Quantum Mechanical Studies of Carbonyl Impurities in Dielectric Polyethylene

A. Huzayyin, S. Boggs(1,2)
(1) The Edward S. Rogers Sr. Dept of Electrical and Computer Engineering
University of Toronto
10 King's College Road
Toronto, ON M5S 3G4, Canada

and **R. Ramprasad**
(2)Institute of Material Science, University of Connecticut
97 North Eagleville Road
Storrs, CT 06269-3136, USA

ABSTRACT

The effect of carbonyl impurities on the solid state physics of polyethylene has been studied through the use of density functional theory. Impurity formation energy, local physical disorder, effect on polyethylene electronic structure, and enhancement of interchain interaction were determined. Estimates of deep traps introduced directly by carbonyl and shallow traps introduced indirectly by carbonyl induced local disorder are in agreement with experimental data and other computational studies.

Index Terms — **Polymers, polyethylene, high field phenomena, carbonyl impurities, computational quantum mechanics, density functional theory.**

1 INTRODUCTION

POLYMERS are used widely as insulation in power apparatus such as capacitors and cables. As a result of the ever increasing design electric fields at which polymer dielectrics are employed, understanding of high field phenomena therein is increasingly important. The present understanding of the physical basis of high field conduction in common insulating polymers, such as polyethylene (PE), is incomplete [1,2] in that an atomic level understanding of the role played by chemical impurities, disorder in the amorphous region, etc. is lacking. High field conduction is generally explained in terms of charge transfer between traps which results from the combined effect of thermal and electric fields [1, 3]. Yet a clear identification of the physical basis of traps is lacking, in spite of extensive effort [1, 2, 4]. Chemical impurities, such as carbonyl groups, are believed to introduce localized states in PE band gap which can act as traps [2]. Discussions with experts indicate that concentration of carbonyl in commercial PE can range to 0.1% as a result of oxygen impurities during polymerization. The presence of carbonyl groups affects high field conduction [5, 6], which is usually attributed to the formation of deep and shallow traps.

In an attempt to improve the fundamental understanding of the effect of chemical impurities on conduction properties, computational studies at the quantum mechanical level, primarily using density functional theory (DFT), have been undertaken. In previous work, C-C and C-H bond lengths, the C-C-C and H-C-C bond angles, and the lattice constants of bulk orthorhombic crystalline PE have been reproduced to acceptable levels of accuracy using DFT [7,8]. While the DFT determinations of the band structure of bulk PE is in good agreement with experiments, the band gap is underestimated by about 25% relative to the experimental value of 8.8 eV [8-12]. This type of an underestimation is typical of DFT. However, changes in electronic structure and band gap relative to the adjacent band edge are well captured by DFT [7, 8, 13]. Excitation energies, such as the electron affinity, have also been calculated using DFT, both for PE-like molecules of varying sizes [14] as well as bulk PE [15]. These computations reproduce correctly the slightly negative electron affinity of PE of -0.5±0.5 eV based on measurements [15]. The negative electron affinity has been correlated with the valence band edge wavefunctions being localized along the polymer chains and the conduction band edge wavefunctions being localized between chains [9, 10].

Few DFT studies have considered the effect of chemical impurities in PE, especially in the context of dielectric applications. Trap depths of chemical (e.g., carbonyl) and physical (e.g., conformational) impurities in PE have been determined within molecular (but not bulk) models of PE [16-18]. The DFT determined energies of neutral and -1 charged molecules, with and without impurities, were used to calculate trap depths. Estimates of trap depths were included in a dc conduc-

---

Manuscript received on 23 September 2009, in final form 17 December 2009.

tion model based on electron mobilities determined from a multiple trapping electron transport model and macroscopic integration of Poisson equation and current density expressed in terms of electric field. The model provided realistic estimates for fields from 10 to 60 kV/mm [19]. The effect of carbonyl groups on crystalline PE has been studied through computation of the energy band diagram and density of states (DOS) using DFT [20]. The present work includes refinement of the preliminary data in [20] through improved representation of the crystalline bulk PE in which impurities are studied.

In this paper, we address the impact of carbonyl impurities on the electronic structure of bulk PE in an amorphous-like setting. Bulk PE is modeled within the constraint of the orthorhombic crystal structure and when this constraint is removed through use of a Core-Shell model which provides a more accurate representation of the impact of carbonyls in amorphous PE. Our objective is to provide a quantum mechanical based description of the impurity states introduced by carbonyl and to discuss their relevance to high field phenomena. Our DFT quantum mechanical computations demonstrate that states created by chemical impurities can act as deep and shallow traps (or hopping sites) and provide estimates of the trap depths. Enhancement of interchain interaction in the vicinity of the carbonyl impurity is established. The methodology adopted in this paper can be applied to study the effect of other chemical impurities on PE.

2 COMPUTATIONAL METHODOLOGY

The ground state configuration of a system of electrons and nuclei forming a molecule or solid can be determined though a combination of DFT (for the electronic structure) and optimization of the nuclear positions based on energy minimization by requiring that the atomic forces (calculated according to the Hellman-Feynman theorem) are small. In the present work, the quantum mechanical part of the electron-electron interaction is approximated using the local density approximation (LDA). In SIESTA, the DFT code employed in the present research [21], the unit cell containing the system of interest is repeated periodically in space through periodic boundary conditions. Pseudopotentials of the Troullier-Martins type [22] are used to eliminate the core electrons, and wavefunctions are expanded using a double zeta plus polarization (DZP) basis set. Geometry optimization is based on requiring each component of the force on each atom to be smaller than 0.05 eV/Å. SIESTA determines the electronic eigenvalues and wavefunctions (i.e., eigenstates) from which various electronic properties and atomic features of the system can be determined, including the electron density, density of states (DOS), and the projected density of states (PDOS). The DOS is the number of electronic states per unit energy and unit cell, as a function of energy. The PDOS is the contribution of any orbital, atom or group of atoms to the DOS of the system. While DFT involves numerous approximations, it remains the most successful implementation of computational quantum mechanics for systems involving hundreds of atoms, as it represents the best tradeoff between the computational time and accuracy [23, 24]. The limitations of DFT are reasonably well understood as a result of its widespread use.

The primitive unit cell of bulk crystalline orthorhombic PE consists of two chains (a and b in Figure 1), with each chain containing two ethylene groups [8]. With the above choice of approximations and parameters, we have determined the lattice constants of bulk PE to be 0.662 nm, 0.457 nm and 0.253 nm, the C-C and C-H bond lengths to be 0.151 nm and 0.112 nm, and the C-C-C and the H-C-H bond angles to be 105.13 and 113.7 degrees, all in good agreement with prior work [8]. The computed band gap of bulk PE was 6.39 eV, within 1% of other LDA estimates [8-11]. The vacuum level was identified according to the procedure described in [25], resulting in an electron affinity of -0.17 eV, in excellent agreement with prior DFT work [10], and within the range of the experimental value of -0.5±0.5 eV [15]. Based on the computed structure, band gap, and electron affinity, and taking into consideration the limitations of DFT, our predictions for bulk orthorhombic PE are satisfactory.

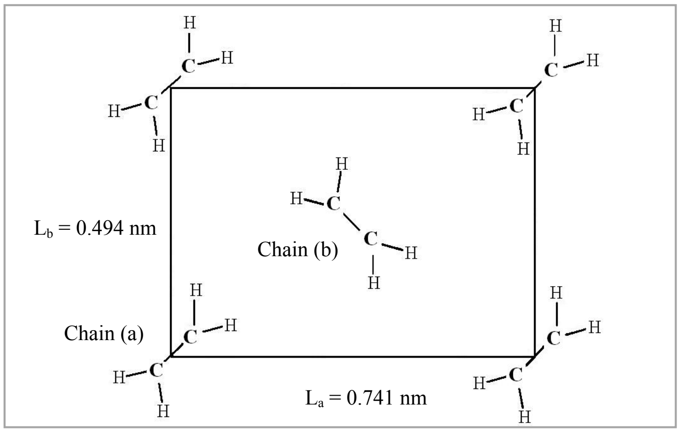

Figure 1. Orthorhombic crystalline structure of PE. Unit cell, formed of chains (a) and (b) shown in XY plane, Z direction is in the paper with a lattice constant L_c = 0.254 nm. Figure modified from [8].

Impurities in the bulk are handled using the supercell approach [26], in which the impurity is placed in an enlarged bulk unit cell, so that the impurity does not interact appreciably with its periodic image. In the present work, an enlarged 192-atom unit cell (or supercell) consisting of eight PE chains, each having eight ethylene groups, was employed to model crystalline PE with an impurity (Figure 2). In addition to the 192-atom supercell which is constrained by the outer orthorhombic boundaries, a second supercell was employed in which the PE chains have considerably more freedom to relax. This structure, shown in Figure 3, consists of a "Core" chain, to which the chemical impurity is added, surrounded by six "Shell" chains. The seven chains are in a supercell large enough to prevent interaction with chains in neighboring replicas. Each of the seven chains consists of 40 carbon atoms and is terminated by a methyl group ($C_{40}H_{82}$). PDOS analysis shows that the terminal methyl group orbitals do not contribute to the CBM and VBM states of short PE chains. Past experimental and theoretical results [2], DFT studies of PE [17-19], and the present DFT computations indicate that a $C_{40}H_{82}$ chain provides a good approximation to the electronic properties of an infinite PE chain. The rationale behind the core-shell model is to study a chemical impurity in a PE chain which is sufficiently long to behave as infinite, while including the effect of neighboring chains in an amorphous like environment in which the chains have freedom to deform as a result of introduction of the impurity. The impurity formation energy is defined as

$$E^{f}[CO] = E[PE+CO] - E[PE] - \tfrac{1}{2} E[O_2] + E[H_2] \qquad (1)$$

where E[PE+CO] is the total energy of the bulk PE including the carbonyl impurity, E[PE] is the total energy of bulk PE without impurities, while $E[O_2]$ and $E[H_2]$ are the energies of an oxygen molecule and a hydrogen molecule respectively in PE [26].

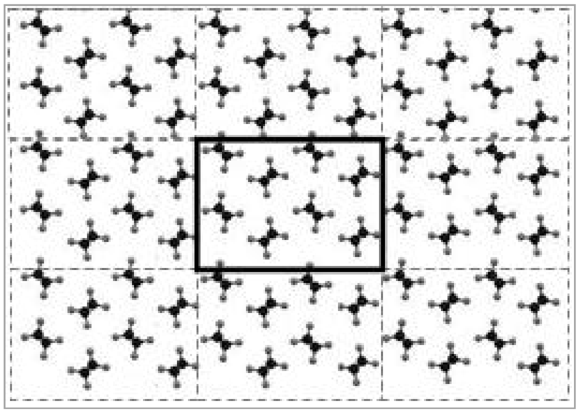

Figure 2. Crystalline bulk unit cell of PE in black frame which creates an infinite bulk through periodic repetitions. Each chain has 8 ethylene groups in z direction (into the paper).

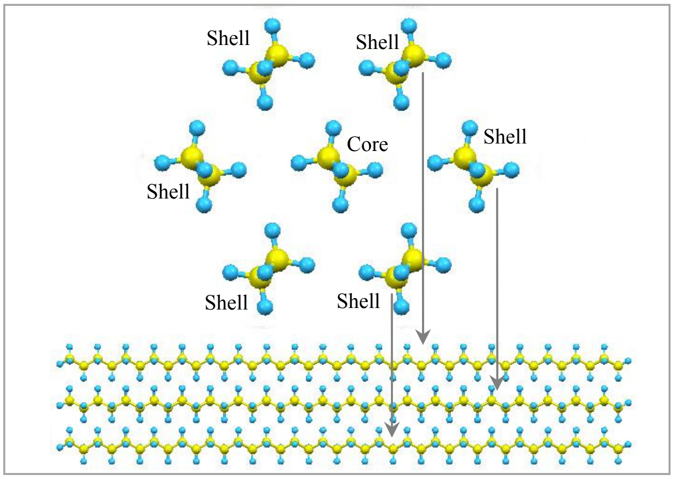

Figure 3. Core-Shell initial structure, in XY plane (above) and ZY plane (below).

3 RESULTS AND DISCUSSION

3.1 CARBONYL IMPURITY IN PE MODELS

3.1.1 CRYSTALLINE ENVIRONMENT

Two hydrogen atoms of an ethylene group are replaced by an oxygen atom in the bulk crystal optimized unit cell. The minimum energy structure of the unit cell with the impurity is determined through DFT and geometry optimization. The resulting O=C bond is a π planar double bond, as confirmed by the bond length, angles, and PDOS, all of which indicate the formation of a carbonyl group. The CBM and VBM energies are within 0.7% of those of the structure without the impurity. The perturbation of the PE structure and band gap caused by the impurity is less than that in [20] as a result of modeling which more closely approximates a single, isolated defect in an infinite solid [26]. On the basis of equation (1), the carbonyl formation energy in the crystal bulk model is 1.77 eV. The carbonyl impurity introduces local disorder in the PE structure, as the ethylene groups close to the carbonyl impurity have shorter carbon-carbon bond lengths than those further away. In the context of amorphous PE, the crystal bulk model is over constrained with an artificial periodicity. In the crystal bulk model with carbonyl, symmetry is preserved, and the PE chain backbones are parallel with almost fixed separations. Such features are not characteristic of amorphous regions. In the next section we study carbonyl impurity in the "Core-Shell" model which was developed to study chemical impurity states in amorphous PE by capturing more features of the amorphous state.

3.1.2 CORE-SHELL ENVIRONMENT

The Core chain is surrounded by the Shell chains which constitute the first layer of neighboring chains in a crystalline environment. The Shell chains provide the Core chain with a reasonable approximation of a surrounding amorphous environment in that the Shell chains are free to distort around the impurity without the constraint of a surrounding crystalline environment. When an impurity is added to the Core chain, the minimum energy structure, as determined through DFT and geometry optimization, involves distortion of the Core and Shell chains in the vicinity of the impurity from crystalline periodicity. The minimum energy structure of a Core-Shell model with a Core chain which includes a carbonyl impurity is shown in Figure 4 along with the structure of a similar part of the crystal bulk model. The carbonyl formation energy in the Core-Shell model is 1.63 eV, slightly lower than that in the crystalline environment, as would be expected, as the Core-Shell system has more opportunity to decrease its energy through relaxation. The disorder caused by introduction of a carbonyl group is more pronounced in the Core-Shell model than the crystal bulk model.

3.2 EFFECT ON ELECTRONIC STRUCTURE

The DOS of the Core-Shell structure with the carbonyl impurity is shown in Figure 5. The DOS plots are generated by fitting Gaussian functions of 0.1 eV width to the energy eigenvalues determined using DFT. The carbonyl group introduces two impurity states into the band gap, an occupied state above the VBM and unoccupied state below the CBM. These states were identified as carbonyl states through comparison with the DOS of PE without the impurity and the PDOS which determines how much each atom and orbital in the structure contributes to each state. The PDOS and wavefunction plots show that the unoccupied impurity state is a π anti-bonding 2p (π^{*}_{2p}) orbital, and the occupied impurity state is a π bonding 2p (π_{2p}) orbital. The square of the unoccupied impurity state wavefunction, which indicates the spatial distribution of the electron location probability for that state, is shown in Figure 6.

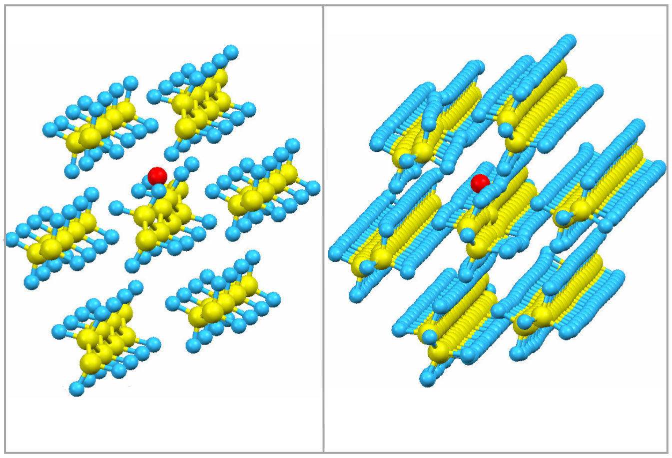

Figure 4. To the right, final Core-Shell structure including a carbonyl impurity in the Core chain. To the left, an equivalent part of the crystal bulk structure. Bending of the Shell chains in the vicinity of the carbonyl group is evident as compared to the crystal bulk model or the initial Core-Shell structure without impurities in Figure 3.

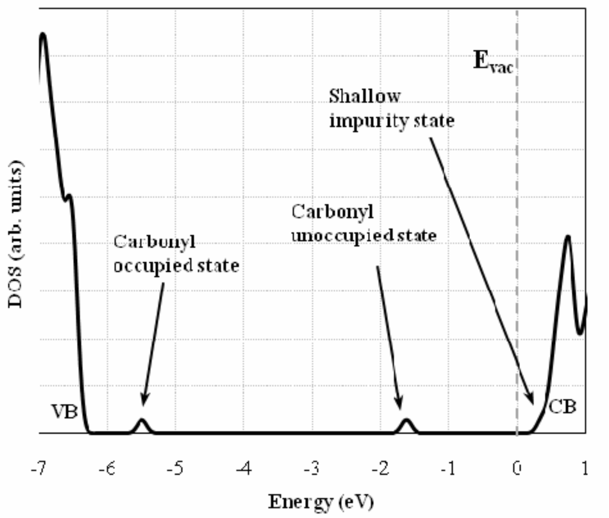

Figure 5. DOS of Core-Shell structure showing impurity states from carbonyl group. The vacuum level is taken as reference energy.

The DOS of the Core-Shell model with carbonyl impurity is similar to that of the crystal bulk model but with a slightly larger band gap of 6.78 eV. The energy of carbonyl impurity states relative to the closest band edge in the Core-Shell environment is very close (within 8%) to that in a crystalline environment. The similar effect of the carbonyl impurity on the DOS of both the over constrained crystal bulk model and the under constrained Core-Shell model suggests that the DOS of both models provides reasonably accurate data for semi-crystalline PE. We feel that the Core-Shell model represents an acceptable approximation to amorphous PE which can be implemented with a reasonable number of atoms and periodic boundary conditions. Since impurities are more likely to be incorporated into the amorphous regions, the following discussion will be based on the Core-Shell model.

The carbonyl impurity is indirectly responsible for introduction of an unoccupied state slightly below the CBM. The PDOS analysis and wavefunction plots show that the orbitals of the carbon atoms adjacent to the carbonyl impurity are the main source of the shallow impurity state. The physical disorder which the carbonyl impurity introduces to neighboring ethylene groups is the main cause of this state. The PDOS of a carbon atom adjacent to the carbonyl impurity and a carbon atom further from it are shown in Figure 7.

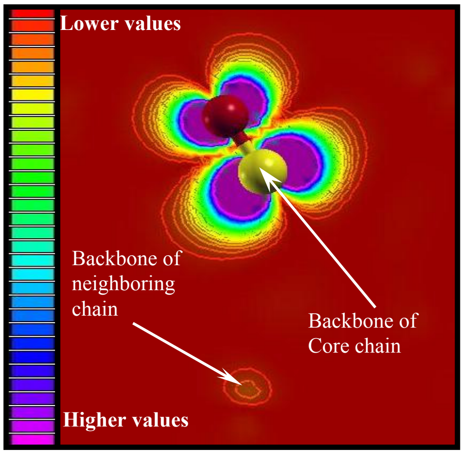

Figure 6. Square of the wavefunction of the unoccupied carbonyl impurity state in the Core-Shell structure plotted in the XY plane at a Z plane passing through the carbonyl group. The plot scale and location were selected to demonstrate the low amplitude peak of the wavefunction at neighboring chain.

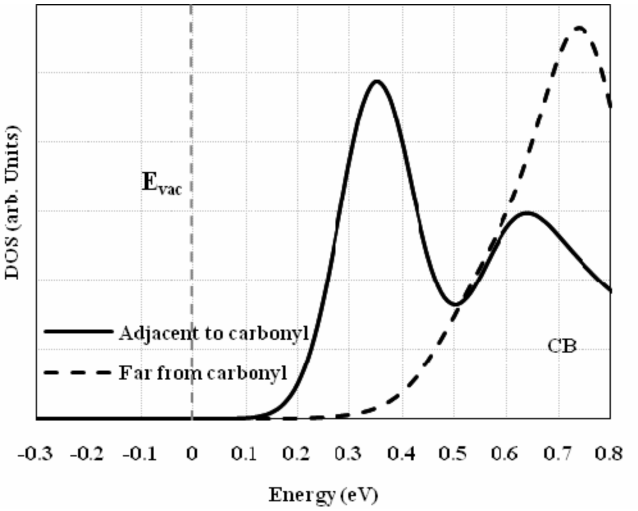

Figure 7. PDOS of a carbon atom adjacent to carbonyl group and a carbon atom far from carbonyl group in the same chain. The vacuum level is taken as reference energy. Distortion of the carbon atoms adjacent to the carbonyl group introduces a shallow impurity state, within 0.4 eV below the CBM.

3.2.1 INTERCHAIN INTERACTION

Interchain interaction in the vicinity of a carbonyl impurity was identified through analysis of PDOS, wavefunctions, and charge density. While the band gap impurity states are caused mainly by the carbonyl orbitals, PDOS analysis shows minor contributions from orbitals associated with neighboring chains. The impurity state wavefunctions have low amplitude peaks around neighboring chains in spite of being localized mainly around the carbonyl group, as shown in Figure 6. As shown in Figure 8, charge density plots reveal an increase of interchain interaction caused by the carbonyl impurity [27]. The charge density contour lines are extended across the chains only in the vicinity of the carbonyl group. The interchain interaction introduced by carbonyl should enhance interchain charge transfer and thereby affect high field conduction. This effect will be a topic of future investigation.

3.3 HIGH FIELD PHENOMENA

The carbonyl impurity introduces a deep trap at ~2 eV and a shallow hopping state within 0.4 eV below the CBM. The latter is of much greater practical significance than the former and probably accounts for the effect of carbonyl on conduction in PE [6]. We have preliminary results for other very common chemical impurities which introduce traps at about 0.9 and 1.1 eV below the CBM, which is in the range of the experimentally determined "effective trap depth" in PE. The combination of carbonyl and other common impurities which act as chemical substituent in or as side groups to the polyethylene backbone or defects therein, and the states which they introduce into the band gap, may account for the high field conduction properties of PE. In addition, the overlap between impurity state wavefunctions and those of adjacent polymer backbones promotes tunneling between such states which is also relevant to high field conduction [1,3].

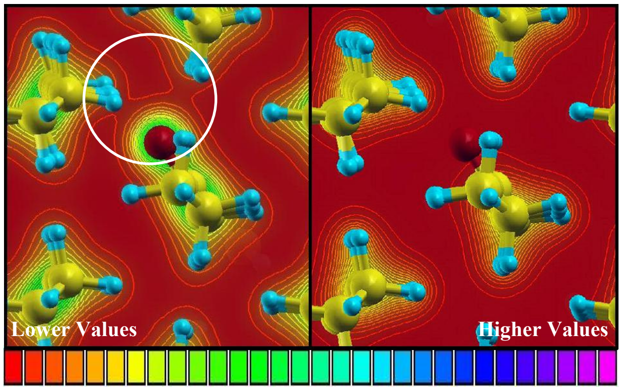

Figure 8. To the left, charge density contour plot in the vicinity of the carbonyl impurity. To the right, charge density away from the carbonyl impurity. The plot scale was chosen to demonstrate the effect of carbonyl impurity in increasing interchain charge density. The plots are in the XY plane where the Z direction is along the chain backbone and into the paper.

4 FUTURE WORK

Future work, much of which is already complete and nearly ready for submission, includes investigating the effects of other chemical impurities commonly found in PE. As noted above, we have preliminary results which identify chemical impurities which create trap states at ~0.9 and ~1.1 eV below the CBM, which is close to the experimentally determined effective trap depth for PE.

REFERENCES

[1] S. Boggs, "Very High Field Phenomena in Dielectrics", IEEE Trans. Dielectr. Electr. Insul., Vol. 12, pp.929-938, 2005.

[2] G. Teyssedre and C. Laurent, "Charge Transport Modeling in Insulating Polymers: From Molecular to Macroscopic Scale", IEEE Trans. Dielectr. Electr. Insul., Vol. 12, pp.857-874, 2005.

[3] M. Meunier, N. Quirke and A. Aslanides, "Characterisation of Charge Carrier Traps in Polymeric Insulators", IEEE Conf. Electr. Insul. Dielectr. Phenomena (CEIDP), pp.21-24, 2000.

[4] H. J. Wintle, "Charge Motion and Trapping in Insulators Surface and Bulk Effects", IEEE Trans. Dielectr. Electr. Insul., Vol. 6, pp.1-10, 1999.

[5] C. Banmongkol, T. Mori and T. Mizutani, "High Field Phenomena in LDPE with Various Physical and Chemical Properties", IEEE Conf. Electr. Insul. Dielectr. Phenomena (CEIDP), Minneapolis, USA, pp.556-559, 1995.

[6] M. M. Perlman and A. Kumar, "Injection-limited trap modulated hopping conduction in carbonyl doped polyethylene", J. Appl. Phys. Vol. 72, pp.5265-5268, 1992.

[7] B. Montanari and R.O. Jones, "Density Functional Study Of Crystalline Polyethylene", Chem. Phys. Letts., Vol. 272, pp.347-352, 1997.

[8] M. S. Miao, M-L. Zhang, V. E. Van Doren, C. Van Alsenoy and J. L. Martins, "Density Functional Calculations on the Strucutre of Crystalline Polyethylene Under High Pressure", J. Chem. Phys., Vol. 115, pp.11317-11324, 2001.

[9] S. Serra, E. Tosatti, S. Iarlori, S. Scandolo and G. Santoro, "Interchain Electron states in Polyethylene", Phys. Rev. B, Vol. 62, pp.4389-4393, 2001.

[10] M. C. Righi, S. Scandolo, S. Serra, S. Iarlori, E. Tosatti and G. Santoro, "Surface States and Negative Electron Affinity in Polyethylene", Phys. Rev. Letts., Vol. 87, pp.076802-076806, 2001.

[11] F. Picaud, A. Smogunov, A. Dal Corso and E. Tosatti1, "Complex Band Structures And Decay Length In Polyethylene Chains", J. Phys. Condensed Matter, Vol. 15 p.3731-3740, 2003.

[12] J. M. Andre, D. P. Vercauteren, V. P. Bodart and J. G. Fripiat, "Ab Initio Calculations of the Electronic Structure of Helical Polymers", J. Computational Chem., Vol. 5, pp.535-547, 1984.

[13] M. S. Miao, P. E. Van Camp, V. E. Van Doren, J. J. Ladik and J. W. Mintmire, "Conformation and Electronic Structure of Polyethylene: A Density-Functional Approach", Phys. Rev. B, Vol. 54, pp.10430-10435, 1996.

[14] M. Meunier, N. Quirke and D. Binesti, "The Calculation of the Electron Affinity of Atoms and Molecules", Moelcular Simulation, Vol. 23, pp.109-125, 1999.

[15] R. Dudde and B. Reihl, "Complete Electronic Strucutre of Oriented Films of Hexatriacontane", Chem. Phys. Letts., Vol. 196, pp. 91-96, 1992.

[16] M. Meunier, N. Quirke and A. Aslanides, "Molecular Modeling of Electron Traps in Plymer Insulators: Chemical Defects and Impurities", J. Chem. Phys., Vol. 115, pp.2876-2881, 2001.

[17] M. Meunier, N. Quirke and D. Binesti, "Electron Trapping in Polymer Insulators: A New Approach Using Molecular Modelling", Intern. Conf. Electric Charge in Solid Insulators, Tours, France, pp.66-72, 1998.

[18] M. Meunier, N. Quirke, D. Binesti, G. Martic and J. M. Fourmigue, "Identification of Space Charge in Cable Insulator: A New Approach Using Molecular Simulation", IEEE Conf. Electr. Insul. Dielectr. Phenomena (CEIDP), Minneapolis, USA, 1997, pp.68-71, 1997.

[19] J. A. Anta, G. Marcelli, M. Meunier and N. Quirke, "Models of Electron Trapping and Transport in Polyethylene: Current-Voltage Characteristics", J. Appl. Phys., Vol. 92, pp.1002-1008, 2002.

[20] A. Huzayyin, S. Boggs, R. Ramparsad, "Effect of Carbonyl Impurities on Polyethylene Band Structure Using Density Functional Theory", IEEE Conf. Electr. Insul. Dielectr. Phenomena (CEIDP), Québec City, Canada, pp.343-356, 2008.

[21] SIESTA 2.0 User Guide, 2006.

[22] N. Troullier and J. L. Martins, "Efficient Pseudopotentials for Plane-Wave Calculations", Phys. Rev. B. Vol. 43, pp.1993-2006, 1991.

[23] K. Capelle, "A Bird's-Eye View of Density Functional Theory", Brazilian J. of Phys., Vol. 36, pp.1318-1343, 2006.

[24] M. H. Gordon and E. Artacho, "Chemistry on the Computer", Physics Today, pp.58-63, 2008.

[25] R. Ramprasad, P. von Allmen and L. R. C. Fonseca, "Contributions to the Work Function: A Density Functional Study of Adsorbates at Graphene Ribbon Edges", Phys. Rev. B, Vol. 60, pp.6023-6027, 1999.
[26] C. G. Van de Walle and J. Neugebauer, "First-Principles Calculations for Defects and Impurities: Applications to III-Nitrides", Appl. Phys. Rev., Vol. 95, pp.3851-3879, 2004.
[27] K. G. Nakamura, K. Ishioka, M. Kitajima, A. Endou, M. Kubo and A. Miyamoto, "Theoretical Calculation of Hydrogen Molecule in Silicon", J. Chem. Phys., Vol. 108, pp. 3222-3225, 1998.

A. A. Huzayyin (S'03) was born in Cairo, Egypt. He is a Ph.D. student at the ECE Department, University of Toronto. He received the B.Sc. degree in electrical power & machines engineering in 2001 and the M.Sc. degree in 2004 from Cairo University, Egypt. His M.Sc. research work was in the field of magneto-hydrodynamics. From 2001 to 2005, Mr. Huzayyin worked as a research assistant, a demonstrator and later as an assistant lecturer at the Faculty of Engineering, Cairo University. During that period he was involved in various research projects most of which was related to low frequency electromagnetic applications in energy systems. In his Ph.D. research, he is applying computational quantum mechanics and molecular modeling in studying high field phenomena in insulating polymers.

S.A. Boggs (F'92) was graduated with a B.A. from Reed College in 1968 and received the Ph.D. and MBA degrees from the University of Toronto in 1972 and 1987, respectively. He spent 12 years with the Research Division of Ontario Hydro, Canada. He was elected an IEEE Fellow for his contributions to understanding of SF6-insulated systems. From 1987 to 1993, he was Director of Research and Engineering at Underground Systems, Inc. He is presently Director of the Electrical Insulation Research Center and Research Professor of Materials Science, Electrical Engineering, and Physics at the University of Connecticut as well as an Adjunct Professor of Electrical and Computer Engineering at the University of Toronto.

R. Ramprasad graduated from the Indian Institute of Technology, Madras, India, with a B.Tech. in metallurgical engineering, and from the University of Illinois, Urbana-Champaign, with a Ph.D. in materials science and engineering. After six years at Motorola, Inc., where he worked on problems related to field emission for flat panel display applications, advanced dielectric and magnetic materials, and metamaterials for RF and microwave applications, he joined the Department of Materials Science and Engineering at the University of Connecticut as a faculty member. Dr. Ramprasad's area of expertise is in the first principles modeling of materials using density functional theory. He is the author of about 50 peer-reviewed journal papers, numerous invited presentations and conference papers, and four issued patents.