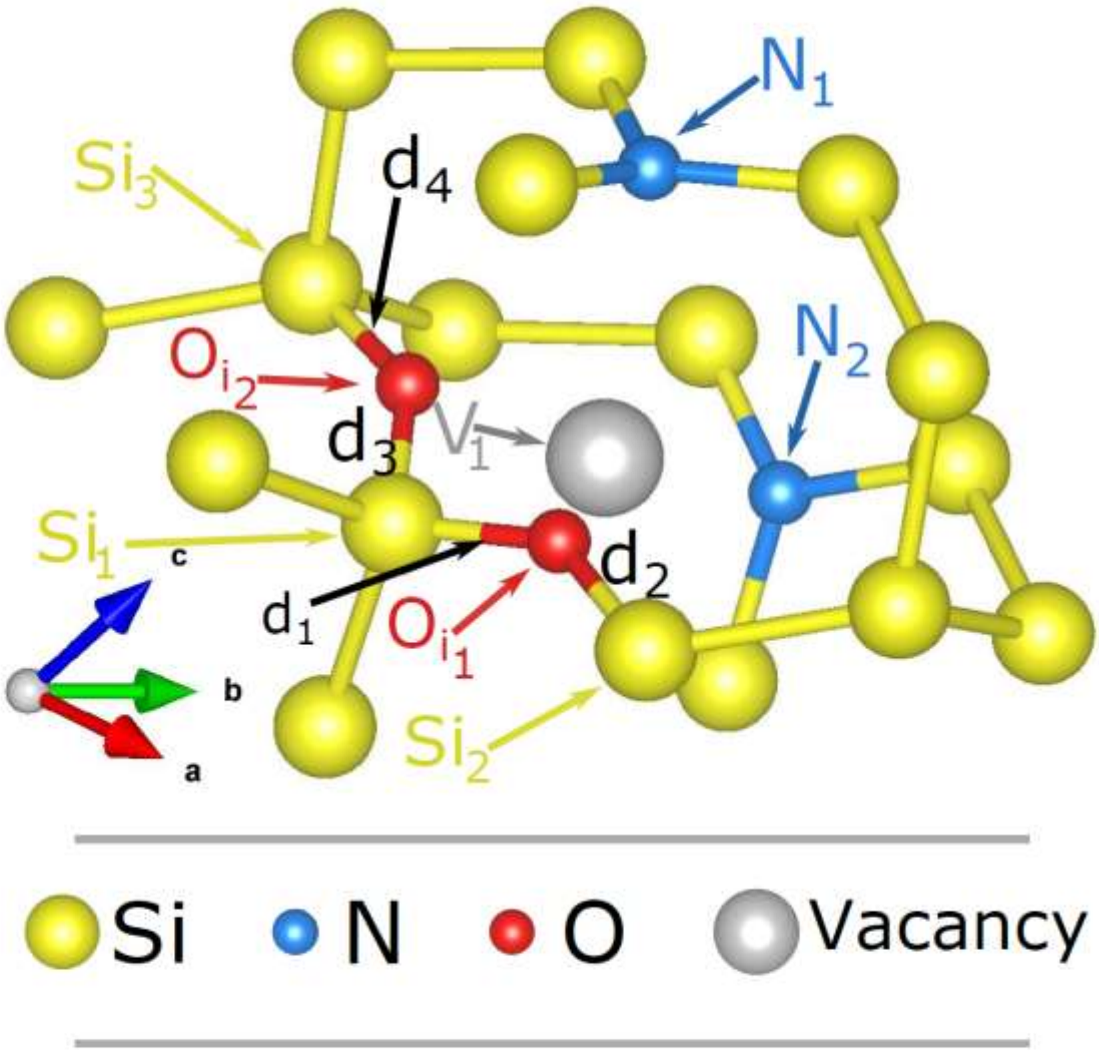

Figure 3. Schematic representation of the energetically favourable VN_2O_2 defect.

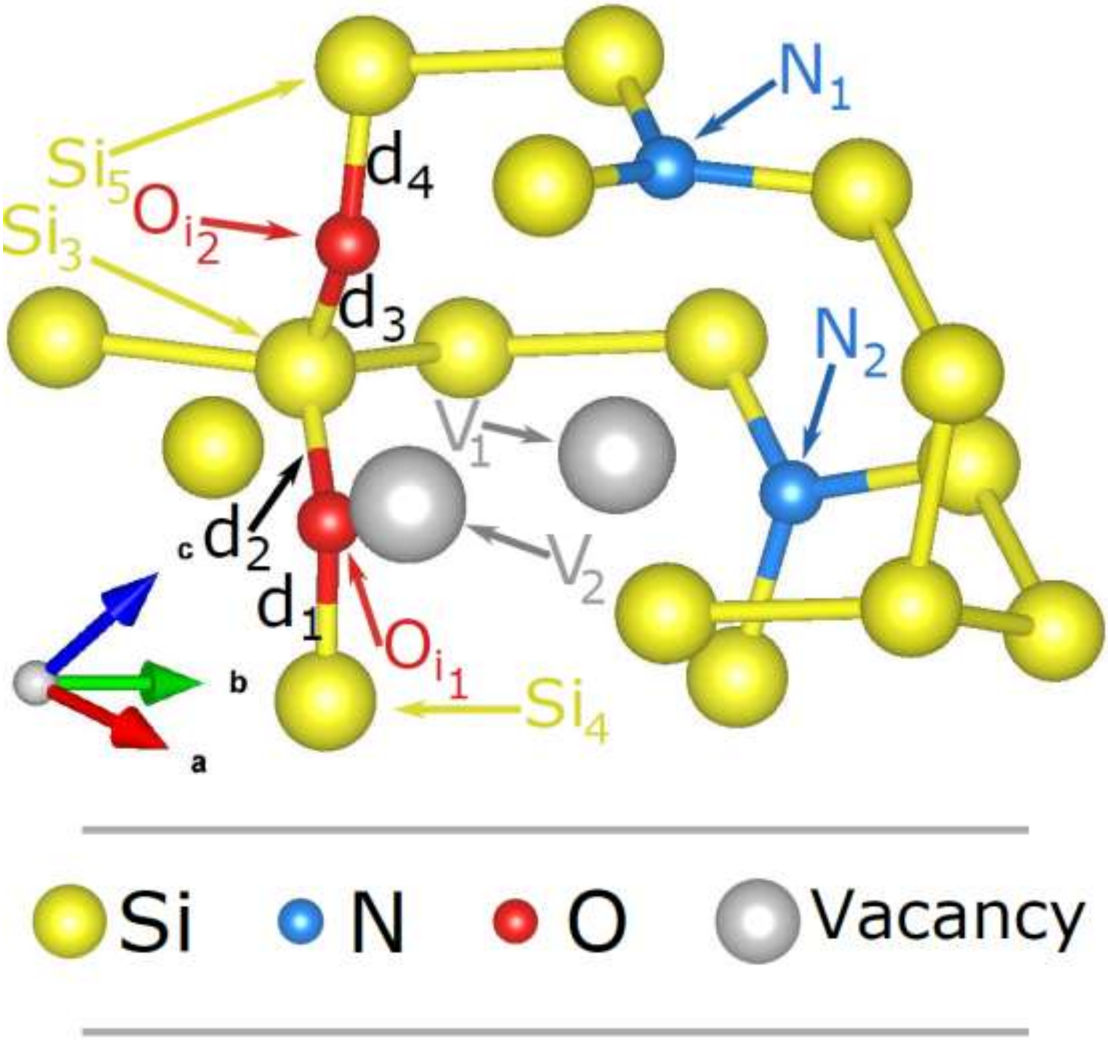

Figure 4. Schematic representation of the energetically favourable $V_2N_2O_2$ defect.

In Cz-Si there are two competing aggregation processes: (a) the formation of voids (i.e. accumulation of vacancies) and (b) the formation of oxygen precipitates. The formation of oxygen precipitates is enhanced by N doping and it has been determined experimentally that N is present in oxygen precipitates.[24] Nitrogen-vacancy complexes have been proposed to capture numerous oxygen atoms.[24,30,46] In particular, previous DFT (employing local density functionals) calculations by Kageshima *et al.*[30] confirm the formation of the V_2N_2O complex in Si. A route to the formation of the V_2N_2O is via the capture of the oxygen interstitial atom by a V_2N_2 complex. The latter is stable at over 1000 °C.[30] It is proposed that these defects can act as heterogeneous nucleation sites at 1000 °C that could in turn lead to extended precipitates (diagonal of up to 50 nm) during the crystal cooling process.[26,30,46]

The overall picture is that the $V_mN_2O_n$ (m, n = 1, 2) complexes will form and will be strongly bound. This is supporting the experimental and theoretical viewpoint that related complexes will form and act as nucleation sites for oxygen precipitates.[24,26,30,33] This in turn will impact the properties of Si. The present approach is to consider binding energies so we do not consider the energies to form the constituent defects in the first place or the kinetics that are required to form the complexes. Both these aspects would be necessary to form experimentally detectable concentrations of the $V_mN_2O_n$ complexes. These concentrations will depend upon the initial concentration of oxygen, nitrogen and vacancies. Under equilibrium condition the concentration of vacancies will be very low as their formation energy is very high (activation energy of diffusion of 4.5-4.6 eV).[47] In that respect the high concentrations of vacancies can be achieved under non-equilibrium conditions (i.e. irradiation or implantation). Finally, atomistic modelling work and the use of thermodynamic models (for example mass action analysis)[44] is required to determine which defects will be prevalent from a concentration viewpoint. The present transferable methodology aiming to understand nitrogen-vacancy complexes in Si will be of interest to related defect issues in other semiconductor systems.[48,49]

4. Conclusions

In the present study, we used systematic DFT calculations to find the minimum energy structure of $V_mN_2O_n$ (m, n=1, 2) complexes. Here we provide the structure and relative energetics of these defects offering complementary information to previous experimental work. The present result can be used as a basis for further work on these extended clusters both at a more advanced theoretical level (state-of-the-art hybrid functionals) and experimental studies. Here we focus on the binding energies and it is anticipated that this approach will yield the right trends. Nevertheless, kinetics in these systems can play a vital role whether the formation of these defects will be realized in concentrations that can be detected by experiment.

References

1. Z. Liu, X. Fu, M. Li, F. Wang, Q. Wang, G. Kang, and F. Peng, J. Mater. Chem. A **3**, 3289 (2015).
2. B. Guan, H. Siampour, Z. Fan, S. Wang, X. Y. Kong, A. Mesli, J. Zhang, and Y. Dan, Sci. Rep. **5**, 12641 (2015).
3. J. Mullins, V. P. Markevich, M. Vaqueiro-Contreras, N. E. Grant, L. Jensen, J. Jablonski, J. D. Murphy, M. P. Halsall, and A. R. Peaker, J. Appl. Phys. **124**, 035701 (2018).
4. T. Müller, G. Kissinger, D. Kot, M. Gehmlich, M. Boy, A. Vollkopf, A. Sattler, and A. Miller, Phys. Status Solidi A **218**, 2100210 (2021).
5. H. Sawada and K. Kawacami, Phys. Rev B **62**, 1851 (2000)
6. H. Kageshima, A. Taguchi and K. Wada, Appl. Phys. Lett. **76**, 3718 (2000)
7. J. P. Goss, I. Hahn, and R. Jones, P. R. Briddon, S. Oberg, Phys. Rev. B **67**, 045206 (2003)
8. A. Platonenko, F. S. Gentille, F. pascale, A. M. Ferrari, M. D’Amore, and R. Dovesi, Physical Chemistry Chemical Physics, **21**, 20939 (2019)
9. H. Kageshima, A. Taguchi and K. Wada, Defect and Impurity Engineered Semiconductors and Devices III, edited by S. Ashok, J. Chevallier, N. M. Johnson, B. L. Sopori, and H. Okushi, MRS Symposia Proceedings No. **719**, (Material Research Society, Pittsburgh, 2002) p. 79

10. T. Sinno, E. Dornberger, W. von Ammon, R. A. Brown,F. Dupret, Material Science and Engineering **R28**, 149 (2000)

11. W. von Ammon, A. Sattler, G. Kissinger, in Springer Handbook of Electronic and Photonic Materials, (Chapter 5, Defects in Monocrystalline Silicon, S. Kasap and P. Kapper, (Eds) 111-132 (2017)

12. A. Dornen, G. Pensl, R. Sauer, Phys. Rev. B **17**, 9318 (1987)

13. X. Yu, J. Chen, X. Ma, D. Yang, Material Science and Engineering **R74**, 1-33 (2013)

14. S. Yuan and D. Yang, Nitrogen Impurity in Crystalline Silicon, in Handbook of Photovoltaic Silicon, Edited by D.Yang, Springer-Verlag Gmbh Germany (2019) 1-32

15. N. Fujita, R. Jones, S. Oberg, P.R. Briddon, Physica B, **401-402**, 159-162 (2007)

16. C. P. Ewels, R. Jones and S. Oberg, in Early Stages of Oxygen Precipitation in Silicon, edited by R. Jones, Kluwer Academic Publishers (NATO ASI Series), **Vol. 17**, 141-162 (1996)

17. K. Papadopoulou, A. Chroneos, S.-R. G. Christopoulos, Physica B **643**, 414184 (2022)

18. G.A Rozgonyi, R. P. Doysher, and C. W. Pearce, J. Electrochem. Soc. **123**, 910 (1976)

19. F. Shimura, and R. S. Hokket, Appl. Phys. Lett. **48**, 224-226, (1986)

20. P. Pichler, Intrinsic point defects, impurities, and their diffusion in silicon, in Computational microelectronics, S. Selberherr , Editor, Springer , New York, 378-390 (2004)

21.N. Fujita, R. Jones, J. P. Goss, P.R. Briddon, T. Frauenheim, S. Oberg, Appl. Phys. Lett. **87**, 021902 (2005)

22. X. Ma, X. Yu, D. Yang , Appl. Phys. Lett.**81**, 496 (2002)

23.D. Yang and X. Yu. Nitrogen in Silicon, Defect and Diffusion Forum, **230-232**, 199-220 (2004)

24.K. Nakai, Y. Inoue, H. Yokota, A. Ikari, J. Takahashi, A. Tacikawa, K. Kitahara, Y. Ohta, and W. Ohashi, J. Appl. Phys. **89**, 4301 (2001)

25.Q. Sun, K. H. Yao, H. C. Gatos, and J. Lagowski, J. App. Phys. **71**, 3760 (1992)

26. X. Yu, D. Yang, X. Ma, J. Yang, L. Li, and Q. Que, J. Appl. Phys. **92**, 188 (2002)

27. Y. Yamanaka, H. Harada, K. Tanahashi, T. Mikayama, and N. Inoue, Solid State Phenomena **82-84**, 63-68, (2002)

28. A. Karoui, F. S. Karoui, G. A. Rozgonyi, M. Hourai, and K. Sueoka, J. Electrochem. Soc. **150**, G771-G777 (2003)

29. F. S. Karoui, A. Karoui, G. A. Rozgonyi, M. Hourai, and K. Sueoka, Solid State Phenomena, **95-96**, 99-104 (2003)

30. H. Kageshima, A. Taguchi and K. Wada, Physica B **340- 342**, 626-629 (2003)

31. A. Karoui, and G. A. Rozgonyi, J. Appl. Phys. **96**, 3264 (2004)

32. F. S. Karoui, A. Karoui, J. Appl. Phys. **108**, 033513 (2010)
33. A. Taguchi, H. Kageshima, and K. Wada, J. Appl. Phys. **97**, 053514 (2005)
34. C. Cui, X. Ma, and D. Yang, J. Appl. Phys. **104**, 123523 (2008)
35. M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, J. Phys. Condens. Matter, **14**, 2717 (2002)
36. J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865–3868 (1996)
37. D. Vanderbilt, Phys. Rev. B **41**, 7892–7895 (1990)

38. H. J. Monkhorst, J. D. Pack, Phys. Rev. B **13**, 5188–5192 (1976)
39. S. R. G. Christopoulos, K. A. Papadopoulou, A. Konios, D. Parfitt, Comput. Mater. Sci., **202**, 110976 (2022)
40. A. Chroneos, C. A. Londos, H. Bracht, Mater. Sci. Eng. **176**, 453–457 (2011)
41. S. R.G. Christopoulos, E. N. Sgourou, R. V. Vovk, A. Chroneos, and C. A. Londos, Materials **11**, 612 (2018)
42. A. Chroneos, C. A. Londos, J. Appl. Phys. **107**, 093518 (2010)
43. A. Chroneos, E. N. Sgourou, C. A. Londos, U. Schwingenschlögl, Appl. Phys. Rev. **2**, 021306 (2015)
44. A. Chroneos, R. W. Grimes, and H. Bracht, J. Appl. Phys. **105**, 016102 (2009)

45. E. N. Sgourou, D. Timerkaeva, C. A. Londos, D. Aliprantis, A. Chroneos, D. Caliste, P. Pochet, J. Appl. Phys. **113**, 113506 (2013)

46. K. Wada, H. Nakanishi, H. Takaoka, N. Inoue, J. Cryst. Growth **57**, 535 (1982).

47. H. Bracht and A. Chroneos, J. Appl. Phys. **104**, 076108 (2008).

48. U. I. Erkaboev, G. Gulyamov, J. I. Mirzaev, and R. G. Rakhimov, Int. J. Mod. Phys. B **34**, 2050052 (2020).

49. J. J. Zhu, M. Vasilopoulou, D. Davazoglou, S. Kennou, A. Chroneos, and U. Schwingenschlögl, Sci. Rep. **7**, 40882 (2017).