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FINAL TECHNICAL REPORT FOR CONTRACT N00014-85-K-0460:

THEORY OF AGGREGATE DEFECTS IN SILICON

Gary G. DeLeo and W. Beall Fowler

Department of Physics  
Lehigh University  
Bethlehem, Pennsylvania 18015

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The research summarized in this final technical report was supported under ONR contract N00014-85-K-0460 during the period 1 June 1985 to 28 February 1989. Included are (i) a brief (two-page) summary of contract-period research accomplishments, and (ii) an appendix listing publications and presented papers. [Reprints of published papers are appended to selected copies of this report; otherwise, they are available upon request.]

During the contract period, our efforts were focussed on point defects in silicon which exhibit large structural departures ("relaxations") from the high-symmetry geometry, and defects which combine to form defect aggregates. The primary goals were to understand on an atomic scale the electronic characteristics of selected defects and defect reactions and, in so doing, reveal physical phenomena basic to defect systems. The project consisted of both electronic-structure-method development, and the application of existing and locally developed methods to specific defect systems. Apart from these categories, we also elucidated the connection between pseudo-Jahn-Teller and chemical-rebonding descriptions of spontaneous off-center displacements.

During the contract period, we developed a semiempirical tight-binding Green's function (TBGF) method which filled both a critical need in our research program and a gap in established electronic-structure methods for defects. This method was developed to provide single-particle energies as functions of atomic positions for off-center and aggregate defects. It was constructed upon a framework developed by Li and Lin-Chung and adapted by us to the defect problem. We applied it first to the problems of substitutional nitrogen and oxygen in silicon, which are well studied experimentally and which are known to exhibit substantial off-center displacements. Here, the splitting of the critical single-particle states was revealed for the first time unclouded by cluster-termination effects. This success encouraged us to apply this method to studies of aggregates.

The aggregate defects of primary interest in this project have been members of the class which passivate silicon dangling bonds; i.e., those combinations which would render a silicon lattice vacancy electrically inactive. Our TBGF treatment of the oxygen-oxygen pair represented a necessary follow-up to our earlier semiempirical MNDO-and scattered-wave-X $\alpha$ -cluster studies. These cluster calculations revealed a stable <100>-oriented pair. The O-O interactions were found to be very weak; hence, the oxygens effectively passivated the four vacancy dangling bonds. Furthermore, these calculations suggested that a lattice-strain-compressed version of this defect might push a doubly occupied state into the conduction band. This then could be responsible for the thermal double donor activity observed in silicon and associated with oxygen. With the TBGF method, we were able to monitor computed electrical-level positions as functions of O-O interaction. The thermal-donor features were observed quite clearly with increasing O-O interaction. This model remains a candidate for the thermal donor. We also note that our treatments of the oxygen-oxygen pair as well as those of



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substitutional nitrogen and oxygen predict metastability, a phenomenon of current interest.

Most of our efforts during this contract period were devoted to computational treatments of interstitial hydrogen and the hydrogen-related complexes, H-B, H-Al, and H-P, in silicon. Furthermore, we were asked to contribute the theory chapter on H-related complexes which will appear in a volume of the Willardson and Beer series on "Semiconductors and Semimetals." The interstitial H and the H-acceptor pairs show evidence of metastability. The H-acceptor and H-donor pairs not only deactivate the shallow acceptor or donor, but appear to fully passivate the vacancy dangling bonds.

Our TBGF studies of the H-B pair enabled us to examine the atom-atom interactions and determine how such a defect could be electrically inactive even though one might expect the B p-orbital to introduce a deep-acceptor level. This we accomplished by monitoring the deep level as a function of H-B interaction strength. It became quite clear that the presence of even a small H-B interaction would serve to push the unoccupied B p-orbital into the conduction band.

We have continued our MNDO-cluster studies of H-acceptor defects by considering issues such as metastable versus unstable sites. We were the first to argue that the antibonding site to the boron was unstable, contrary to the model of Assali and Leite, and that the Si-antibonding site might be metastable. In a more recent treatment of the deuterium-boron pair, we revealed for the first time in a defect system (and perhaps in any solid-state system) the presence of a Fermi resonance. Here, we have interpreted the infrared spectrum of Pajot, et al. in terms of an anharmonic interaction between the axial motion of the deuterium atom and the perpendicular second-harmonic of the boron. We have continued our attempt to understand the low frequency sidebands to the H vibrational frequency in the H-Al pair.

Still more recently, we have applied our MNDO-cluster electronic-structure method to the H-P pair in silicon. This complex also exhibits dangling-bond passivation. We have reported frequencies and possible metastable geometries.

The isolated interstitial hydrogen defect is interesting as a precursor to the H-related complexes as well as in its own right. We have reported the bond-centered site as the stable location for the hydrogen and suggested, based on computational results, that the hydrogen is off-center toward one silicon and tunneling between equivalent silicons. A pseudo-Jahn-Teller description of this is also presented. We have also calculated the level position of interstitial H in a tetrahedral site by means of a Green's function approach due to Haldane and Anderson as modified by Fowler and Elliott.

Other related projects during this contract period include a treatment of the isolated interstitial carbon in silicon. We have reported for the first time the stability of the  $\langle 100 \rangle$  split interstitial geometry and commented on possible metastability. This too is an important precursor defect to a known metastable system, the C-C pair in silicon.

## APPENDIX

## PUBLICATIONS DURING CONTRACT PERIOD

## IN PRINT-

G. G. DeLeo and W. B. Fowler. (1986). Hydrogen-acceptor pairs in silicon. *Phys. Rev. Lett.* **56**, 402.

M. Besson, G. G. DeLeo, and W. B. Fowler. (1986). Tight-binding Green's function approach to off-center defects: Nitrogen and oxygen in silicon. *Phys. Rev. B* **33**, 8188.

G. G. DeLeo, W. B. Fowler, G. W. Barry, and M. Besson. (1986). Electronic structures of substitutional off-center and small-aggregate defects in silicon by semiempirical Green's function methods. *Materials Science Forum* **10-12**, 31.

W. B. Fowler. (1986). Defect calculations in a modified Haldane-Anderson model. *Materials Science Forum* **10-12**, 91.

G. G. DeLeo, G. D. Watkins, and W. B. Fowler. (1988). Relationship between the pseudo-Jahn-Teller effect and chemical rebonding. *Phys. Rev. B* **37**, 1013.

G. G. DeLeo, M. J. Dorogi, and W. B. Fowler. (1988). Bond-centered interstitial hydrogen in silicon: Semiempirical electronic-structure calculations. *Phys. Rev. B* **38**, 7520.

M. Besson, G. G. DeLeo, and W. B. Fowler. (1988). Band structure of silicon from the semiempirical modified neglect of diatomic differential overlap method. *Phys. Rev. B* **38**, 13422.

W. B. Fowler, G. G. DeLeo, and M. J. Dorogi. (1989). Semiempirical electronic-structure calculations of bond-centered interstitial hydrogen in silicon. *Materials Science Forum* **38-41**, 985.

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G. G. DeLeo and W. B. Fowler. (1989). Computational studies of hydrogen-containing complexes in semiconductors. To appear in "Semiconductors and Semimetals," Edited by R. K. Willardson and A. C. Beer, Volume xx (Academic Press, Boston).

## IN PREPARATION-

M. Besson, G. G. DeLeo, and W. B. Fowler. (1989). Electronic structure calculations of interstitial carbon in silicon.

G. D. Watkins, W. B. Fowler, G. G. DeLeo, M. Stavola, S. J. Pearton, J. Lopata, and D. M. Kozuch. (1989). Identification of a Fermi resonance in the deuterium-boron pair defect in silicon.

#### DISSERTATIONS COMPLETED DURING CONTRACT PERIOD

M. Besson. (1986). New Green's function defect electronic structure methods with applications to oxygen and nitrogen in silicon. Ph. D. Thesis, Lehigh University, Bethlehem, PA.

#### PAPERS PRESENTED AT MEETINGS DURING CONTRACT PERIOD

G. G. DeLeo, M. Besson, and W. B. Fowler. (1986). Electronic structures of off-center defects using semiempirical Green's function methods. Bull. Am. Phys. Soc. 31, 198.

G. G. DeLeo and W. B. Fowler. (1986). Electronic structures of substitutional off-center and small-aggregate defects in silicon by semiempirical Green's function methods. Fourteenth International Conference on Defects in Semiconductors, Paris, Paper M1-9.

W. B. Fowler. (1986). Defect calculations in a modified Haldane-Anderson model. Fourteenth International Conference on Defects in Semiconductors, Paris, Paper P1-9.

M. Besson, G. G. DeLeo, and W. B. Fowler. (1987). Electronic structure of interstitial carbon in silicon. Bull. Am. Phys. Soc. 32, 404.

G. G. DeLeo and W. B. Fowler. (1987). Electronic-structure calculations of interstitial hydrogen in silicon. Bull. Am. Phys. Soc. 32, 841.

G. G. DeLeo. (1987). Calculations of vibrational properties of hydrogen-related defects. Gordon Research Conference on Point Defects, Line Defects, and Interfaces in Semiconductors, Plymouth, NH (invited paper).

G. G. DeLeo, M. J. Dorogi, and W. B. Fowler. (1988). Bond-centered interstitial hydrogen in silicon: An MNDO study of the energy surface. Bull. Am. Phys. Soc. 33, 698.

M. Besson and G. G. DeLeo. (1988). Electronic structure of interstitial carbon in silicon. Bull. Am. Phys. Soc. 33, 580.

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## PAPERS SUBMITTED FOR MEETINGS DURING CONTRACT PERIOD

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G. G. DeLeo and W. B. Fowler. (1989). Hydrogen-donor and -acceptor pairs in silicon: An MNDO study of the energy surface. *Bull. Am. Phys. Soc.* **34**, 834.

## RELATED WORK PUBLISHED PRIOR TO CONTRACT PERIOD

G. G. DeLeo, W. B. Fowler, and G. D. Watkins. (1984). Electronic structure of hydrogen- and alkali-metal-vacancy complexes in silicon. *Phys. Rev. B* **29**, 1819.

G. G. DeLeo, W. B. Fowler, and G. D. Watkins. (1984). Theory of off-center impurities in silicon: Substitutional nitrogen and oxygen. *Phys. Rev. B* **29**, 3193.

G. G. DeLeo and W. B. Fowler. (1985). Alternative dangling-bond passivation at a lattice vacancy in silicon. *J. Elect. Mater.* **14a**, 745.

G. G. DeLeo, C. S. Milsted, Jr., and J. C. Kralik. (1985). Substitutional oxygen-oxygen pair in silicon. *Phys. Rev. B* **31**, 3588.

G. G. DeLeo and W. B. Fowler. (1985). Hydrogen-acceptor pairs in silicon: Pairing effect on the hydrogen vibrational frequency. *Phys. Rev. B* **31** (Rapid Commun.), 6861.