

Final report proposal for the project “Silicon Carbide Derived Carbons: Experiments and Modeling” (Grant DE-FGOI-05ER05-01 and Grant DE-FG02-07ER46472) submitted to the DOE, Office of Basic Energy Sciences

This report has been submitted to DoE in 2010 as part of a renewal proposal. It is being resubmitted in 2013 upon request from DoE and the Georgetown University Sponsored Office.

1. Results from the previously funded research (2007 – 2010)

In the past 2.5 years, we investigated silicon carbide derived carbons at a comprehensive level and moved towards titanium carbide.

As for the modeling carried out at Georgetown University, the newly developed computer algorithms were successfully used to study carbon formation. It was assumed, sp^3 bonded carbon forms upon chlorination of SiC.^{8; 19; 20} Therefore, a study was carried out for large vacancy clusters / pores in diamond (up to V_{65}). It was found, that open pores on the nanoscale level show a tendency for graphitization^{21; 22}. This has great effect on the physicochemical behavior of the carbon material, for example, in regard to sorption and provides a basis for comparison with experimental data.

Over the course of the last years, we succeeded in establishing highly reproducible treatment processes for CDC with tunable pore size and nanostructure. CDC formation in vacuum was studied and it was found that carbon nanotube (CNT) growth can be continued by the addition of CO_2 to the atmosphere. In agreement with previous results, this shows the great potential of SiC CDC (and carbide derived carbon in general) because of its tunability in terms of layer thickness, carbon nanostructures, pore size, pore volume and the corresponding physico-chemical (sorption, conductivity) and mechanical properties.

1.1. Theoretical studies (Georgetown University)

Work progressed along parallel fronts at the Georgetown subgroup. (1) We have developed new computer programs and installed commercial programs with the support of the grant. (2) We performed extensive testing and validation studies on carbon phases and carbon compounds with unusual bonding situations. (3) We established qualitative differences with respect to the better known Si systems. (4) We have performed an extensive and comprehensive study of vacancy clusters in diamond starting from V_1 to V_{65} . (5) We have developed a new measure (energy averaged Fukui index, EAFI)^{15; 23} for the characterization of open carbon structures with high reactivity. (6) We have developed and confirmed the hypothesis regarding local “graphitization” tendencies of small and medium vacancy clusters. (7) We have discovered novel structures of vacancy clusters and obtained an accurate atomistic description of

the diffusion of a vacancy in diamond. Below we summarize the developments in the modeling area in some detail.

1.1.1. New programs and infrastructure

We developed a specialized software using the tight binding density functional theory (TBDFT)²⁴ and a genealogical algorithm extending the philosophy of Baker et al.²⁵ to the realm of computer modeling.²¹ The algorithm maintains full structural diversity without prejudice for high symmetry and it generates in principle all, for larger pores the most stable vacancy clusters and pores extending previous work^{26; 27} on pores with very limited structural diversity allowing to obtain realistic modeling of complex and unbiased pores shapes with varying sizes. We also applied for and obtained supercomputer time for this project and strengthened the local multiprocessor infrastructure and available software through funds of this grant and with Georgetown University funding.

1.1.2. Testing and validation

A significant fraction of the work was devoted, as planned, to validations and comparisons of different methods with each other and with available experiments. We have successfully modeled and interpreted experimental data on simple known carbon structures and their energetics. We systematically compared different supercells within TBDFT, VASP (Vienna *ab initio* Simulation Package) and Brenner-type modeling. We have extensively tested the Brenner-type approach and concluded that for carbon vacancies it is inferior to the DFT approaches both at the full self consistent level (using plane wave, VASP code, and atomic orbital basis sets, Gaussian 03 and DMol codes) and the geometry optimized TBDFT level. The primary testing criteria were formation energy and structural features. TBDFT proved adequate and very fast and, therefore, it became the basis of the production runs.

This part of the project aims at keeping our modeling as honest as possible. We are finding molecular analogs of the otherwise unusual chemical environments found around vacancies and vacancy clusters, in particular elongated CC bonds with changing hybridization. In contrast to modeling based on classical force fields (including Brenner-Tersoff-type) we do not find sp hybridized segments or chains because these are highly unsaturated and tend to anneal in the QM treatment.

1.1.3. Qualitative differences between C and Si systems

The problems for the purposes with Brenner-type potentials²⁸ for modeling carbon materials are due to the significant differences between Si and C in terms of the relative importance of sp^2/sp^3 hybridization^{29;30} that are present and change within one material. For carbons, the π -delocalization, an essentially quantum mechanical (QM) effect, provides the driving force toward graphitization. Since the characterization surface reorganizations inside the pores in carbons is a key objective of this project we had to develop our version of the TBDFT, rather than pursuing the Brenner approach which is faster and would have allowed a larger statistical sampling of structural models.

1.1.4. Comprehensive study of vacancy clusters in C

We have completed the optimization of structure with vacancy clusters, V_n with $n=1,2,\dots,65$. These large scale calculations were done mostly with TBDFT, based on the validation mentioned under 2. All structures up to $n=7$ were fully modeled. Structures for $n>7$ were generated by our own unique algorithm based on selecting the lowest energy structures for n and the generating all structures for $n+1$, starting with $n=7$. The characterization of these larger V_n species includes energetics, structural parameters (connectivity polyhedra, sp^2/sp^3 characterization, Jahn-Teller and Peierls distortions) and comparisons with available experimental data. It is surprising how few of these clusters have been characterized so far in the literature^{26;31} most likely due to the fact that appropriate methods were lacking, as mentioned above.

Based on the completed modeling, we are making generalizations for the low energy local graphitized environments and structures. These are highly unusual bonding environments, and often show a signature motif that we termed as the Tetrahedron Of Local Graphitization (TOLG, Fig. 1) with a tendency toward planarization and local states in the gap.^{22;32}

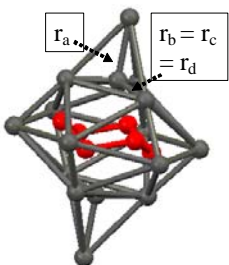


Fig. 1: Illustration of the graphitization trend for the V_6 vacancy cluster. (Red atoms in the center are the vacancy atoms missing.) Relaxation using TBDFT reduces r_a from the van der Waals distance of 3.35 Å to the unusual value of 1.99 Å. Most significant change is the displacement of two carbon atoms just above and under the cyclohexane-like ring. This is the region of the tetrahedron of local graphitization we observed in most of the relaxed structures around the internal surfaces of pores.

This planarization occurs with a concomitant increase of the r_a bond along a sp^3 to sp^2 path creating completely unusual C-C distances not seen in chemistry and which fall in the 1.8 to 2.6 Å range. These unique bonding environments will play an important role in the

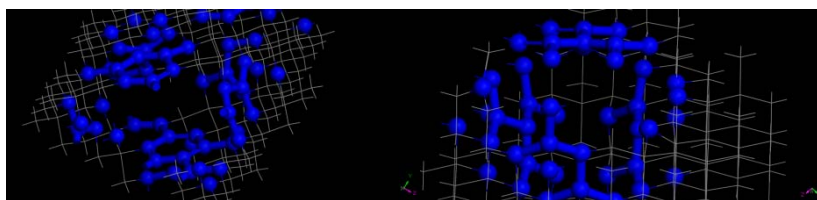


Fig. 2: The most stable V_{37} vacancy cluster indicates a graphitized region, shown by the blue atoms that all have near sp^2 hybridization. The sp^3 carbons and their σ -bonds are represented by a wireframe.

planned research. These unusual structures are stabilized by the surrounding network. The graphitization tendency has two key aspects: graphitization distorts small and medium size vacancy clusters, and it distorts the shapes of larger vacancy clusters, such as V_{37} (see Fig. 2, Ref. ³³). The latter tendency is the basis of slit pores ¹⁸ being preferred over more spherically shaped pores, a trend unique to C and not present in Si.

1.1.5. Characterization of complex non-periodic structures

We have approached the problem of characterizing complex structures by focusing on well developed indices that have dual utility: they can identify the unusual structural regions and convey information on their various (electrophilic, nucleophilic and radical) reactivities. We have developed a new measure (energy averaged Fukui index, EAFI)²³ for the characterization of open carbon structures with high reactivity, to be used in the planned modeling. These reactivity indices supplement the ring statistics, angular distributions and pair correlation measures used in characterizing these structures.³⁴ We find that due to the developing aromatic rings, the relaxed structures are less reactive than would be expected from the large number of dangling bonds in the unrelaxed structures. This auto-passivation of the locally graphitized structures is an important new insight into the understanding of CDCs.

1.1.6. The hypothesis of “graphitization” tendencies in vacancy clusters in C

The completed modeling described before led to the hypothesis that the internal surfaces of cavities and pores in carbons favor and tend toward locally “graphitized” structures (not planar enough to be called which in turn greatly affect their chemical and absorption properties. The number of dangling bonds in the high energy environment is significantly reduced according to this hypothesis in turn reducing chemical reactivity of these internal surfaces.

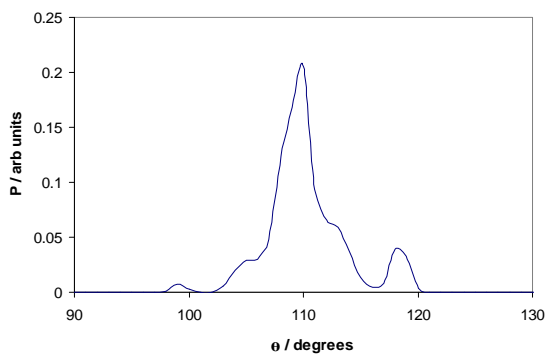


Fig. 3: Calculated angle distribution for V_{30} .

often
 sp^2),

the

Fig. 3 displays the calculated angle distribution for V_{30} . As an illustration of the graphitization tendencies, note the emerging peak near 120° in the angle distribution function of the most stable vacancy cluster for $n=30$, chosen for illustrative purposes here.³⁵ Besides from the dominant tetrahedral peak at 109.5° the additional peaks and shoulders indicate highly strained local environments in the relaxed carbon network.

This hypothesis needs to be further studied and confirmed for the formation of new carbon phases in the proposed work. The implication of this local graphitization for the properties of relatively open carbon structures such as pores, nanotubes and graphene is that it has the potential to change our thinking about the chemi- and physisorption properties of these open carbon phases. A similar analysis on silicon reveals that neighboring three-coordinated atoms move toward each other leaving only four-

coordinated atoms on the void surface. For carbon, only QM treatment can produce sufficiently reliable energetics that reflects this local graphitization.

1.1.7. Unusually stable traps, local formations and diffusion of a vacancy

We have discovered a stable divacancy cluster (2C in Fig. 4) that displays a nearly ordinary C=C bond and should be detectable by resonance Raman spectroscopy. We also found barriers to the motion of monovacancies and divacancies which are necessary in order to better understand the structures of carbide derived carbons. We have discovered that the 1I hypothetical divacancy structure is not stable toward the V_2 . Simulations that often display 2 connected carbons, such as in 1I, are obtained by non-quantum mechanical force fields and are less stable than the non-QM modeling would indicate (Fig. 4).³⁶ The diffusion mechanism we revealed by QM modeling agrees with basic data on the activation energies and provides novel insights into the transformations that occur in the highly reactive environments that forms the core of the new plans presented in this proposal.

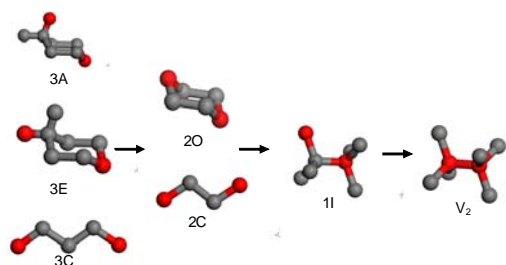


Fig. 4: Stepwise diffusion mechanism of one monovacancy moving toward another. 2C is a stable trap, V_2 is the most stable structure, barriers indicate that the only viable mechanism toward V_2 has to start from 3A or 3E (3^{rd} axial or equatorial neighbor). Red sites indicate the migrating

Appendix: Bibliography & References Cited as listed in the 2010 renewal request and report with updates as appropriate.

- ¹T. Kyotani, J. Chmiola, and Y. Gogotsi, "Carbide Derived Carbon and Templated Carbons," pp. 77 - 113. In *Carbon Materials for Electrochemical Energy Storage Systems*. Edited by F. Beguin and E. Frackowiak. CRC Press/Taylor and Francis, Boca Raton, 2009.
- ²G. Laudisio, R. K. Dash, J. P. Singer, G. Yushin, Y. Gogotsi, and J. E. Fischer, "Carbide-derived carbons: A comparative study of porosity based on small-angle scattering and adsorption isotherms," *Langmuir*, 22 [21] 8945-8950 (2006).
- ³G. Yushin, R. Dash, J. Jagiello, J. E. Fischer, and Y. Gogotsi, "Carbide-derived carbons: effect of pore size on hydrogen uptake and heat of adsorption," *Advanced Functional Materials*, 16 [17] 2288 - 2293 (2006).
- ⁴P. Simon and Y. Gogotsi, "Materials for electrochemical capacitors," *Nature Materials*, 7 845 - 854 (2008).
- ⁵Y. Gogotsi, "Nanomaterials Handbook," pp. 800). Boca Raton: CRC Press / Taylor & Francis. (2006).
- ⁶G. Cheng, D.-H. Long, X.-J. Liu, and L. C. Ling, "Fabrication of hierarchical porous carbide-derived carbons by chlorination of mesoporous titanium carbids," *New Carbon Materials*, 24 [3] 243 - 249 (2009).

- ⁷J. Huang, B. G. Sumpter, and V. Meunier, "A Universal Model for Nanoporous Carbon Supercapacitors Applicable to Diverse Pore Regimes, Carbon Materials, and Electrolytes," *Chemistry - A European Journal*, 14 [22] 6614 - 6626 (2008).
- ⁸T. X. Nguyen, J. S. Bae, and S. K. Bhatia, "Characterization and Adsorption Modeling of Silicon Carbide-Derived Carbons," *Langmuir*, 25 [4] 2121 - 2132 (2009).
- ⁹J. S. Bae, T. X. Nguyen, and S. K. Bhatia, "Influence of Synthesis Conditions and Heat Treatment on the Structure of Ti₃SiC₂-Derived Carbons," *Journal of Physical Chemistry C*, 114 [2] 1046 - 1056 (2010).
- ¹⁰M. Inagaki, "Pores in carbon materials-Importance of their control," *New Carbon Materials*, 24 [3] 193-222 (2009).
- ¹¹M. Kormann, H. Ghanem, H. Gerhard, and N. Popovska, "Processing of carbide-derived carbon (CDC) using biomorphic porous titanium carbide ceramics," *Journal of the European Ceramic Society*, 28 [6] 1297 - 1303 (2008).
- ¹²M. Latt, M. Kaarik, L. Permann, H. Kuura, M. Arulepp, and J. Leis, "A structural influence on the electrical double-layer characteristics of Al₄C₃-derived carbon," *Journal of Solid State Electrochemistry*, 14 [4] 543 - 548 (2010).
- ¹³S. Pathak, Z. G. Cambaz, S. R. Kalidindi, J. G. Swadener, and Y. Gogotsi, "Viscoelasticity and high buckling stress of dense carbon nanotube brushes," *Carbon*, 47 [8] 1969-1976 (2009).
- ¹⁴Z. G. Cambaz, G. Yushin, S. Osswald, Y. Mochalin, and Y. Gogotsi, "Noncatalytic synthesis of carbon nanotubes, graphene and graphite on SiC," *Carbon*, 46 [6] 841 - 849 (2008).
- ¹⁵J. Martinez, "Local reactivity descriptors from degenerate frontier molecular orbitals," *Chemical Physics Letters*, 478 [4 - 6] 310 - 322 (2009).
- ¹⁶C. Portet, G. Yushin, and Y. Gogotsi, "Electrochemical performance of carbon onions, nanodiamonds, carbon black and multiwalled nanotubes in electrical double layer capacitors," *Carbon*, 45 [13] 2511 - 2518 (2007).
- ¹⁷Y. Gogotsi, C. Portet, S. Osswald, J. M. Simmons, T. Yildirim, G. Laudisio, and J. E. Fischer, "Importance of pore size in high-pressure hydrogen storage by porous carbons," *International Journal of Hydrogen Energy*, 34 [15] 6314 - 6319 (2009).
- ¹⁸S. K. Bhatia and A. L. Myers, "Optimal Conditions for Adsorptive Storage," *Langmuir*, 22 [4] 1688 - 1700 (2006).
- ¹⁹Z. G. Cambaz, G. N. Yushin, Y. Gogotsi, K. L. Vyshnyakova, and L. N. Pereselentseva, "Formation of Carbide-Derived Carbon on beta-Silicon Carbide Whiskers," *Journal of the American Ceramic Society*, 89 [2] 509 - 514 (2006).
- ²⁰Y. G. Gogotsi, S. Welz, D. A. Ersoy, and M. J. McNallan, "Conversion of silicon carbide to crystalline diamond-structured carbon at ambient pressure," *Nature*, 411 [6835] 283 - 287 (2001).
- ²¹D. J. Twitchen, M. E. Newton, J. M. Baker, T. R. Anthony, and W. F. Banholzer, "Electron-paramagnetic-resonance measurements on the divacancy defect center R4/W6 in diamond," *Physical Review B*, 59 [20] 12900 - 12910 (1999).
- ²²I. Laszlo, M. Kertesz, and Y. Gogotsi, "Simulations of Multi-atom Vacancies in Diamond," *Materials Research Society Symposium Proceedings*, 978 [GG] 13 - 15 (2007).
- ²³I. Laszlo, B. Slepetz, and M. Kertesz, "Energy averaged Fukui index for characterization of bulk matter: application to carbon nanostructures," *in preparation* (2010).
- ²⁴T. Frauenheim, G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, and R. Scholz, "A self-consistent charge density-functional based tight-binding method for predictive materials simulations in physics, chemistry and biology," *Physica Status Solidi B*, 217 [1] 41-62 (2000).
- ²⁵J. M. Baker, "Deducing atomic models for point defects in diamond: The relevance of their mechanism of formation," *Diamond and Related Materials*, 16 [2] 216 - 219 (2007).
- ²⁶N. Fujita, R. Jones, S. Öberg, and P. R. Briddon, "Large spherical vacancy clusters in diamond – Origin of the brown colouration?," *Diamond and Related Materials*, 18 [5 - 8] 843 - 845 (2009).

- ²⁷A. T. Blumenau, R. Jones, T. Frauenheim, B. Willems, O. I. Lebedev, G. Van Tendeloo, D. Fisher, and P. M. Martineau, "Dislocations in diamond: Dissociation into partials and their glide motion," *Physical Review B*, 68 [014115] 1 - 9 (2003).
- ²⁸D. W. Brenner, "Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films," *Physical Review B*, 42 [15] 9458 - 9471 (1990).
- ²⁹R. F. Curl, M. K. Lee, and G. E. Scuseria, "C₆₀ buckminsterfullerene high yields unraveled," *Journal of Physical Chemistry A*, 112 [46] 11951 - 11955 (2008).
- ³⁰B. Sahat, S. Shindo, S. Irlle, and K. Morokuma, "Quantum Chemical Molecular Dynamics Simulations of Dynamic Fullerene Self-Assembly in Benzene Combustion," *Acs Nano*, 3 [8] 2241 - 2257 (2009).
- ³¹L. S. Hounsoume, R. Jones, P. M. Martineau, D. Fisher, M. J. Shaw, P. R. Briddon, and S. Oberg, "Origin of brown coloration in diamond," *Physical Review B*, 73 [12] 125203/125201 - 125203/125208 (2006).
- ³²I. Laszlo, B. Slepetz, M. Kertesz, and Y. Gogotsi, "Simulations of large Multi-atom Vacancies in Diamond," *Diamond and Related Materials*, submitted (2010).
- ³³D. Hyde-Volpe, B. Slepetz, and M. Kertesz, "The [V-C=C-V] Divacancy and the Interstitial Defect in Diamond: Vibrational Properties," *Journal of Physical Chemistry* (2010).
- ³⁴J. C. Palmer, A. Llobet, S.-H. Yeon, J. E. Fischer, Y. Shi, Y. Gogotsi, and K. E. Gubbins, "Modeling the structural evolution of carbide-derived carbons using quenched molecular dynamics," *Carbon*, 48 [4] 1116 - 1123 (2010).
- ³⁵I. Laszlo, B. Slepetz, M. Kertesz, D. Hyde-Volpe, and Y. Gogotsi, "Characterization of large vacancy clusters in diamond by a generational algorithm and TBDFT: Atomistic Basis of the Slit Pore Model," *Chemistry of Materials*, submitted (2010).
- ³⁶S. K. Jain, R. J.-M. Pellenq, J. P. Pukic, and K. E. Gubbins, "Molecular Modeling of Porous Carbons Using the Hybrid Reverse Monte Carlo Method," *Langmuir*, 22 [24] 9942 - 9948 (2006).
- ³⁷M. I. Katsnelson, "Graphene: carbon in two dimensions," *Materials Today*, 10 [1-2] 20-27 (2007).
- ³⁸S. Shivaraman, R. A. Barton, X. Yu, M. V. S. Chandrashekar, J. Park, P. L. McEuen, J. Parpia, H. G. Craighead, and M. G. Spencer, "Free-Standing Epitaxial Graphene," *Nano Letters*, 9 [9] 3100 - 3105 (2009).
- ³⁹J. Robinson, X. Weng, K. Trumbull, R. Cavallero, M. Wetherington, E. Frantz, M. Labella, Z. Hughes, M. Fanton, and D. Snyder, "Nucleation of epitaxial graphene on SiC(0001)," *Acs Nano*, 4 [1] 153 - 158 (2010).
- ⁴⁰Y. Nakayama, "Synthesis, nanoprocessing, and yarn application of carbon nanotubes," *Japanese Journal of Applied Physics*, 47 [10] 8149 - 8156 (2008).
- ⁴¹C. Portet, G. Yushin, and Y. Gogotsi, "Effect of Carbon Particle Size on Electrochemical Performance of EDLC," *Journal of the Electrochemical Society*, 155 [7] A531 - A536 (2008).
- ⁴²S. Osswald, C. Portet, Y. Gogotsi, G. Laudisio, J. P. Singer, J. E. Fischer, V. V. Sokolov, J. A. Kukushkina, and A. E. Kravchik, "Porosity control in nanoporous carbide-derived carbon by oxidation in air and carbon dioxide," *Journal of Solid State Chemistry*, 182 [7] 1733-1741 (2009).
- ⁴³J. Chmiola, G. Yushin, R. Dash, and Y. Gogotsi, "Effect of pore size and surface area of carbide derived carbons on specific capacitance," *Journal of Power Sources*, 158 [1] 765 - 772 (2006).
- ⁴⁴Y. Shi, "A mimetic porous carbon model by quench molecular dynamics simulation," *Journal of Chemical Physics*, 128 [1] 234707-234701 - 234707 (2008).
- ⁴⁵J. C. Palmer, S. J. Jain, K. E. Gubbins, J. E. Fischer, R. K. Dash, and Y. Gogotsi, "Hybrid Reverse Monte Carlo Simulations of Microporous Carbons," pp. 56 - 63. In *Characterization of Porous Solids VIII*. Edited by S. Kaskel, P. Llewellyn, F. Rodriguez-Reinoso, and N. A. Seaton. RSC Publishing, Cambridge, 2009.
- ⁴⁶R. Dash, J. Chmiola, G. Yushin, Y. Gogotsi, G. Laudisio, J. Singer, J. Fischer, and S. Kucheyev, "Titanium carbide derived nanoporous carbon for energy-related applications," *Carbon*, 44 [12] 2489 - 2497 (2006).

- ⁴⁷G. N. Yushin, E. N. Hoffman, A. Nikitin, H. Ye, M. W. Barsoum, and Y. Gogotsi, "Synthesis of nanoporous carbide-derived carbon by chlorination of titanium silicon carbide," *Carbon*, 43 [10] 2075 - 2082 (2005).
- ⁴⁸R. K. Dash, G. Yushin, and Y. Gogotsi, "Synthesis, structure and porosity analysis of microporous and mesoporous carbon derived from zirconium carbide," *Microporous and Mesoporous Materials*, 86 [1-3] 50 - 57 (2005).
- ⁴⁹S. Brunauer, P. H. Emmett, and E. Teller, "Adsorption of Gases in Multimolecular Layers," *Journal of the American Chemical Society*, 60 [2] 309 - 319 (1938).
- ⁵⁰E. H. Kisi, J. A. A. Crossley, S. Myhra, and M. W. Barsoum, "Structure and crystal chemistry of Ti_3SiC_2 ," *Journal of Physics and Chemistry of Solids*, 59 [9] 1437 - 1443 (1998).
- ⁵¹K. Becker and F. Ebert, "Die Kristallstruktur einiger binärer Carbide und Nitride," *Zeitschrift für Physik*, 31 [1] 268 - 272 (1925).
- ⁵²A. H. Gomes de Mesquita, "Refinement of the Crystal Structure of SiC Type 6H," *Acta Crystallographica*[23] 610 - 617 (1967).
- ⁵³Y. G. Gogotsi and M. Yoshimura, "Low-Temperature Oxidation, Hydrothermal Corrosion, and Their Effects on Properties of SiC (Tyranno) Fibres," *Journal of the American Ceramic Society*, 78 [6] 1439 - 1450 (1995).
- ⁵⁴V. Presser, A. Loges, Y. Hemberger, and K. G. Nickel, "Microstructural Evolution of Silica on Single-Crystal Silicon Carbide. Part I: Devitrification and Oxidation Rates," *Journal of the American Ceramic Society*, 92 [3] 724 - 731 (2009).
- ⁵⁵Y. Zhou and Z. Sun, "Electronic structure and bonding properties in layered ternary carbide Ti_3SiC_2 ," *Journal of Physics: Condensed Matter*, 12 [1] L457 - L462 (2000).
- ⁵⁶K. Christiansen and R. Helbig, "Anisotropic oxidation of 6H-SiC," *Journal of Applied Physics*, 79 [6] 3276 - 3281 (1996).
- ⁵⁷K. Christiansen, S. Christiansen, M. Albrecht, H. P. Strunk, and R. Heibig, "Anisotropic oxidation of silicon carbide," *Diamond and Related Materials*, 6 [1] 1467 - 1471 (1997).
- ⁵⁸M. Syväjärvi, R. Yakimova, A.-L. Hysten, and E. Janzen, "Anisotropy dissolution and defect revealing on SiC surfaces," *Journal of Physics: Condensed Matter*, 11 [49] 10041 - 10046 (1999).
- ⁵⁹H. Harima, "Raman scattering characterization on SiC," *Microelectronic Engineering*, 83 [1] 126 - 129 (2006).
- ⁶⁰S. Irle, G. Zheng, M. Elstner, and K. Morokuma, "From C₂ Molecules to Self-Assembled Fullerenes in Quantum Chemical Molecular Dynamics," *Nano Letters*, 3 [12] 1657 - 1664 (2003).
- ⁶¹C. H. Park, B.-H. Cheong, K.-H. Lee, and K. J. Chang, "Structural and electronic properties of cubic, 2H, 4H, and 6H SiC," *Physical Review B*, 49 [7] 4485 - 4493 (1994).
- ⁶²D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, "Construction of tight-binding-like potentials on the basis of density-functional theory: Application to carbon," *Physical Review B*, 51 [19] 12947 - 12957 (1995).
- ⁶³G. Zheng, H. A. Witek, P. Bobadova-Parvanova, S. Irle, D. G. Musaev, R. Prabhakar, K. Morokuma, M. Lundberg, M. Elstner, C. Köhler, and T. Frauenheim, "Parameter Calibration of Transition-Metal Elements for the Spin-Polarized Self-Consistent-Charge Density-Functional Tight-Binding (DFTB) Method: Sc, Ti, Fe, Co, and Ni," *Journal of Chemical Theory and Computation*, 3 [4] 1349 - 1367 (2007).
- ⁶⁴S. Yang and M. Kertesz, "Energetics of Linear Carbon Chains in One-dimensional Restricted Environment," *Physical Chemistry Chemical Physics*, 11 [2] 425 - 430 (2009).
- ⁶⁵S. Yang, M. Kertesz, V. Zolyomi, and J. Kürti, "Application of a Novel Linear/Exponential Hybrid Force Field Scaling Scheme to the Longitudinal Raman Active Mode of Polyynes," *Journal of Physical Chemistry A*, 111 [12] 2434 - 2441 (2007).
- ⁶⁶J. Baker, A. A. Jarzecki, and P. Pulay, "Direct Scaling of Primitive Valence Force Constants: An Alternative Approach to Scaled Quantum Mechanical Force Fields," *Journal of Physical Chemistry A*, 102 [8] 1412 - 1414 (1998).

- ⁶⁷Y. H. Hu, "Simulations of Aberration-Corrected High-Resolution Transmission Electron Microscope Images for Carbyne Chains," *Journal of Physical Chemistry C*, 113 [41] 17751 - 17754 (2009).
- ⁶⁸J. J. P. Stewart, "Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements," *Journal of Molecular Modeling*, 13 [12] 1173 - 1213 (2007).
- ⁶⁹N. Mizorogi and J.-I. Aihara, "PM3 localization energies for the isolated-pentagon isomers of the C₈₄ fullerene," *Physical Chemistry Chemical Physics*, 5 [1] 3368 - 3371 (2003).
- ⁷⁰B. Saha, S. Shindo, S. Irle, and K. Morokuma, "Quantum Chemical Molecular Dynamics Simulations of Dynamic Fullerene Self-Assembly in Benzene Combustion," *Acs Nano*, 3 [8] 2241- 2257 (2009).
- ⁷¹W. Gruber, U. Geckle, M. Bruns, and H. Schmidt, "Si diffusion in magnetron sputtered silicon carbide films deposited on silicon and carbon substrates" *Thin Solid Films*, 518 [1] 396 - 398 (2009).
- ⁷²M. Sabisch, P. Krüger, and J. Pollmann, "Ab initio calculations of structural and electronic properties of 6H-SiC(0001) surfaces," *Physical Review B*, 55 [16] 10561 - 10570 (1997).
- ⁷³L. Pizzagalli, A. Catellani, G. Galli, F. Gygi, and A. Baratoff, "Theoretical study of the (3x2) reconstruction of β -SiC(001)," *Physical Review B*, 60 R5129 - R5132 (1999).
- ⁷⁴S. Osswald, E. Flahaut, and Y. Gogotsi, "In situ Raman spectroscopy study of oxidation of double- and single-wall carbon nanotubes," *Chemistry of Materials*, 18 [6] 1525 - 1533 (2006).
- ⁷⁵J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna, "Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer," *Science*, 313 [5794] 1760 - 1763 (2006).

Appendix: Papers that acknowledged funding from DOE BES for this proposal

Published:

1. T. Tiang, J. Huang, M. Kertesz, Fluxional sigma-Bonds of 2,5,8-Tri-tert-butyl-1,3-diazaphenalenyl Dimers: Stepwise [3,3], [5,5] and [7,7] Sigmatropic Rearrangements via pi-Dimer Intermediates, *Physical Chemistry Chemical Physics*, accepted (2010).
2. S. Yang, M. Kertesz, Energetics of Linear Carbon Clusters in One-dimensional Restricted Environment, *Phys. Chem. Chem. Phys.* 11, 425-430 (2008).
3. I. Laszlo, M. Kertesz, Y. Gogotsi, Simulations of Multi-atom Vacancies in Diamond, *Mater. Res. Soc. Symp. Proc.* **978E**, GG13-15 (2007).
4. I. Laszlo, B. Slepetz, M. Kertesz, Y. Gogotsi, Simulations of large Multi-atom Vacancies in Diamond, *Diamond and Related Materials*, 2010, 19, 1153-1162.
5. D. Hyde-Volpe, B. Slepetz, M. Kertesz, The [V-C=C-V] Divacancy and the Interstitial Defect in Diamond: Vibrational Properties, *J. Phys. Chem. C*, 2010, 114, 9563-9567.
6. I. Laszlo, B. Slepetz, M. Kertesz, D. Hyde-Volpe, Y. Gogotsi, Characterization of large vacancy clusters in diamond by a generational algorithm and TBDFT: Atomistic Basis of the Slit Pore Model, *Mater. Chem. Phys. Chem. Chem. Phys.* 2010, 12, 14017-14022.

Submitted or in preparation:

1. B. Slepetz, M. Kertesz, Divacancy in diamond: a stepwise formation mechanism. In preparation for publication.