

Defense Threat Reduction Agency 8725 John J. Kingman Road, MS 6201 Fort Belvoir, VA 22060-6201



TECHNICAL REPORT

Doped boron carbide-based polymers: Fundamental studies of a novel class of materials for enhanced neutron detection

Distribution Statement A. Approved for public release; distribution is unlimited.

March 2016

HDTRA1-09-1-0060

Jeffry A. Kelber and Peter A. Dowben

Prepared by: University of North Texas 1155 Union Circle Denton, TX 76203

DESTRUCTION NOTICE:

Destroy this report when it is no longer needed. Do not return to sender.

PLEASE NOTIFY THE DEFENSE THREAT REDUCTION AGENCY, ATTN: DTRIAC/ J9STT, 8725 JOHN J. KINGMAN ROAD, MS-6201, FT BELVOIR, VA 22060-6201, IF YOUR ADDRESS IS INCORRECT, IF YOU WISH IT DELETED FROM THE DISTRIBUTION LIST, OR IF THE ADDRESSEE IS NO LONGER EMPLOYED BY YOUR ORGANIZATION.

R	EPORT DO	Form Approved					
		wing instructions	OMB No. 0704-0188 searching existing data sources, gathering and maintaining the				
data needed, and completing a this burden to Department of D 4302. Respondents should be valid OMB control number. PL	and reviewing this collection of befense, Washington Headqua aware that notwithstanding ar EASE DO NOT RETURN YOU	information. Send comments reg ters Services. Directorate for Info	arding this burden estimate or an rmation Operations and Reports n shall be subject to any penalty	y other aspect of th (0704-0188) 1215	is collection of information, including suggestions for reducing Jefferson Davis Highway, Suite 1204, Arlington, VA 22202- v with a collection of information if it does not display a currently		
1. REPORT DATE (DD	D-MM-YYYY)	2. REPORT TYPE			3. DATES COVERED (From - To)		
4. TITLE AND SUBTIT	LE				5a. CONTRACT NUMBER		
				-	5b. GRANT NUMBER		
					5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)					5d. PROJECT NUMBER		
			5e. TASK NUMBER				
				-	5f. WORK UNIT NUMBER		
7. PERFORMING ORG	GANIZATION NAME(S		8. PERFORMING ORGANIZATION REPORT NUMBER				
9. SPONSORING / MC			10. SPONSOR/MONITOR'S ACRONYM(S)				
					11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT							
13. SUPPLEMENTARY NOTES							
14. ABSTRACT							
15. SUBJECT TERMS							
				18. NUMBE	R 19a. NAME OF RESPONSIBLE PERSON		
16. SECURITY CLASSIFICATION OF:				OF PAGES			
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)		

U.S. Customary Units	Multiply by Divide by [†]		International Units	
Length/Area/Volume				
inch (in)	2.54	$ imes 10^{-2}$	meter (m)	
foot (ft)	3.048	$ imes 10^{-1}$	meter (m)	
yard (yd)	9.144	$ imes 10^{-1}$	meter (m)	
mile (mi, international)	1.609 344	$\times 10^3$	meter (m)	
mile (nmi, nautical, U.S.)	1.852	$\times 10^3$	meter (m)	
barn (b)	1	$ imes 10^{-28}$	square meter (m ²)	
gallon (gal, U.S. liquid)	3.785 412	$\times 10^{-3}$	cubic meter (m ³)	
cubic foot (ft ³)	2.831 685	$\times 10^{-2}$	cubic meter (m ³)	
Mass/Density				
pound (lb)	4.535 924	$ imes 10^{-1}$	kilogram (kg)	
unified atomic mass unit (amu)	1.660 539	$\times 10^{-27}$	kilogram (kg)	
pound-mass per cubic foot (lb ft ⁻³)	1.601 846	$ imes 10^1$	kilogram per cubic meter (kg m ⁻³)	
pound-force (lbf avoirdupois)	4.448 222		newton (N)	
Energy/Work/Power				
electron volt (eV)	1.602 177	$\times 10^{-19}$	joule (J)	
erg	1	$\times 10^{-7}$	joule (J)	
kiloton (kt) (TNT equivalent)	4.184	$ imes 10^{12}$	joule (J)	
British thermal unit (Btu) (thermochemical)	1.054 350	$\times 10^3$	joule (J)	
foot-pound-force (ft lbf)	1.355 818		joule (J)	
calorie (cal) (thermochemical)	4.184		joule (J)	
Pressure				
atmosphere (atm)	1.013 250	$\times 10^{5}$	pascal (Pa)	
pound force per square inch (psi)	6.984 757	$\times 10^3$	pascal (Pa)	
Temperature				
degree Fahrenheit (°F)	$[T(^{\circ}F) - 32]/1.8$		degree Celsius (°C)	
degree Fahrenheit (°F)	[T(°F) + 459.67]/1.8		kelvin (K)	
Radiation		10		
curie (Ci) [activity of radionuclides]	3.7	$\times 10^{10}$	per second (s^{-1}) [becquerel (Bq)]	
roentgen (R) [air exposure]	2.579 760	$\times 10^{-4}$	coulomb per kilogram (C kg ⁻¹)	
rad [absorbed dose]	1	$\times 10^{-2}$	joule per kilogram (J kg ⁻¹) [gray (Gy)]	
rem [equivalent and effective dose]	1	$ imes 10^{-2}$	joule per kilogram (J kg ⁻¹) [sievert (Sv)]	

UNIT CONVERSION TABLE U.S. customary units to and from international units of measurement $\!\!\!\!\!^*$

*Specific details regarding the implementation of SI units may be viewed at <u>http://www.bipm.org/en/si/</u>. *Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.

Please answer all sections of the document. You are welcome to use figures and tables to complement or enhance the text. For annual reports, please only describe work for the period of performance (July 1, 2013 - June 30, 2014). For final reports, please describe the comprehensive effort.

Grant/Award #: HDTRA1-09-1-0060 PI Name: Jeffry. A. Kelber and Peter A. Dowben Organization/Institution: University of North Texas and University of Nebraska-Lincoln Project Title: Doped boron carbide-based polymers: Fundamental studies of a novel class of materials for enhanced neutron detection

What are the major goals of the project?

List the major goals of the project as stated in the approved application or as approved by the agency. If the application lists milestones/target dates for important activities or phases of the project, identify these dates and show actual completion dates or the percentage of completion. Generally, the goals will not change from one reporting period to the next. However, if the awarding agency approved changes to the goals during the reporting period, list the revised goals and objectives. Also explain any significant changes in approach or methods from the agency approved application or plan.

The overall goal of this basic research has been to develop novel, boron carbide-based polymers with novel chemical and electronic structures to enhance sensitivity to neutron detection. This will be accomplished by the following:

1) Developing Novel Boron-Carbide Materials consisting of carborane precursors connected by systematically varied linking units (e.g., benzene, pyridine, diaminobenze), thus systematically altering such electronic structure properties as band gap and electron-hole separation lifetime.

2) Determining how the electronic properties of these materials impact sensitivity to thermal neutron detection, especially at low or zero detector bias, while maintaining gamma blindness.

3) Determining and controlling metal/boron carbide interactions to minimize Schottky barrier formation and metal diffusion into the boron carbide. These are essential issues to the implementation of boron carbide-based films in practical detector structures.

What was accomplished under these goals?

For this reporting period describe: 1) major activities; 2) specific objectives; 3) significant results, including major findings, developments, or conclusions (both positive and negative); and 4) key outcomes or other achievements. Include a discussion of stated goals not met. As the project progresses, the emphasis in reporting in this section should shift from reporting activities to reporting accomplishments.

I) Major Activities:

1. <u>Film deposition and spectroscopic characterization of chemical and electronic structure</u> This activity focused on deposition of films by two methods: (a) co-condensation of orthocarborane and aromatic precursors in UHV followed by electron bombardment to induce cross-linking, and (b) plasma-enhanced chemical vapor deposition (PECVD) of films using ortho-carborane or meta-carborane (ortho or meta $B_{10}C_2H_{12}$) precursors and benzene, diaminobenzene, or pyridine. Spectroscopic characterization has involved ultraviolet photoemission spectroscopy (UPS) for understanding valence band density of states, and x-ray excited photoemission (XPS) in concert with FTIR for understanding chemical structure, and how carborane and aromatic species are bonded to each other.

The deposition of thin films (< ~ 200 Å) by e-beam bombardment has been useful for investigating chemical bonding interactions and effects on electronic structure and electron-hole separation. The ability to deposit films of consistent composition at thicknesses >> 1000 Å— requiring PECVD-- is critical to the formation of films of sufficient thickness for effective neutron detection. The goal of consistent composition was recently addressed with the addition of mass-flow controllers for the PECVD chamber, to replace manually-controlled leak valves.

2. <u>Electronic Structure Calculations (collaboration with Prof. Jincheng Du, UNT Dept. of Mat.</u> <u>Sci.</u>): Spectroscopic characterizations were analyzed with the help of density functional theory (DFT)-based theoretical calculations carried out in collaboration with Prof. Jincheng Du and students within the Dept. of Materials Science and Engineering at UNT. These results were used to gain greater insight into the experimental results regarding chemical bonding interactions and valence band electronic structure.

3. <u>Diode Detector Formation and testing</u>: Diode structures were assembled from PECVD of ortho-carborane/aromatic films (p-type) on n-type Si substrates. Ti/Au electrodes were then deposited, and I-V behavior determined in the forward and backward bias directions to test for leakage current (reverse bias) and potential Schottky barrier formation (forward bias).

4. Neutron voltaic measurements: thermal and non-thermal neutrons: Neutron voltaic measurements, initiated during the previous reporting period, have been continued and extended. This effort relates film electronic structure (band gap, electron-hole separation) to charge sweep out efficiencies by measuring sensitivity to neutrons from a D-T neutron source (Thermo Scientific MP 320 neutron generator), with added value obtained by using a Cd filter to test for gamma blindness. Studies have focused on ortho-carborane/aromatic composite films, with a particular focus on pyridine-containing films and the role of N in the detection of non-thermal neutrons.

II) Specific Objectives

1. Film deposition and spectroscopic characterization of chemical and electronic structure

The specific objectives were to deposit thin films by electron beam-induced cross linking in order to study chemical and electronic structure, and to deposit, by PECVD, carborane and carborane/aromatic-derived films of sufficient thickness (>>1000 Å) to make diode structures for neutron detection, and to focus on bonding interactions for carborane-derived films containing pyridine. Possible differences in electron beam-induced cross linking and PECVD films arise from the fact that pyridine readily polymerizes under PECVD conditions, and larger relative concentrations of pyridine compared to the boron carbide icosahedra can be obtained under these conditions. Core level photoemission yields insights into pyridine/boron carbide relative composition and chemical bonding, while valence band spectra provided information regarding valence band structure. Additionally, spectra acquisition with every ~ 1000 Å or so added film thickness (to total film thickness up to ~ 7000 Å) provided confirmatory information on the consistency of film compositions with depth.

2. <u>Electronic Structure Calculations (collaboration with Prof. Jincheng Du, UNT Dept. of Mat.</u> <u>Sci.)</u> The specific objective here was to compare experimental core level binding energies with binding energies calculated by various methods for specific bonding configurations. This provided substantial insight concerning chemical bonding in films containing aromatic species. This exercise involved several different basis sets in order to determine which basis set gave the best results in terms of agreement. Additionally, limited DFT calculations were carried out for valence band structures of boron carbide and aromatic/boron carbide films. This allows us to assign specific features of the valence band spectra in terms of C or B related carboranederived states, as opposed to aromatic- derived states.

3. <u>Diode detector formation</u> I-V curves were acquired to determine the possible existence of Schottky barriers, as well as to examine the effects of possible defect states on leakage

currents—both important factors governing detector sensitivity, especially at low biases. Additionally, such measurements reveal whether metal diffusion into the boron carbide can occur under conditions of voltage bias.

4. <u>Neutron Voltaic Measurements.</u> The goal here was to determine (a) if pyridine or other aromatic additions would enhance charge collection resulting from thermal neutron interactions, while (b) still being blind to gamma radiation and with the hope (c) the incorporation of N into the films permitted detection of non-thermal neutrons, because of the small but persistent neutron cross-section of nitrogen to higher neutron energies.

III) Significant Results

1. <u>Film deposition and spectroscopic</u> <u>characterization of chemical and electronic</u> <u>structure</u>



Figure 1. Representative structures for (a) PECVD BC, (b) PECVD BC:DAB and (c) PECVD BC:PY with a high pyridine/orthocarborane ratio. (Hydrogen atoms omitted for clarity.)

The types of structures developed by electron beam induced cross linking are shown schematically in Fig. 1a, b. Such boron carbide films containing either B-B bonding or interstitial C (Fig. 1a) [1]. The dominance of B-B bonding rather than direct bonding to carborane C sites (Fig. 1a) is consistent with gas phase studies showing that near-threshold ionization of $B_{10}C_2H_{12}$ icosahedra induces B-H bond scission and H₂ elimination at B sites directly opposite C sites in the icosahedron [2]. Electron beam-induced cross linking of orthocarboranes with benzene or 1,4-diaminobenzene or pyridine species yields structures of the type shown schematically in Fig. 1b, with carborane/aromatic ratios ~ 1:1 [3-5].

UPS spectra of electron beaminduced cross linking created films with different aromatic units are shown in Fig. 2. In all cases (benzene (BNZ); 1, 4diaminobenzene (DAB); and pyridine



Figure 2: UPS valence band measurements for PECVD BC ($B_{10}C_2H_x$) and orthocarborane copolymers with benzene (BNZ); pyridine (py) and 1,4-diaminobenzene (DAB). Numbers and arrows mark position of valence band maximum relative to Fermi level. For the aromatically modified films, the carborane/aromatic ratio is ~ 1/1. From [5]



Figure 3. Enhanced hole separation in BC:aromatic copolymers and composites (BC:DAB shown). Schematic showing that (a) electron-hole pair creation in BC:aromatic copolymer or matrix should result in (b) electron-hole separation on adjacent carborane-aromatic units (DAB shown), resulting in (c) enhanced electron pulse height in neutron detection. From [5]. (PY)) the boron carbide/aromatic ratio is ~ 1:1. The data in Fig. 2 indicate that the states near the valence band maximum (VBM) are associated with the aromatic moiety and that the states deeper within the valence band are associated with the carborane moiety [5]. The data in Fig. 2 therefore strongly suggest that the states near the conduction band minimum (CBM) should be associated with carborane moiety. leading the situation shown schematically in Fig. 3 [5]. Promotion of an electron across the band gap should result in a hole localized on the aromatic moiety and an electron on the carborane moiety (Fig. 3a,b). This would result in greater electron-hole

(e-h) separation, and therefore enhanced signal in neutron voltaic experiments for aromatic films relative to pure carborane-derived boron carbide $(B_{10}C_2H_x)$ (Fig. 3c,d).

Experimental evidence that enhanced e-h separation does occur in boron carbide: aromatic (BC:aromatic) films is shown in Fig. 4. $B_{10}C_2H_x$ (BC) and BC:DAB films were deposited by ebeam crosslinking on Co patterned substrates for subsequent magnetoresistance measurements [6]



Figure 4. Evidence of enhanced e-h separation in BC:aromatic copolymer from magnetoresistance measurements. I-V Curves with an external magnetic field of 0 T (black line), 0.1 T (purple line), 0.5 T (blue line), 0.8 T (green line) and 1 T (red line) for thin films of cross-linked ortho-carborane with (a) and without (b) 1,4-diaminobenzene (DAB). (The inset in (a) shows the structural model of $B_{10}C_2H_x$: DAB.) Formation of an e-h dipole (c) provides a potential barrier to charge motion, accounting for the low current plateau near zero bias in (a) but not observed in (b) (arrows). Adopted from [6]

I-V magnetoresistance (MR) curves for the BC:DAB film exhibit a plateau at low bias voltage values (Fig. 4a). This plateau region is not observed for pure BC films (Fig. 4b). The data indicate that the BC:DAB film exhibits a potential barrier to e-h transport under applied field consistent with formation of an e-h dipole (Fig. 4c). The data in Fig. 4 thus indicate that BC:DAB films do exhibit the enhanced e-h physical separation predicted (Fig. 3) by the trends in valence band electronic structure (Fig. 2). BC:aromatic films of sufficient thickness should therefore exhibit enhanced sensitivity to thermal neutrons in neutron voltaic measurements.

In order to obtain films sufficiently thick for neutron voltaic studies (~ 5000 Å or more), PECVD is required. PECVD BC films exhibit many structural similarities to films created by electron beam-induced crosslinking, except with a greater concentration of C and B in exicosahedral enviroments (as in Fig. 1a), and with a VBM ~ 1.5 eV closer to the Fermi level than

corresponding than films formed by electron beam induced crosslinking, probably due to a greater concentration of defects [7]. Importantly, we have obtained PECVD BC:PY films with pyridine>carborane ratios well in excess of 1:1[8]. Valence band UPS studies show that increasing pyridine:carborane ratio yields a decrease in VBM binding energy relative to the Fermi level, as shown in Fig. 5.

The data in Fig. 5 are consistent with a ptype semiconducting nature for these films [8], and indicate that increasing pyridine content should yield a smaller band gap.

Some caution should be exercised with regard to the above results in that the thicknesses of PECVD films deposited for neutron detection purposes (generally > 1000 Å) greatly exceed valence band or core level photoemission sampling depths (typically ~ 10 Å - 100Å). This problem was generally addressed by acquiring spectra at various points in the deposition process. Variations in elemental composition with



Figure 5 Comparison of the UPS spectra of the valence bands of (i) pure PECVD o-carborane film (black line), (ii) o-carborane and pyridine PECVD film with N/B atomic ratio of 0.73 (pyridine/carborane ratio of ~ 1:7; red line), and (iii) orthocarborane and pyridine PECVD film with N/B atomic ratio of 2.27 (pyridine/carborane ratio of ~ 1:22; blue line). Black arrows/number mark the positions/energies of the various valence band maxima below the Fermi level ($E_F=0$). All films are on clean Si. Peak maxima are set at 7 eV. From ref. [8]

thickness sometimes occurred during deposition, but the addition of automated mass flow controllers, recently installed is expected to yield films of highly uniform composition.

The interactions of PECVD films with transition metals have also been examined, both by I-V measurements with capacitive detector structures [8] (vide infra), and by photoemission [7]. Core level XPS studies of Cu thin films or nanoclusters on PECVD Cu films were used to measure both the total Cu $2p_{3/2}$ and Cu 3p photoemission intensities as a function of annealing for a PECVD BC film. The rate of attenuation of a photoemission signal by an overlayer film increases with decreasing core level kinetic energy [9]. The attenuation of intensity of the photoemission signal (I) scales as:

(1)
$$I = I_0 \exp(-d/\lambda)$$

In (1) d is the thickness of the (in this case) Cu overlayer, and λ is the inelastic mean free path for a core level photoelectron of specific kinetic energy going through an overlayer of specific electron density [9]. Since calculated λ values for the Cu 2p_{3/2} and Cu 3p photoelectrons through boron carbide are 10.1 Å and 20.1 Å, respectively [7, 10], significant diffusion of Cu atoms or particles into the ~ 1000 Å thick PECVD BC film should result in a significant increase in the Cu 3p/Cu 2p_{3/2} intensity ratio, as well as a decrease in the Cu 2p_{3/2}/B 1s intensity ratio. In



Figure 6 Evolution of XPS ratios with annealing temperature; (a) the Cu(2p3=2)/B(1s) atomic ratio and (b) the Cu (3p)/Cu(2p3=2)intensity ratio as a function of annealing temperature. The datapoints with the circle indicate the extended annealing at 1000 K for 60 min. From ref [7].

contrast, simple agglomeration of Cu on the film surface, without diffusion, would yield a decrease in the Cu $2p_{3/2}/B$ 1s ratio without significant change in the Cu $3p/Cu 2p_{3/2}$ ratio. As shown in Fig. 6, annealing a PECVD BC film with a thin Cu overlayer in UHV results in negligible change in the Cu $3p/Cu 2p_{3/2}$ ratio for temperatures below ~ 1000 K. This indicates that Cu/PECVD BC/Cu layers

should not exhibit thermallyinduced diffusion of Cu at temperatures < ~ 1000 K [7].

2. <u>Electronic Structure</u> <u>Calculations (collaborations</u> with Prof. Jincheng Du, UNT <u>Dept. of Mat. Sci., Prof. Wai-</u> <u>Ning Mei, UNL</u>)

Ab initio Density Functional Theory (DFT) calculations were carried out to determine lowest energy structures for BC:aromatic films, with an assumed BC:aromatic ratio of ~ 1:1 (as in Fig. 1b). Calculations for were carried out for test structures of BC:BNZ (Fig. 7a,b) and



Figure 7 Possible structures for (a,b) BC:BNZ and (c,d) BC:DAB. White spheres= H; orange spheres =B, grey spheres=C, blue spheres= N. From ref [11].

BC:DAB (Fig. 7c,d) polymers, assuming either a single bond between each carborane and aromatic unit (Fig. 7a,c) or a double-bonded structure (Fig. 7b,d) [11]. These calculations found the single-bonded structures to be energetically favorable, in full agreement with experiment [4, 5, 7]. Valence densities of states calculated for the structures in Fig. 1a,b) also yield results in close agreement with experimental results [3, 5].

A further tool for theoretical analysis is to compare calculated core level binding energies

with those of experiments. Shifts in core level binding energies for an atom A ($\Delta E(A)$) relative to some elemental standard are roughly proportional to changes in the corresponding ground valence charge population of A (q(A)) according to [12]:

(2)
$$\Delta E(A) = kq(A) + \sum_{B \neq A} q_b / r_{ab}$$

where k is a proportionality constant and the second term sums up point charge interactions with neighboring atoms. In covalent solids such as boron carbide, the second term is generally constant, and the shifts in experimental B 1s binding energies should be linearly proportional to calculated ground state charge densities obtained from a population analysis. Previous work [4] indicated that varying results for calculated binding energies could be obtained,



Figure 8. Linear correlation between experimental and calculated B 1s core level binding energies using a DFT-based Mulliken charge population analysis and minimal basis set, with structures from Fig. 4 and eqn. (1). Data from ref. [4]

depending on the method of population analysis and the basis set used in the calculations. The current work determined that the optimum basis set used depended on the method of population analysis—Mulliken, Hirshfeld, atoms-in-molecules, or Natural Bond Order [11]. In particular, best results for a Mulliken charge population analysis were found to require the use of a minimal basis set—essentially, atomic orbitals, in agreement with previous results [4]. The excellent linear correlation obtained between experimental B 1s binding energies and energies calculated using the minimal basis set/Mulliken population analysis is shown in Fig. 8. The data demonstrate that this method can be used to analyze experimental data from emerging boron carbide polymers based on carboranes and other aromatic or non-aromatic species, including high concentrations of pyridine.

3. <u>Diode detector formation</u> In order to compare film electronic characteristics and sensitivities to thermal and non-thermal neutrons, diode detector structures were fabricated as shown schematically in Fig. 9 Diodes were fabricated for the following test structures [8].

Diode test structures were fabricated for the following film compositions and estimated thicknesses, derived from XPS-based growth rates for thinner films:

(a) pure orthocarborane $(B_{10}C_2H_x)$ films with an estimated thickness 1650 Å

Au/Ti Orthocarborane/aromatic polymer n-type Si Au/Ti

(b) orthocarborane/pyridine film with ratio ~ 1:3 and an estimated thickness 3500 Å Figure 9 Diode detector structure using PECVD orthocarborane or orthocarborane/pyridine films. Electrodes were Au with Ti adhesion layers. The films are p-type, deposited on n-type Si.

(c) orthocarborane/pyridine ratio ~ 1:10 and an estimated film thickness 7200 Å

providing a relative boron content in the film (with respect to the film fabricated from pure carborane of B content) of 84% and 56% respectively.

The I(V) curves for the three diode test structures formed from the above films (a, b and c) are shown in Fig. 10. These heterojunction diodes fabricated from these films show no evidence of Schottky barrier formation or of significant leakage current in reverse bias [8].

These data indicate that films with orthocarborane/pyridine ratios << 1 yield diodes with negligible reverse-bias leakage current and retain excellent rectification, suitable candidates for neutron detection studies.



Figure 10. The I(V) curves of (a) $B_{10}C_2H_x$, (b) $B_{10}C_2H_x$:Py ratio approximately (1:3), and (c) $B_{10}C_2H_x$:Py ratio approximately 1:10 on 30 Ohm.cm n-type silicon. From ref. [8].

4. Neutron voltaic measurements

The diode structures were used for neutron voltaic studies at zero detector bias, using a d-T neutron source (Thermo Scientific MP 320 Neutron Generator) Results

320 Neutron Generator). Results recorded at zero diode bias are shown in Figure 11 for the pure orthocarborane film (Fig. 11a) and the orthocarborane/pyridine 1:10 film (Fig. 11b) both with ($\bullet \bullet \bullet \bullet \bullet$) and without (+++++) a Cd foil cover. The data in Fig. 11 demonstrate three important conclusions:

(i) <u>The films are "gamma blind</u>" as count rates in the presence of a Cd shield are substantially lower at all channel numbers than in the absence of such shielding and the cadmium foil bocks neutrons while neutron capture in Cd generates X-ray and gamma radiation

(ii) <u>Higher count rates are obtained for the</u> <u>orthocarborane: pyridine</u> film (Fig. 11b), even though this film has comparable or even less (56%) B content than the pure orthocarborane film (Fig. 8a). This indicates that even at zero bias, pyridinedoped films display excellent electron-hole separation, and possibly substantially higher charge mobility, than pure orthocarborane films. This finding is consistent with the proposed multidentate pyridine/carborane structure (Fig. 1c), as such multidentate polypyridine ligands are



Figure 11 Experimental neutron pulse height spectra of (a) $B_{10}C_2H_X$ (b) $B_{10}C_2H_X$:Py ratio approximately 1:10 both obtained at 0 Bias. (•••••) represents data taken with a Cd foil cover and (+++++) data with no Cd cover. Data from ref. [8]

known to lead to enhanced luminescence and electron-hole lifetimes [13].

(iii) Potential for Enhanced detection of non-thermal neutrons

In Fig. 11 channel number increases roughly with increasing neutron energy, though this has yet to be precisely calibrated. However, the data show that the pyridine-containing film (Fig. 11b) exhibits significantly higher count rates at higher channel numbers (without Cd shielding) than the pure carborane film (Fig.11a). This is may be attributable to the significant N content in the pyridine-containing film. N has significant cross sections for the resonant absorption of neutrons at energies > 1 MeV [13-15]:

(3)
$${}^{14}N+{}^{1}n \rightarrow {}^{14}C + {}^{1}H$$

This indicates that boron carbide films containing pyridine or other N-containing species, with favorable electron transport characteristics, may be capable of the sensitive detection of non-thermal neutrons even at zero detector bias.

Conclusions:

The data provided here show that pyridine, and possibly other N-containing aromatic species, can form films in which the aromatic moiety is not a linking unit, but more properly a semiconducting matrix for boron carbide (Fig. 1c). Such films are p-type, and yield diode test structures on n-type Si with excellent I(V) characteristics indicating no Schottky barrier formation with Ti/Au electrodes, and negligible reverse-bias leakage current, indicating no metal diffusion or defect-induced leakage, consistent with photoemission studies. The polydentate nature of the high pyridine-content film yields enhanced electron-hole separation, and enhanced, gammablind sensitivity to both thermal and non-thermal neutrons. These conclusions are illustrated schematically in Fig. 12.



Fig.12 Schematic diagram showing neutron capture and enhanced electron transport for detection in a boron carbide/pyridine cluster. (pink=B; grey=C; blue=N, white = H). From ref. [8,16]

What opportunities for training and professional development has the project provided? If the research is not intended to provide training and professional development opportunities or there is nothing significant to report during this reporting period, state "Nothing to Report." Describe opportunities for training and professional development provided to anyone who worked on the project or anyone who was involved in the activities supported by the project. "Training" activities are those in which individuals with advanced professional skills and experience assist others in attaining greater proficiency. Training activities may include, for example, courses or one-on-one work with a mentor. "Professional development" activities result in increased knowledge or skill in one's area of expertise and may include workshops, conferences, seminars, study groups, and individual study. Include participation in conferences, workshops, and seminars not listed under major activities.

not listed under major activities.

The following students have obtained their PH.D's or B.Sc.'s during this grant.

<u>AT UNT</u>

1. <u>Frank L. Pasquale</u> (Ph.D in Chemistry/UNT.; Sept., 2013, US Citizen) is now at LAM Research/ Tualatin, OR. Frank was the key person in applying XPS and UPS to the

study of BC:aromatic film chemical and electronic structure, and in developing an effective apparatus for the PECVD of thicker films. He is the lead author on four papers in this area.

- <u>Swayambhu Behera</u>, (Ph.D. in Physics/UNT, Jan. 2011)-- Now Development Engineer, Applied Materials Corp./Santa Clara, CA Swayambhu Behera wrote the initial paper in this group on characterization of vicinal and modified boron carbide films (S. Behera, et al. "Photo-induced site-specific nitridation of plasma-deposited B₁₀C₂H_x films: a new pathway toward post-deposition doping of semiconducting boron carbides", Surf. Sci. 604 (2010) L51-L54)
- Justin. Wilks, (PhD. In Chemistry/UNT—US Citizen, May 2009)-- Now a process development engineer at Novellus/Lam (Tualitin, OR) (now Lam research). Justin initiated this work in the group, helped to set up much of the experimental apparatus, and is 2nd author on the Surf. Sci. paper cited above. His work on thin film deposition, modification, and characterization was critical to the initiation of this work.
- 4. <u>Sawyer Foyle</u> (Texas Academy of Math and Science (TAMS) Student, Univ. of North Texas, US Citizen) Sawyer helped analysis spectra with the direction of Frank Paquale, as well as help perform several experiments pertaining to the development of the ortho-carborane:pyridine films. As a TAMS student—a high school student spending junior and senior years in residence and UNT, Sawyer entered the University of Alabama in 2013 were he is now an undergraduate research assistant in the Department of Chemistry.
- 5. <u>Raymond Welch</u> (B.Sc., Chem. 2014) Raymond Welch initiated efforts in sputter deposition of ultra-smooth films in this group and assisted in PECVD studies under the direction of F. Pasquale and R. James. Raymond is now in graduate school in the Dept. of Chemistry at the University of Texas at Dallas.

At UNL:

- J<u>uan Colon-Santa</u>: recently obtained his doctorate (Ph.D., Physics, UNL, 2012) under another DTRA funded project at the University of Nebraska (Hispanic, U.S. citizen). Awards include Richard Larson Fellowship (2007-2008); Avery Fellowship (2008); Leo Falicov Prize from the American Vacuum Society (2011); Folsom Dissertation Award (2012). He has working with Elena Echeverria on making reliable contacts on boron carbide for transport measurements; also working on the e-beam deposited boron carbide from ortho and para-carborane and measuring the Schottky barrier heights with gold contacts. Helped rebuild the UHV system all of summer 2012 for this purpose. Related project work: measuring the electronic structure and the surface oxide of thorium oxide ThO₂ with Tony Kelly of AFIT. Juan has also looking at radiation hardness effects in materials like boron carbide. Dr. Santana is now an Assistant Prof. of Physics at Northern Illinois University.
- Jing Liu, recently obtained her doctorate (2011) in physics in this DTRA funded project at the University of Nebraska: post-doc, Northeastern University and staff, National Synchrotron Light Source; Thesis: "Photo-fragmentation Processes of the closo-Carboranes and the Local Structure of Transition Metal Doped Semiconducting Boron

Carbide Thin Films". Student prizes: Chinese National Award for Outstanding Students Studying Abroad (2011)

- 3. <u>George Peterson</u> (undergraduate, U.S. citizen). He has been working on GEANT IV Monte Carlo simulations of neutron capture efficiencies, versus gamma production for various transition metal dopants in boron carbide and lithium tetraborates. He has also performed some high altitude balloon measurements of solar neutrons using both boron carbide and lithium tetraborate detectors. Now a graduate student in Mechanical Engineering with Prof. Nastasi, continuing work on neutron detection in collaboration with Los Alamos National Laboratory.
- 4. <u>Stephanie M. Rodriguez Marmol</u> (B.Sc., University of Puerto-Rico Humacao; expected May 2017; U.S. Citizen, Hispanic, female). Worked with Elena Echeverria on making reliable contacts on boron carbide for transport measurements in the summer of 2014.

Students currently working in this area (now under HDTRA1-14-1-0041)

<u>At UNT.</u>

- 1. <u>Robinson James (Ph.D./Chemistry, expected May 2015)</u> Robinson has done much of the initial characterization of PECVD thin films (Fig. 1a, c) and made significant improvements to the PECVD chamber.
- <u>Bin Dong</u> (Ph.D./Chemistry expected May 2017, female) is taking over from Robinson. She has already made substantial contributions to the control of precursor partial pressure during the PECVD process for better control of film composition.
- <u>Marcus Sky Driver</u> (Postdoc: Ph.D., 2014 from U. Missourri-KC/Physics,—U.S. Citizen) Marcus has helped with detailed analysis of photoemission spectra, made substantial improvements to the photoemission instrumentation, and is now helping with the development of optical probes of charge transport in BC:aromatic films.
- 4. <u>Brock Beauclaire</u> (Undergraduate, Physics, B.Sc. expected May 2016) is working under Dr. Driver in the development of optical probes of charge carrier transport in these materials.

At UNL:

 <u>Elena Echeverria</u>: (Ph.D., Physics, UNL, expected December 2015; Hispanic, female). Elena Echeverria is working on making reliable contacts on boron carbide for transport measurements; also working on the e-beam deposited boron carbide from ortho and para-carborane and measuring the Schottky barrier heights with gold contacts. Helped rebuild the UHV system all of summer 2012 for this purpose. Supervised Stephanie M. Rodriguez Marmol, (B.Sc., University of Puerto-Rico – Humacao; expected May 2017; U.S. Citizen, Hispanic, female).

How have the results been disseminated to communities of interest?

If there is nothing significant to report during this reporting period, state "Nothing to Report." Describe how the results have been disseminated to communities of interest. Include any outreach activities that have been undertaken to reach members of communities who are not usually aware of these research activities, for the purpose of enhancing public understanding and increasing interest in learning and careers in science, technology, and the humanities.

Results have been disseminated in the form of both published scientific papers and presentations at scholarly meetings. In addition, a number of patents have originated from this work.

Publications

2010

- Eckart Rühl, Norman F. Riehs, Swayambhu Behera, Justin Wilks, Jing Liu, H.-W. Jochims, Anthony N. Caruso, Neil M. Boag, Jeffry A. Kelber and Peter A. Dowben, "Photo-fragmentation of the *closo*-carboranes Part II: VUV assisted dehydrogenation in the *closo*-carboranes and semiconducting B₁₀C₂H_x films", *J. Phys. Chem.* A 114 (2010) 7284-7291.
- Swayambhu Behera, Justin Wilks, Peter Dowben, Anthony Caruso, M. Driver, Jeffry Kelber, "Photo-Induced Site-Specific Nitridation of Plasma-Deposited B₁₀C₂H_x Films: A New Pathway Toward Post-Deposition Doping of Semiconducting Boron Carbides", *Surface Science* 604 (2010) L51-L54

2011

 Jing Liu, P. A. Dowben, Guangfu Luo, Wai-Ning Mei, Anil Kumar Rajapitamahuni, Andre Sokolov, Sudarshan Karki and Anthony N. Caruso, "The Local Structure and I-V Characteristics of Chromium Doped Semiconducting Boron Carbide", MRS Symposium Proceedings 1307 (2011) DOI:10.1557/opl.2011.503

2012

- Frank Pasquale and Jeffry A. Kelber, "Site-specific electron-induced cross-linking of ortho-carborane to form semiconducting boron carbide", *Applied Surface Science* 258 (2012) 2639-42
- F. Pasquale, J. Liu, P. A. Dowben and J. A. Kelber "Novel semiconducting alloy polymers formed from ortho-carborane and 1,4-diaminobenzene", *J. Mater. Chem. and Phys.* 133 (2012) 901-906

2013

 Frank L. Pasquale, Yun Li, Jincheng Du and Jeffry A. Kelber, "Novel alloy polymers formed from *ortho*-carborane and benzene or pyridine", *J. Phys.: Cond. Matt.* 25 (2013) 105801

- Robinson James, Frank L. Pasquale and Jeffry A. Kelber, "Plasma-enhanced chemical vapor deposition of *ortho*-carborane: structural insights and interaction with Cu overlayers", *J. Phys.: Cond. Matt.* 25 (2013) 355004
- Frank. L. Pasquale, Robinson James, Raymond Welch, Elena Echevarria, P. A. Dowben and J. A. Kelber, "Novel Cross-linked Ortho-Carborane and Ortho-Carborane:Y (Y=1,4-diaminobenzene, pyridine, benzene) Polymer Films: A New Class of Carborane-Based Materials with Tunable Electronic Structure", *ECS Trans.* 53 (2013) 303-310
- 9. Elena Echevarria, Frank L. Pasquale, Juan A. Colón Santana, Le Zhang, Robinson James, Andre Sokolov, Jeffry A. Kelber and P. A. Dowben, "Significant magneto-resistive effects in boron carbide thin films", *Matt. Lett.* **110** (2013) 20-23

2014

- Elena Echeverría, Robinson James, Umesh Chiluwal, Frank L. Pasquale, Juan A. Colón Santana, Richard Gapfizi, Jae-Do Tae, M. Sky Driver, A. Enders, Jeffry A. Kelber and P.A. Dowben, "Novel semiconducting boron carbide/pyridine polymers for neutron detection at zero bias", Applied Physics A (2014), in press; doi: 10.1007/s00339-014-8778-4
- 11. Jing Liu, Eckart Rühl, Adam P. Hitchcock, David N. McIlroy, John D. Bozek, Tolek Tyliszczak, A. Knop-Gericke, Neil M. Boag, and P.A. Dowben, "Double cation formation from the photo-fragmentation of the *closo*-carboranes", *Zeitschrift für Physikalische Chemie* **228** (2014) 421–436
- 12. Yun Li, Jessica M. Rimsza, Frank. L. Pasquale, Jeffry A. Kelber and Jincheng Du, Chemical bonding in carborane/aromatic co-polymers: a first-principles analysis of experimental photoemission spectra (submitted for publication).
- 13. Robinson James, Umesh Chiluwal, Jae-Do Tae, Frank. L. Pasquale and Jeffry A. Kelber Boron carbide films fabricated by plasma-enhanced chemical vapor deposition or ebeam induced cross-linking of meta-carborane: chemical bonding and electronic structure (in preparation).
- 14. Elena Echeverría, Robinson James, Frank L. Pasquale, Juan A. Colón Santana, M. Sky Driver, A. Enders, Jeffry A. Kelber and P.A. Dowben, "Neutron Detection Signatures at Zero Bias in Novel Semiconducting Boron Carbide/Pyridine Polymers", submitted to an MRS Symposium Proceedings

Presentations:

2011

- Frank L Pasquale and Jeffry A Kelber, "Novel Boron Carbide-Based Semiconducting Polymers for Enhanced Electronic Properties", AVS 58th Annual International Symposium and Exhibition, 2011
- "The local Structure of Transition metal doped semiconducting boron carbides", The Nebraska Academy of Sciences, One hundred-twenty first annual meeting, April 15, 2011, Nebraska Wesleyan University [presented by Jing Liu]

2012

- Frank L Pasquale, Robinson James, Raymond Welch, Sawyer Foyle, Jing Liu, P. A. Dowben, and J.A. Kelber, Metallization of Electron-Induced Novel Thin-Orthocarborane Derived Polymer Films for Neutron Detecting and Nanoelectronic Applications, Techon 2012.
- "The History and Development of Boron Carbon Alloy Devices and Rare Earth Heterojunction Neutron Detectors", Seminar, 20 November 2012, BAE Systems Maritime – Submarines at Waterlooville

2013

- 5. Elena Echeverria, Guangfu Luo, J Liu, Wai-Ning Mei, FL Pasquale, J Colon Santanta, PA Dowben, Le Zhang, JA Kelber, "Magneto-Resistance in thin film boron carbides", APS March Meeting 2013.
- "Magneto-resistance in thin boron carbide films", Nebraska Academy of Science, 133rd Annual Meeting, April 19, 2013, Nebraska Wesleyan University [presented by Elena Echevarria]
- Robinson James, Frank L Pasquale, Umesh Chiluwal, Elena Echeverria, P.A. Dowben, and Jeffry A. Kelber "Boron Carbide Films Fabricated using Plasma Enhanced Chemical Vapor Deposition of ortho-Carborane for Diffusion Barrier and Device Applications SRC- TECHCON 2013.
- "Magneto-Resistance in thin film boron carbides", APS March Meeting 2013 Baltimore, Maryland, Bulletin of the American Physical Society 58 (2013) 147; Abstract: B16.00014; Session B16: Focus Session: Spin-Dependent Physics in Graphene, Room: 318; 1:51 PM–2:03 PM [presented by Elena Echeverria]
- Elena M. Echeverria, Frank L. Pasquale, Juan A. Colon Santana, Le Zhang, Robinson James, Andre Solkolov, Jeffry A. Kelber, Peter Dowben "<u>Significant</u> <u>Magneto-Resistance in Thin Films of Boron Carbide</u>" Techcon 2013.

- R. James, U. Chiluwal, E. Echeverria, R. Gapfizi, J. Tae, P.A. Dowben and J.A. Kelber "Novel Composite Materials Fabricated by Plasma-enhanced CVD of Carboranes and Pyridine or Benzene", AVS 61st International Symposium & Exhibition November 2014.
- 11. Chuting Tan, Bin Dong, Robinson James, Jeffry Kelber, Danyal Turkoglu, Greg Downing and Lei R. Cao "Characterization of Boron Carbide Based Polymer Neutron Sensor with Neutron Depth Profiling" Submitted abstract for 2015 Mid-America Regulatory Conference.
- Neutron Detection Signatures at Zero Bias in Novel Semiconducting Boron Carbide Containing Pyridine Polymers "Neutron Detection Signatures at Zero Bias in Novel Semiconducting Boron Carbide Containing Pyridine Polymers", 2014 IEEE Nuclear Science Symposium.
- 13. E. Echeverria, F. L. Pasquale, R. James, S. Adenwalla, J. A. Kelber and P. A. Dowben *"Semiconducting boron carbide polymer devices for neutron detection"*. March meeting of the American Physical Society (March 6, 2014) Denver, CO.
- 14. "Significant Magneto-Resistance in Thin Films of Boron Carbide", UNL Research Fair, Lincoln, Nebraska, 15-16 April 2014. [presented by Elena Echeverria]
- P. A. Dowben, "The history and development of boron carbon alloy devices and rare earth heterojunction neutron detectors" Ohio State Colloquium, Columbus, OH. Jan. 31, 2014
- P.A. Dowben, "Boron Carbide Semiconductors: So Many Devices and Applications, So Little Understanding", 118th International Symposium on Boron, Borides and Related Materials, (http://www.soest.hawaii.edu/ISBB2014/), September 5, 2014 in Honolulu, Hawai'i, USA
- 17. "Real Time Identification and Interdiction of Fissile Material", Seminar, Battelle, Columbus, Ohio, August 1, 2014
- "Neutron Detection Signatures at Zero Bias in Novel Semiconducting Boron Carbide/Pyridine Polymers", 2014 MRS Fall Meeting & Exhibit December 3, 2014, Boston, Massachusetts; Symposium DD: Materials for Advanced Nuclear Technologies; DD12.14 [presented by Elena Echeverria], Elena M Echeverria, Robinson James, Frank L. Pasquale, Juan A. Colon Santana, Axel Enders, Jeffry A. Kelber, Peter A. Dowben

Patent Applications:

QNTM-0004-PCT Novel Semiconducting Alloy Polymers Formed from Orthocarborane and 1,4-Diaminobenzene PCT/US12/40681 filed June 4, 2012 (PENDING)

QNTM-0004-USNATL Novel Semiconducting Alloy Polymers Formed from Orthocarborane and 1,4-Diaminobenzene 14/115,104 filed November 1, 2013 (PENDING)

QNTM-0023-UT1 Boron Carbide Films Exhibiting Extraordinary Magnetoconductance and Devices Based Thereon 14/098,759 filed December 6, 2013 (PENDING)

QNTM-0029-PR1 Novel Semiconducting Boron Carbide Polymers for Neutron Detection at Zero Bias 61/991,707 filed May 12, 2014 (PENDING)

What do you plan to do during the next reporting period to accomplish the goals? If there are no changes to the agency-approved application or plan for this effort, state "No Change." Describe briefly what you plan to do during the next reporting period to accomplish the goals and objectives.

This is the final report for HDTRA1-09-1-0060. The work is being extended and broadened under HDTRA1-14-1-0041. The focus is on preparation of films with novel aromatic groups to enhance charge carrier properties, and on the development of a deeper insight as to how aromatic-carborane chemical interactions quantitatively impact electron-hole separation lifetime and carrier mobility, as well as gamma-blindness, sensitivity to thermal neutrons, and possible sensitivity to non-thermal neutrons.

References

[1] F. Pasquale, J. Kelber. Semiconducting boron carbide films by electron beam induced crosslinking. Appl Surf Sci. 258 (2012) 2639-2642.

[2] E. Ruhl, N. Riehs, S. Behera, J. Wilks, J. Liu, H.-. Joachim, A.N. Caruso, N.M. Boag, J.A. Kelber, P.A. and Dowben. *Photo-fragmentation of the closo-carboranes part II: VUV-assisted dehydrogenation in the closo-carboranes and semiconductiong* $B_{10}C_2H_x$ *films.* J Phys Chem A. 114 (2010) 7284-7291.

[3] F. Pasquale L., J. Liu, P.A. Dowben, J.A. Kelber. *Novel semiconducting alloy polymers formed from ortho-carborane and 1,4-diaminobenzene. Mat Chem and Phys.* 133 (2012) 901-906.

[4] F.L. Pasquale, Y. Lin, J. Du, J.A. Kelber. *Novel alloy polymers formed from ortho-carborane and benzene or pyridine.* J Phys: Cond Matt. 25 (2012) 105801.

[5] F.L. Pasquale, R. James, R. Welch, E. Echeverria, P.A. Dowben, J.A. Kelber. *Novel cross-linked ortho-carborane and ortho-carborane:* Y (*Y*=1,4-diaminobenzene, pyridine, benzene) polymer films: A new class of carborane-based materials with tunable electronic structure. ECS Trans. 53 (2013) 303-310.

[6] E. Echeverria, F.L. Pasquale, J.A. Colon-Santana, L. Zhang, R. James, A. Sokolov, J.A. Kelber, P.A. Dowben. *Significant magneto-resistance in thin films of boron carbide*. Mat Lett. 110 (2013) 20-23.

[7] R. James, F.L. Pasquale, J.A. Kelber. *Plasma-enhanced chemical vapor deposition of orthocarborane: structural insights and interaction with Cu overlayers.* J. Phys.: Cond. Matt. 25 (2013) 355004.

[8] E. Echeverria, R. James, U. Chiluwal, F.L. Pasquale, J.A. Colon-Santana, R. Gapfizi, J. Tae, M. Driver, A. Enders, J. Kelber, P. Dowben. *Novel semiconducting boron carbide polymers for neutron detection at zero bias.* Appl Phys A. in press (2014).

[9] D. Briggs, M.P. Seah. "*Practical surface analysis, second edition, volume 1-- Auger and X-ray photoelectron spectroscopy*" **1** (1990) 657.

[10] S. Tanuma, C.J. Powell, D.R. Penn. *Calculation of electron inelastic mean free paths (IMFPS) VII. reliability of the TPP-2M predictive equation*: Surface and Interface Analysis. 35 (2003) 268-275.

[11] Y. Li, J.M. Rimsza, F. Pasquale, J. Kelber, J. Du. Chemical bonding in carborane/aromatic copolymers: a first-principles analysis of experimental photoemission spectra. Submitted for Publication. (2014).

[12] U. Gelius. Binding energies and chemical shifts in ESCA. Phys Scipta. 9 (1974) 133-147.

[13] L. Hammarstrom, O. Johansson. *Expanded bite angles in tridentate ligands. improving the photophysical properties in bistridentate Ru^{II} polypyridine complexes.* Coord Chem Rev. 254 (2010) 3546-2559.

[14] F.A. Valente, H.I. Zagar. Fast neutron resonance with nitrogen. Phys Rev. 69 (1946) 55-59.

[15] H.I. Zagar, F.A. Valente. *Heavy particle groups from the neutron disintegrations of nitrogen and neon*. Phys Rev. 67 (1945) 133-142.

[16] "Neutron Detection Signatures at Zero Bias in Novel Semiconducting Boron Carbide/Pyridine Polymers", 2014 MRS Fall Meeting & Exhibit December 3, 2014, Boston, Massachusetts; Symposium DD: Materials for Advanced Nuclear Technologies; DD12.14 [presented by Elena Echeverria], Elena M Echeverria, Robinson James, Frank L. Pasquale, Juan A. Colon Santana, Axel Enders, Jeffry A. Kelber, Peter A. Dowben

DEPARTMENT OF DEFENSE

DEFENSE THREAT REDUCTION AGENCY 8725 JOHN J. KINGMAN ROAD STOP 6201 FORT BELVOIR, VA 22060 ATTN: D. PETERSEN

DEFENSE TECHNICAL INFORMATION CENTER 8725 JOHN J. KINGMAN ROAD, SUITE 0944 FT. BELVOIR, VA 22060-6201 ATTN: DTIC/OCA

DEPARTMENT OF DEFENSE CONTRACTORS

QUANTERION SOLUTIONS, INC. 1680 TEXAS STREET, SE KIRTLAND AFB, NM 87117-5669 ATTN: DTRIAC