

Ab Initio Identification of the Nitrogen Diffusion Mechanism in SiliconNathan Stoddard,¹ Peter Pichler,² Gerd Duscher,^{1,3} and Wolfgang Windl⁴¹Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695, USA²Fraunhofer IISB, Schottkystrasse 10, 91058 Erlangen, Germany³Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA⁴Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio 43210-1178, USA

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In this Letter, we present *ab initio* results identifying a new diffusion path for the nitrogen pair complex in silicon, resulting in an effective diffusivity of $67 \exp(-2.38 \text{ eV}/kT) \text{ cm}^2/\text{s}$. This nudged elastic band result is compared with other nitrogen diffusion paths and mechanisms, and is determined to have unmatched agreement with experimental results. It is also shown that careful consideration of total energy corrections and use of a fully temperature-dependent diffusion prefactor have modest but important effects on the calculation of diffusivity for paired and for interstitial nitrogen.

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Nitrogen doping of silicon has become a process of increasing importance because of its various effects on the formation of extended defects in silicon. The first prominently reported effect was the complete suppression of void formation in float-zone processed crystals [1]. In Czochralski-grown silicon, because of an additional interaction with oxygen, the mechanism is less effective and a higher density of relatively smaller voids and grown-in oxide precipitates was observed in nitrogen-doped crystals [2]. Finally, nitrogen is known to increase the mechanical strength of silicon by locking dislocations [3] and, when implanted with a sufficient dose, to reduce the oxidation rate [4]. In partial explanation of the above effects, it has been shown that the N_2 pair readily complexes with vacancies, both in a metastable, immobile N_2V configuration, and in the very stable N_2V_2 configuration which can form from either the reaction $\text{N}_2\text{V} + \text{V} \rightarrow \text{N}_2\text{V}_2$ or $\text{N}_2 + \text{V}_2 \rightarrow \text{N}_2\text{V}_2$ [5,6]. The N_2V_2 complex has been shown to attract oxygen into stable complexes, indicating the possibility of further oxygen precipitate nucleation based on the N_2 pair.

As early as the investigations of Stein [7] in 1985, it was concluded from isotope shifts that the nitrogen dimer configuration is prevalent at room temperature. Jones *et al.* [8] confirmed this conclusion using a combination of spectroscopic and *ab initio* investigations. Except for the work of Gali *et al.* [9], who calculated a binding energy of 1.73 eV, all theoretical investigations agree on a rather high binding energy between 3.67 and 4.3 eV [6,10–12]. In contrast, the primary diffusion mechanism for nitrogen, in general, and the N_2 pair, in particular, has been disputed in the literature.

In a variety of experimental investigations based on nitrogen outdiffusion from doped substrates [13] or on the indiffusion of nitrogen from the ambient [14–17], the profiles obtained were interpreted in terms of the diffusion of N_2 as an entity. The diffusion data obtained are shown in Fig. 1 and can be described best by a diffusion constant of

$$D_{\text{N}_2} = 35 \exp(-2.34/kT) \text{ cm}^2/\text{s} \quad (1)$$

with the 90% confidence interval for the activation energy ranging from 2.01 to 2.77 eV. Profiles after ion implantation [18,19] are considerably more complex, and the possibility of a catalytic effect of oxygen on nitrogen diffusion was reported recently [20]. In the analysis of Adam *et al.* [21], nitrogen dimers were not taken into consideration nor apparently needed to obtain an excellent description of the experimental profiles. A later analysis of Voronkov and Falster [22] was based on nitrogen dimers as the prevalent defect, but it was concluded that diffusion proceeded via dissociation and diffusion of the monomers rather than as an entity. Uncertainties remain about this mechanism because the binding energy of N_2 in their analysis, estimated to be between 2.24 and 2.9 eV, is considerably smaller than the bulk of the estimates from theoretical work.

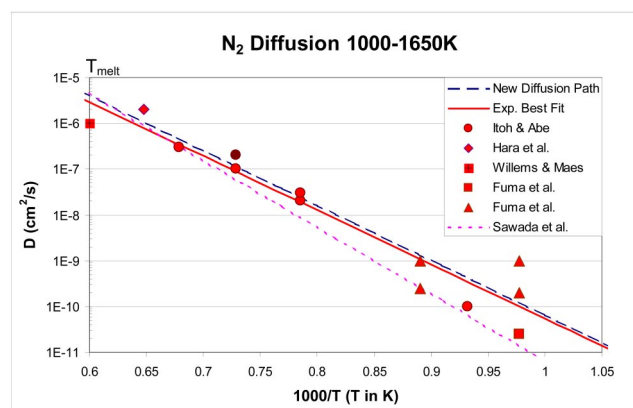


FIG. 1 (color online). Experimental data for the nitrogen diffusion constant in silicon with best fit line and new theoretical diffusion profile. The darker points are FTIR data specific to nitrogen pair diffusion. A theoretical curve is also presented using the activation energy from Sawada *et al.* [24], together with a diffusion prefactor from Itoh and Abe [13].

Concerning nitrogen interstitial (N_i) diffusion, Schultz and Nelson calculated the migration barrier for N_i to be 0.4 eV for a split-interstitial configuration, resulting in very fast diffusion [23].

Sawada *et al.* conducted the only *ab initio* N_2 diffusion study [24]. Both simultaneous and sequential movements of the nitrogen atoms were considered, with reported activation barriers of 3.3 and 2.9 eV, respectively. The second value for the energy barrier is fairly consistent with early data from Itoh and Abe [13], but outside of the confidence range given above. The 2.9 eV diffusion path moves the atoms from the ground state (usually named the antiparallel configuration) to the so-called Humble configuration (see Refs. [8,24] for a description) with a smaller barrier of 1.0 eV to move to a different antiparallel state in a break-and-make bonding motion. Sawada *et al.* make a point of using either known structures or configurations with obvious symmetry. In this Letter, the requirements of symmetry along the diffusion path are dropped, and a new diffusion path is identified with calculations that make use of rigorous corrections to the subtleties of the local density approximation (LDA) and a careful determination of the saddle point. This new path has a lower activation energy than any previously reported path. The diffusion prefactor of nitrogen is calculated for the first time, both for N_2 pairs and for N_i .

Simulations were performed using the Vienna *Ab Initio* Simulations Package (VASP), which employs a self-consistent approach based on density functional theory (DFT) in the LDA [25]. Ultrasoft pseudopotentials [26] with a plane-wave basis set were used both for ionic relaxation and for calculating the total energy at points along the diffusion path. A supercell of 64 silicon atoms, i.e., eight conventional unit cells, plus two nitrogen atoms was first relaxed to the well-known antiparallel N_2 structure; see Fig. 2(a). A similar configuration with the N_2 pair situated in an equivalent nearby position was relaxed, and four to six intermediate positions between these two were interpolated as starting guesses for nudged elastic band calculations; each was locally relaxed to a total energy tolerance of 0.005 eV. Only the neutrally charged case is considered since, in other work, the energy difference between negative and neutral charge states was negligible while the positive charge state had higher energies by a constant energy shift [24]. Throughout the calculations, a $2 \times 2 \times 2$ k -point mesh was generated using the Monkhorst-Pack scheme [27]. Corrections were applied to the total energy in an attempt to correct systematic errors arising from the use of LDA-DFT, including a band gap size correction or “scissors operator” (usually the most significant), a correction due to the finite size of the supercell, and an adjustment for energy levels within the band gap [28]. (This correction makes the $2 \times 2 \times 2$ k -point sampling equivalent to or better than uncorrected $4 \times 4 \times 4$ meshes.) These corrections must be applied

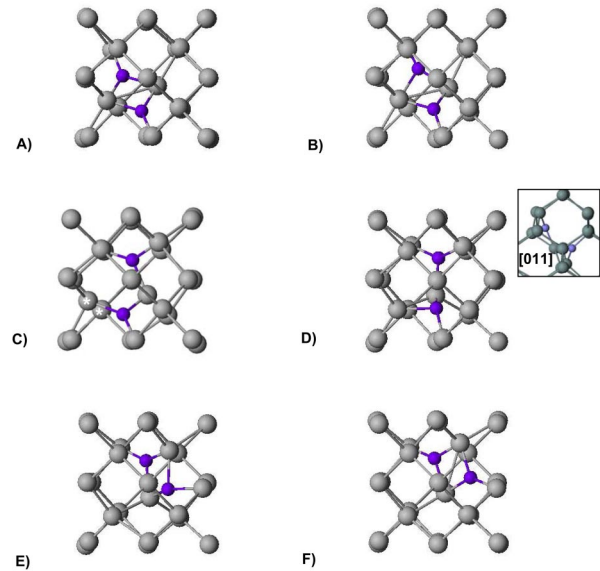


FIG. 2 (color online). Low activation barrier diffusion series for a nitrogen pair (in purple) moving through the silicon lattice (gray) in (100) projection. The first and last configurations are equivalent, and the energetics are provided in Fig. 3. Both atoms move, making their jumps at different times. In the highest energy configuration, (C), the Si atoms marked with a (*) have only three bonds, and the N-N separation is at its maximum. The upper purple atom is N(1).

since nitrogen has electronic states above the valence-band edge.

The different stages along the new diffusion path are illustrated in Fig. 2. The two nitrogen atoms part ways, one moving up while the other moves down, only to meet again on the other side of the cell’s central atoms. The atoms move disjointedly, with the upper atom moving through 2(a)–2(c) before the lower atom does 2(d)–2(f), while the highest energy configurations are those where the nitrogen atoms are the farthest separated. In this [001] projection, it appears that the configurations of Fig. 2(d) may be the pentagonal Humble configuration, but from a different view [Fig. 2(d) inset] this is clearly not the case. The nitrogen atoms maintain threefold coordination in each stage depicted, while the bond length varies within 1.76 ± 0.05 Å (see Table I) except for N(2) in the second stage. For this second stage, the silicon atoms remain close to their equilibrium positions while only N(2) displaces, resulting in a small increase in the total energy. The stage 3 saddle point has the highest energy because two of the Si atoms have only threefold coordination, but the energy is still modest since the nitrogen bond lengths are near equilibrium. The corresponding activation energy for this diffusion series is only 2.36 eV (see Fig. 3), considerably less than any other published value, and a very good match to the experimental fit; see Fig. 1. The diffusion coefficient prefactor, D_0 , was determined by calculating vibrational

TABLE I. Bond lengths (in Å) for the two nitrogen atoms through the different stages of the diffusion path.

Position	Bond length of N(1)			Bond length of N(2)		
1	1.733	1.735	1.778	1.733	1.735	1.778
2	1.73	1.75	1.76	1.67	1.73	1.99
3	1.72	1.80	1.81	1.71	1.76	1.78
4	1.72	1.78	1.81	1.73	1.74	1.77
5	1.71	1.73	1.78	1.74	1.75	1.84
6	1.73	1.74	1.78	1.73	1.74	1.78

frequencies for the saddle point and the ground state, as well as the entropies of formation and configuration:

$$D_0 = 1/12\nu d^2 p e^{-S/k} \text{ cm}^2/\text{s}, \quad (2)$$

where d is the jump distance, p is the multiplicity of jump paths, S is the combined entropy, and ν is the jump frequency. Within harmonic transition-state theory, the jump frequency is the ratio of the products of the real Γ -point frequencies for the ground state over those of the saddle state. The entropy of configuration is just the natural log of the number of possible defect configurations. Within the quasiharmonic approximation, the entropy S of an atomic configuration is given as [29,30]

$$S = k_B \sum_f \sum_i \left\{ \frac{\hbar\omega_{if}}{2k_B T} \coth\left(\frac{\hbar\omega_{if}}{2k_B T}\right) - \ln\left[2 \sinh\left(\frac{\hbar\omega_{if}}{2k_B T}\right)\right] \right\}, \quad (3)$$

where the summation goes over the degrees of freedom, f , for each atom, i , and ω_{if} is the characteristic frequency. The entropy of formation can be determined from the entropy of the N_2 defect, the N_i defect, and perfect silicon by

$$S_f = 2S_{N_i} - S_{N_2} - S_{\text{perfect}}. \quad (4)$$

The temperature dependence of the entropy [Eq. (3)] does not completely cancel out and has a weak effect on the effective migration barrier. For the diffusion path of Fig. 2, the full diffusion constant was calculated, including the entropy temperature dependence, in the temperature range of 800–1400 °C. Using an Arrhenius fit where the prefactor is temperature independent, the data are best described in this temperature range by

$$D_{N_2} = 67 \exp(-2.38/kT) \text{ cm}^2/\text{s}; \quad (5)$$

see Fig. 1. For low temperatures (300–700 °C), values of $D_0 = 117 \text{ cm}^2/\text{s}$ and $E_a = 2.42 \text{ eV}$ better fit the temperature dependence of the theoretical diffusion constant. This Arrhenius fitting approach will be applied throughout.

The most significant way in which this study differs from previous work is in setting aside the use of symmetric arrangements, instead allowing nonobvious detours to lower energy. Given that previous authors' calculations have used the same inherent assumptions in their models,

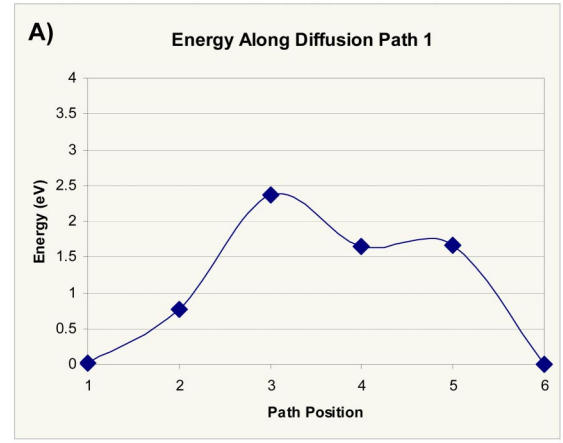


FIG. 3 (color online). Energy profile for the N_2 diffusion path. The migration barrier energy is 2.36 eV.

the fact that this new path has a lower value for the energy barrier must make it the preferred route. Nitrogen is known to introduce deep levels into the electronic band gap; this is the reason that it does not work as a dopant in silicon [31]. Of the corrections applied to these DFT calculations [28], the finite size and gap energy level corrections changed the total energies calculated by less than 0.002 eV. The scissors operator changed the total energies by an average of +0.25 eV, with a net +0.06 eV change in the migration barrier. While the corrections amounted to $\sim 3\%$ in activation energy, and a nonvisible change in Fig. 1, their application is important since they are known to have significant effects in some systems, such as SiO_2 .

A study was also conducted of nitrogen interstitial diffusion in silicon. It was determined that bond-centered and split-interstitial configurations for N_i differ by at least 0.11 eV in their formation energies (depending on defect charge), with the bond-center configuration being more stable. The study by Schultz and Nelson found an energy barrier of 0.4 eV for the diffusion of the split-interstitial nitrogen [23]. Our study of bond-centered nitrogen found a 0.44 eV migration barrier through a simple path, but a calculation of the temperature-dependent prefactor gave that the diffusion constant is best fit by an Arrhenius expression of

$$D_N = 1.7e^{-0.56/kT} \text{ cm}^2/\text{s} \quad (6)$$

in the temperature range from 800–1600 K. At low temperatures, an exponent of 0.50 eV better describes the diffusion constant. With these values, the N_i will diffuse at least 5 orders of magnitude faster than N_2 pairs. Given the strong binding energy of nitrogen pairs and the fast diffusion of N_i , we expect that all of the nitrogen concentration will be paired, complexed, or substituted within a very short time. Subsequent diffusion will be limited by the N_2 mechanism. As for the suggestion of Falster and Voronkov that nitrogen pairs diffuse by dissociation and

interstitial diffusion [22], even their low estimate of the binding energy (less than the commonly quoted range) when added to our migration barrier for N_i diffusion and combined with the N_i diffusion prefactor, results in slower diffusion, with $D = 1.7 \exp(-2.80/kT) \text{ cm}^2/\text{s}$, than the experimental data and the new N_2 diffusion path. For this reason, we believe that N_2 diffusion should proceed as a complex, and the dissociation mechanism should play only a minor role. Furthermore, the proposed mechanism of N-V exchange was calculated to have an energy barrier $\sim 0.8 \text{ eV}$ greater than for N_2 diffusion. As a footnote, we do not find a straight migration path for N-V exchange as previous work did. Rather, the N atom takes a bowed path with the saddle point nitrogen displaced from the bond center by $>0.8 \text{ \AA}$ in a (110) direction. This curved path lowers the energy barrier by $\sim 1.3 \text{ eV}$ compared to previous work [32].

In summary, we have evaluated each of the major proposed routes for nitrogen diffusion in silicon with parameter-free first principles simulations. Our results suggest that, after incorporation into the lattice, a small fraction of nitrogen atoms will remain immobile on substitutional lattice sites due to the displacement energy, while the ground-state interstitial nitrogen will almost instantaneously form complexes due to its low migration barrier (0.44 eV) and very high diffusivity (approximately $1.7 \exp(-0.56/kT) \text{ cm}^2/\text{s}$ between 800 and 1600 K), primarily forming N_2 . The diffusion path that we have identified has a 2.36 eV migration barrier and an effective diffusivity of $67 \exp(-2.38/kT) \text{ cm}^2/\text{s}$ between 800 and 1400 °C, which is lower than any previously reported path for the nitrogen dimer and which has been shown to be more energetically favorable than diffusion by dissociation or N-V site exchange. Furthermore, the excellent match between *ab initio* calculations of the diffusion constant and experimental data over a wide temperature range suggests very strongly that the dominant diffusion mechanism is a simultaneous movement of the two nitrogen atoms.

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- [1] T. Abe, H. Harada, and J.-i. Chikawa, in *Defects in Semiconductors II*, edited by S. Mahajan and J.W. Corbett, MRS Symposia Proceedings 14669 (Materials Research Society, Pittsburgh, 1983), p. 1.
 - [2] K. Nakai, Y. Inoue, H. Yokota, A. Ikari, J. Takahashi, A. Tachikawa, K. Kitahara, Y. Ohta, and W. Ohashi, *J. Appl. Phys.* **89**, 4301 (2001).
 - [3] K. Sumino, I. Yonenaga, M. Imai, and T. Abe, *J. Appl. Phys.* **54**, 5016 (1983).
 - [4] W. J. M. J. Josquin and Y. Tamminga, *J. Electrochem. Soc.* **129**, 1803 (1982).

- [5] A. Karoui, F. S. Karoui, G. Rozgonyi, M. Hourai, and K. Sueoka, *J. Electrochem. Soc.* **150**, G771 (2003).
- [6] H. Kageshima, A. Taguchi, and K. Wada, *Appl. Phys. Lett.* **76**, 3718 (2000).
- [7] H. J. Stein, in *Thirteenth International Conference on Defects in Semiconductors*, edited by L. C. Kimerling and J. M. Parsey, Jr. (The Metallurgical Society of AIME, New York, 1985), p. 839.
- [8] R. Jones, S. Öberg, F. Berg Rasmussen, and B. Bech Nielsen, *Phys. Rev. Lett.* **72**, 1882 (1994).
- [9] A. Gali, J. Miro, P. Deák, C. P. Ewels, and R. Jones, *J. Phys. Condens. Matter* **8**, 7711 (1996).
- [10] H. Sawada and K. Kawakami, *Phys. Rev. B* **62**, 1851 (2000).
- [11] A. Karoui, F. Sahtout Karoui, G. A. Rozgonyi, M. Hourai, and K. Sueoka, in *Semiconductor Silicon 2002*, edited by H. R. Huff *et al.*, Electrochemical Society Proceedings 2002-2 (Electrochemical Society, New York, 2002), p. 670.
- [12] J. P. Goss, I. Hahn, and R. Jones, *Phys. Rev. B* **67**, 045206 (2003).
- [13] T. Itoh and T. Abe, *Appl. Phys. Lett.* **53**, 39 (1988).
- [14] A. Hara, T. Fukuda, T. Miyabo, and I. Hirai, *Appl. Phys. Lett.* **54**, 626 (1989).
- [15] G. J. Willems and H. E. Maes, *J. Appl. Phys.* **73**, 3256 (1993).
- [16] N. Fuma, K. Tashiro, K. Kakumoto, and Y. Takano, *Mater. Sci. Forum* **196–201**, 797 (1995).
- [17] N. Fuma, K. Tashiro, K. Kakumoto, and Y. Takano, *Jpn. J. Appl. Phys.* **35**, 1993 (1996).
- [18] L. S. Adam, M. E. Law, K. S. Jones, O. Dokumaci, C. S. Murthy, and S. Hegde, *J. Appl. Phys.* **87**, 2282 (2000).
- [19] R. S. Hockett, *Appl. Phys. Lett.* **54**, 1793 (1989).
- [20] G. Mannino, V. Privitera, S. Scalsese, S. Libertino, E. Napolitani, P. Pichler, and N. E. B. Cowern, *Electrochem. Solid State Lett.* **7**, G161 (2004).
- [21] L. S. Adam, M. E. Law, O. Dokumaci, and S. Hegde, *J. Appl. Phys.* **91**, 1894 (2002).
- [22] V. Voronkov and R. Falster, *Solid State Phenom.* **95**, 83 (2004).
- [23] P. A. Schultz and J. S. Nelson, *Appl. Phys. Lett.* **78**, 736 (2001).
- [24] H. Sawada, K. Kawakami, A. Ikari, and W. Ohashi, *Phys. Rev. B* **65**, 075201 (2002).
- [25] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); *Phys. Rev. B* **49**, 14251 (1994); G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); *Phys. Rev. B* **54**, 11169 (1996).
- [26] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [27] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [28] W. Windl, *Phys. Status Solidi B* **241**, 2313 (2004).
- [29] D. Chandler, in *Introduction to Modern Statistical Mechanics* (Oxford University Press, New York, 1987), p. 70.
- [30] R. LeSar, R. Najafabadi, and D. J. Srolovitz, *Phys. Rev. Lett.* **63**, 624 (1989).
- [31] H. P. Hjalmarsen, P. Vogl, D. J. Wolford, and J. D. Dow, *Phys. Rev. Lett.* **44**, 810 (1980).
- [32] J. S. Nelson, P. A. Schultz, and A. F. Wright, *Appl. Phys. Lett.* **73**, 247 (1998).