First Principles Calculations for Nitrogen-Vacancy Related Defects in N-CZ Si

A. Karoui[1], F. Sahtout Karoui[1], G. A. Rozgonyi[1], M. Hourai[2] , and K. Sueoka[2]

[1] *North Carolina State University, Raleigh, NC 27695-7916, USA.*

[2] *Sumitomo Metal Industries, Ltd., Sitix Division, Saga, Japan.*

In nitrogen doped CZ Si, VN_2 and V_2N_2 are among the prominent complexes, at crystal growth and wafer processing temperatures. Their structural, energetic, and thermal properties have been investigated using first principle calculations, which included DFT (LDA) quantum mechanics and MNDO-AM1 semi-empirical calculations. Four kinetic reactions are considered:

$$N_{int} + N_{int} \rightarrow N_{2\,int} \quad (R0)$$
$$V + N_{2\,int} \rightarrow VN_2 \quad (R1)$$
$$VN_2 + V \rightarrow V_2N_2 \quad (R2)$$
$$V_2 + N_{2\,int} \rightarrow V_2N_2 \quad (R3)$$

The relaxed geometry of the molecules indicates the lattice expands outward around the V_2N_2 defect and compresses inward around VN_2. The complex energies of formation in their ground states are: -4.09 eV for $N_{2\,int}$, 2.0 eV for VN_2, and -5.2 eV or -1.0 eV for V_2N_2 for reaction paths R2 or R3. The enthalpies and free energies of the reactions were calculated from 298K to 1650K and the latter is shown in Fig.1. We found that VN_2 produced by R1 is not very stable, whereas V_2N_2 produced by R2 and R3 is stable. Although, R3 is the most energetically favorable, since di-vacancies cannot survive temperatures higher than 600K, R3 is not effective. Hence R2 is effective reaction at temperature where void formation is most prevalent, in agreement with Kagashima [1] and Sawada [2] results.

The equilibrium concentration of VN_2 was also investigated by computing the configuration entropy. The thermal entropy was calculated using MNDO-AM1. The equilibrium concentration of VN_2 produced by R1 increases with the available V, see Fig. 2 (a), which appear to be used up at high temperature, see Fig. 2 (b). This is in line with the fact that reaction R1 is slightly endothermic. VN_2 formation temperature increases when [V] decreases. A temperature threshold above which all N pairs associate with the available V appear at high V concentration. Figure 2 (b) shows also that V are used immediately above the temperature threshold, when the N concentration reaches or exceeds that of the vacancies. For low N concentration (i.e., lower than 1E14 cm^{-3}) a complete reaction of V with the N pairs does not occur, see Fig.2 (b). This is in agreement with von-Ammon's analysis of the COP region shrinkage with increasing N level [3].

One expects that in the wafer center, where the V concentration is high, reaction R1 forming VN_2 prevails around temperature of void formation. Thus high concentration of VN_2 is possible and R2, which is spontaneous, can consequently occur.

References:

[1] H. Kageshima, A. Tauguchi, K. Wada, Appl. Phys. Lett., 76, 25 , 3718, (2000).

[2] H. Sawada, and K. Kawakami, Kazuza Academia Forum 99, 105, 1999.

[3] W. von Ammon, et al, J. of Crystal Growth, 226, 19, (2001).

[4] B.J. Coomer, A.Resende, J.P.Goss, R.Jones, S.Oberg, P.R.Briddon, Physica B, 273-274, 520 (1999).

[5] G. D. Watkins and J. W. Corbett, Phys. Rev., 138, 2A, A543 (1965).

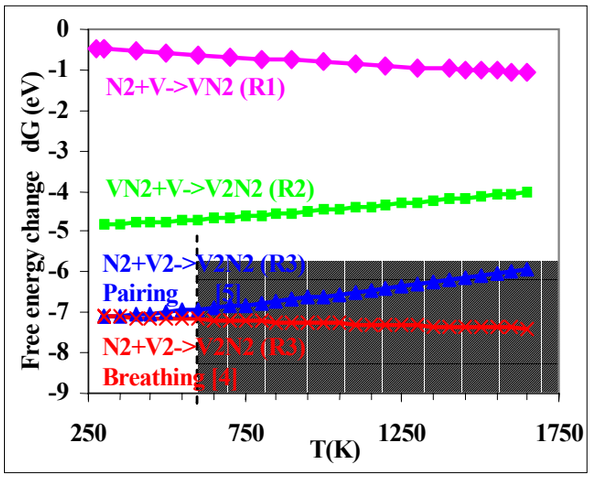
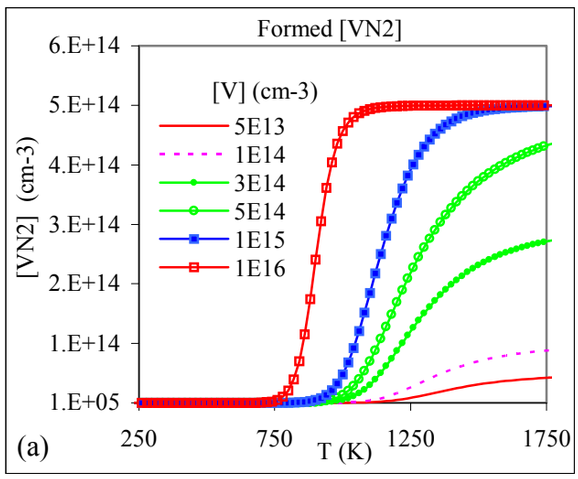


Fig. 1: Calculated Gibbs free-energy change of reactions leading to N-V complexes in N-CZ Si as a function of temperature.



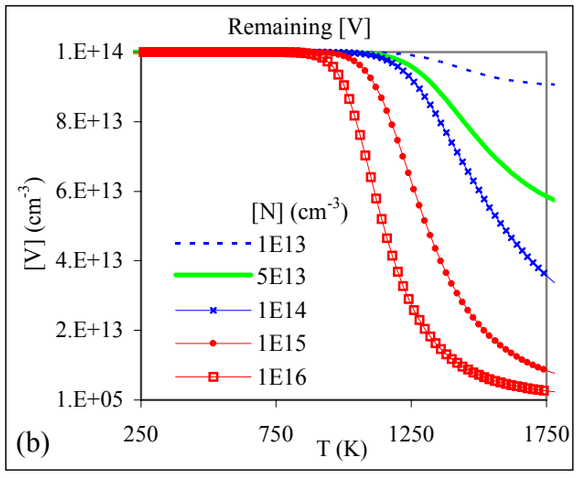


Fig.2: (a) equilibrium concentration of VN_2 produced via R1, for [N]= 5E14 cm^{-3} and (b) free vacancies, versus N doping level for [V]= 1E14 cm^{-3}