

Project No. 12-3834

High Hydrogen Content Graphene Hydride Compounds & High Cross- Section Cladding Coatings for Fast Neutron Detection

Mission Supporting Transformative Research

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Project Title: High Hydrogen content Graphene Hydride Compounds & High Cross-Section Cladding Coatings for Fast Neutron Detection

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Recipient: University of South Carolina

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Co-PI: Adrian Mendez-Torres, Savannah River National Lab

Project Objective: The objective is to **develop and implement a superior low-cost, large area (potentially >32in), easily deployable, close proximity, harsh environment innovative neutron sensor needed for next generation fuel cycle monitoring.** We will exploit recent breakthroughs at the PI's lab on the electrochemistry of epitaxial graphene (EG) formed **on commercial SiC wafers**, a transformative nanomaterial system with superior radiation detection and durability properties to ***develop a new paradigm in detection for fast neutrons, a*** by-product of fission reactors. There are currently few effective detection/monitoring schemes, especially solid-state ones at present. This is essential for monitoring and control of future fuel cycles to make them more efficient and reliable. By exploiting these novel materials, as well as innovative hybrid SiC/EG/Cladding device architectures conceived by the team, will develop low-cost, high performance solutions to fast-neutron detection. Finally, we will also explore 3-terminal device implementations for neutron detectors with built-in electronic gain to further shrink these devices and improve their sensitivity.

1. Major accomplishments in this project and key challenges

There were several major accomplishments in this project that are described in greater detail below:

1. Developed SiC crystal growth techniques using novel chemistries (Dichlorosilane, SiF₄), and surface preparation to reduce cost, as well as improve the thickness and quality of the material, which will eventually lead to thick, radiation hard detectors for a variety of applications, including neutron detection, and other energy applications. Our work has provided the key breakthroughs to realize high quality SiC epitaxy >100um thick to be routinely produced, making us one of a handful of teams in the world that can achieve this (Suda's, Kimoto's team in Japan, Janzen's group in Sweden). The defect reduction technique will lead to a USPTO patent application (USC invention disclosure submitted, and provisional application is being prepared).
2. Developed new graphene window electrode growth technique using SiF₄ that enables the thickness and defect density (Provisional patent USPTO 14/767,095) to be controlled more precisely than ever before. This control is critical for engineering the detector performance for the new architecture described in 4.
3. Developed neutron sensitization technologies using hydrogenation of epitaxial graphene for proton recoil detection of neutrons. We showed the critical role of defects in the multilayer graphene, which are responsible for uptake of hydrogen by electrochemical means. High H-uptake is important for high neutron interaction cross section that leads to proton recoil subsequently detected. Also developed simple neutron absorption layer using ~5um thick sputtered Gadolinium Oxide for incorporation into any charged particle detection device structure. While we have made this Gd-based device, no neutron measurements have been performed.
4. Developed a new device architecture based on a SiC bipolar phototransistor (SBPT) with a thin, radiation transparent graphene window as an electrode. This device provides for current gain>100x, with our analysis suggesting gains >10,000x are possible at low flux of neutrons or charge particles. Such high gain in a low-cost, radiation hard solid-state platform has never been demonstrated in nuclear detection applications. We believe that this approach holds great promise. (Provisional patent submitted USPTO 15/049,743.)
5. 2 undergraduates from my research group involved in developing and characterizing graphene/SiC materials, have been accepted to PhD programs related to semiconductors in the energy space. Ms. Hani Gomez (Latina American) will begin her PhD at UC-Berkeley this Fall, and is the recipient of the prestigious NSF graduate fellowship, while Mr. Joseph Andrews will begin his PhD at Duke University. This is consonant with the workforce development mandate of NEUP.
6. 3PhD graduates, Sabih U. Omar, Shamaita Shithi (female) and Kevin Daniels, were funded directly under this work. Dr. Kevin Daniels (African American) has accepted a prestigious postdoctoral position at the Naval Research Laboratory under the direction of Dr. Rachel Myers-Ward, working on detection technologies using SiC and graphene technologies. Drs. Omar and Shithi are currently device engineers at Intel (Hillsboro, OR). One more, Ms. Anusha Balachandran is expected to graduate in 2017, although her continued funding will be through an NSF grant. This meets the diversity and workforce mandate of NEUP.
7. Published 15 journal articles in high impact journals such as Appl. Phys. Lett., J. Appl. Phys., IEEE Trans. Elec. Dev. as a direct consequence of this funding (see products

below). This was accompanied by >10 conference presentations at the Electronic Materials Conference (2015 plenary talk was given by Dr. S. Nakamura, the 2014 Physics Nobel Laureate), ANS, and IEEE conferences. Some key talks are highlighted below. This work also led to 3 provisional patent applications, which will eventually be converted to full applications through the University of South Carolina, which the Federal government, as always, will have the first right of refusal to.

There were 2 key challenges that would have improved the overall success of the project. These are discussed below in the plans for follow-on studies in section 2.

1. Access to neutron sources. The original co-PI left Savannah River National Lab (SRNL) halfway through the project, at which point USC lost access to the Cf-252 neutron source. The PI is still very interested in pursuing this at no cost, as there are devices that we currently have ready for testing with neutrons. We request the program manager to help us in identifying potential collaborators to bring this very productive project to a tangible nuclear detection application, rather than basic charged particles and UV light.
2. Large dark current in the bipolar structure that due to leakage currents from non-mesa isolated collector junctions in the BJT structure. In recent iterations, we have reduced the dark current by 300x to <1uA, by optimizing the growth of the SiC. Initial calculations indicate that this can be reduced to <1pA through careful mesa isolation (see below).

Accomplishments

1.1 Homoepitaxial Growth of 4H-SiC with on-axis substrates using SiF₄ to reduce cost and defects

SiC epitaxial growth is performed on SiC seed substrates. These seed substrates are cut and polished from SiC boules that are grown using Physical Vapor Transport (PVT) at temperatures >2200°C along the basal <0001> Si-face direction. Due to the extreme temperatures and conditions required for this growth, boules, cylindrically shaped, are often short <3inches in length, unlike the several feet length in the melt-grown silicon industry. Thus being able to cut parallel to the face will enable more wafers to be obtained from a given boule. In fact, for 6in wafers, the current industry bleeding edge, cutting at 0-degrees, as opposed to the 4 degrees standard currently used, would yield 3x more wafers for a given boule, with a corresponding decrease in cost, a true game changer in the industry.

However, epitaxial growth is often performed on 4 degree (or greater) wafers, as cutting off-axis reveals steps that highlight the stacking sequence of the crystal. These steps then enable replication of the underlying crystal structure. However, if only the basal plane is revealed, common wisdom dictates that the underlying stacking is not available to the growing crystal, and therefore, the thermodynamically favorable cubic polytype (low bandgap of 2.3eV, leading to larger leakage) of SiC, 3C, nucleates and grows. This is further complicated by the fact that any nominally on-axis wafer always has a small unintentional miscut (+/- 0.5 degrees) owing to the tolerances in the cutting process. This means there is a competition between step mediated growth and surface nucleation, often leading to a mixture of polytypes of very different bandgaps (3C-2.3eV vs. 4H-3.2eV, the desired wide bandgap structure), a clearly undesirable state of affairs. Therefore, the industry has stalled at a 4 degree standard, with a few startups attempting 2 degree, although at 6in diameter, this still leads to significant boule wastage. Our team has, over the course of this project, developed Chlorine based chemistries to produce >50um thick films (See outputs below) that are at the state-of the art. However, even these films, at high

enough thickness, suffer from Si-liquid puddle formation during growth, which degrades the quality of the films, killing device performance. Fluorine based chemistry provides for more volatile Si-containing vapors that can mediate SiC growth without forming liquid silicon puddles.

In our growth experiments, we grow SiC on commercial on-axis SiC wafers. The growth is performed at 1600°C, 300 Torr, SiF₄ (novel silicon precursor, patent pending for implementation) partial pressure of ~0.1% in an ultrapure hydrogen ambient. Propane (C₃H₈) is used as the carbon source, and is varied to provide C/Si ratios from 0.6-2.5. Under suboptimal conditions i.e. C/Si ratios ~1.5-1.8, mixed polytypes are seen similar to other researchers, where lower C/Si ratios promote polytype replication. However, at C/Si>2, we see very clean step-flow growth, in stark contrast with other researchers in the field. We attribute this to the novel SiF₄ chemistry. This is clearly seen in Fig. 1, which shows Nomarski micrographs of the surface morphology, where unoptimized layers show grain boundaries.

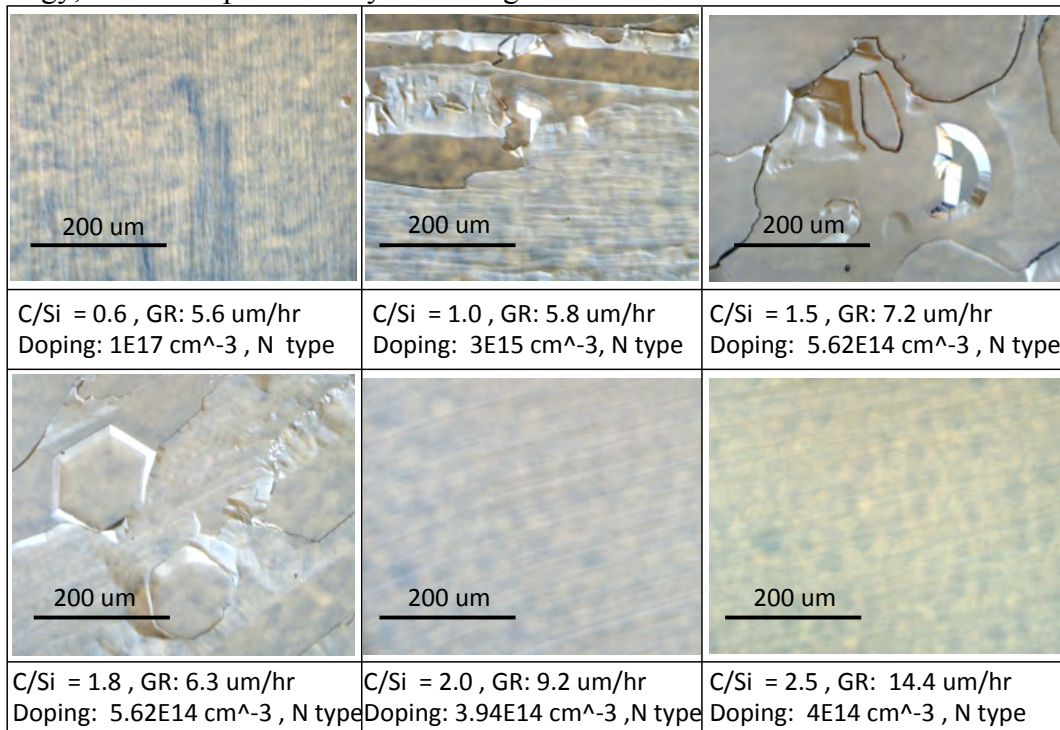
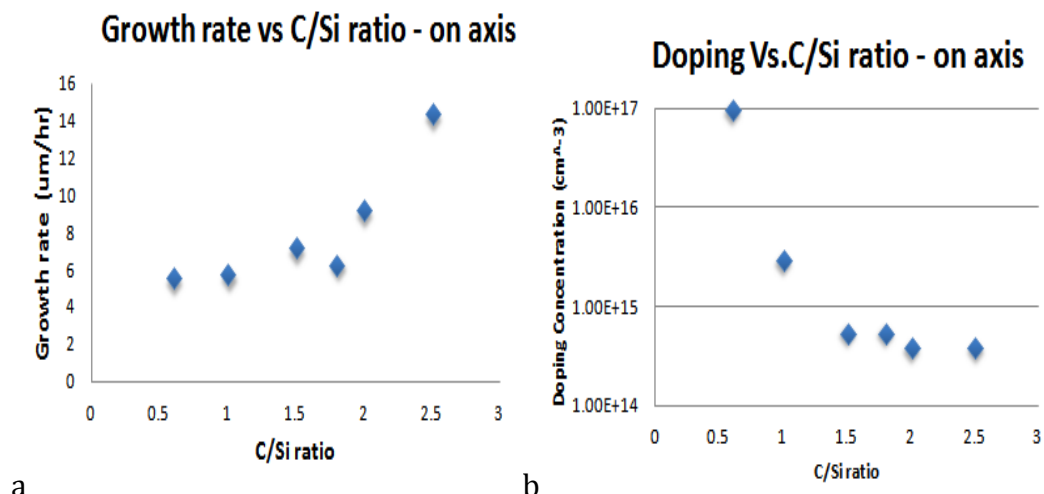


Figure 1: Nomarski micrographs showing SiC homoepitaxial layer morphology as a function of C/Si ratio.

Growth rates as high as 14um/hr, and doping density n-type<10¹⁵cm⁻³ are clearly observed, showing C-limited growth (Fig.2a) controlling growth rate, and site-competition controlling impurity incorporation into the crystal (Fig 2b). While site-competition is routinely observed by many researchers, the C-limited regime is only observed occasionally by researchers using halogenated precursors.



a b
Figure 2 C/Si ratio dependence of a) Growth rate and b) impurity incorporation, or doping density. All dopings are n-type.

Finally, atomic force micrographs (AFM) all reveal clear step-mediated growth, even for sub-optimal samples in the smoother regions between grain boundaries (Fig. 3). The confirmation of step-flow growth provides a key clue to understanding our breakthrough.

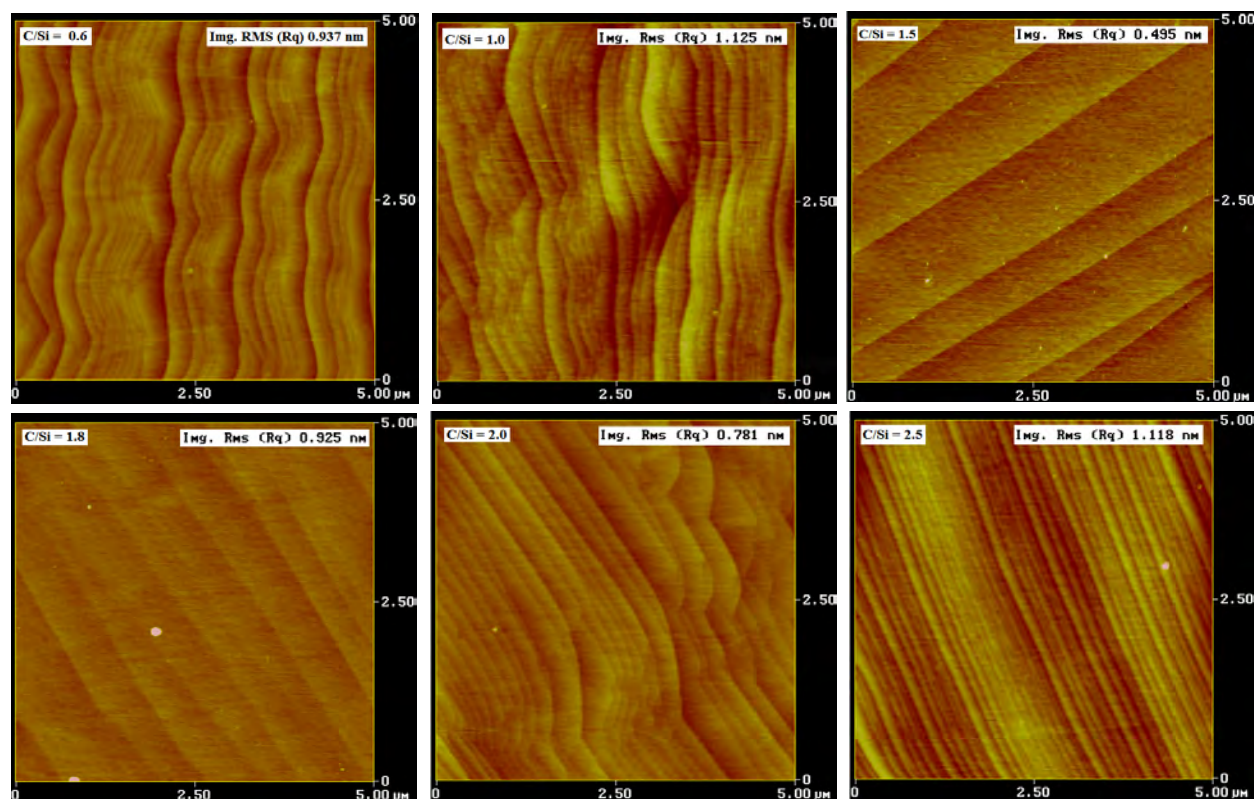


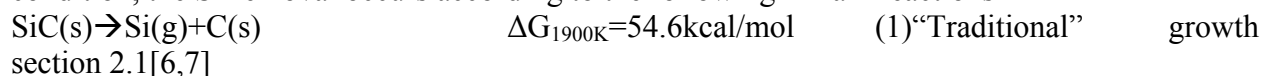
Figure 3: Atomic force micrographs of 4H-SiC surface epitaxial layers as a function of C/Si ratio showing clear step-mediated growth in smooth regions.

1.2 Developed new graphene window electrode growth technique:

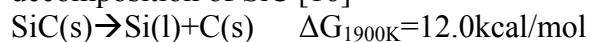
We presented a quantitative study on the growth of multilayer epitaxial graphene (EG) by traditional solid-state decomposition of SiC on polar (c-plane Si and C-face) and non-polar (a and m plane) 6H-SiC faces, with distinctly different defect profiles. The growth rates are slower than expected from a mechanism that involves Si loss from an open and free surface, and much faster than expected for the nucleation of a defect-free EG layer, implying that defects in the EG play a critical role in determining the growth kinetics. Analysis shows that the surface diffusion of Si atoms to the grain boundaries of EG limits the growth on c-plane C-face and non-polar faces, rather than the purely vertical diffusion of Si through the grain boundaries. However, for Si-face c-plane growth, diffusion of Si to the defects, as well as desorption of Si at the grain boundaries are both relevant, leading to a different temperature trend compared to the other faces. This distinct qualitative difference is ascribed to point-defects in Si-face growth, as contrasted with line defects/grain boundaries on the other faces. The size of the EG grains correlates with the surface diffusion length extracted from this model. The longer a Si adatom diffuses, the higher the quality of the grown EG film, an insight that provides valuable information on Si adatom kinetics for optimizing EG growth for growing thin windows for detectors. Other measurements on the electrochemical hydrogenation of graphene showed that the chemical sensitivity of graphene appears to be dominated by defects, a fact we exploited in section 1.3.

Defect Engineering Using Halogen Assisted Graphene (HAG)-In-Diffusion of Fluorinated accelerant and Out-Diffusion of Si -NOVEL PROCESS

In this new process, Si is again removed from the surface, leaving behind excess carbon that rearranges itself into graphene. However, in this process, a chemical Si-removal accelerant, SiF₄, is introduced into the reactor, diluted ~0.1% in Ar at ~300Torr (T=1300-1650°C). Under this condition, the Si-removal occurs according to the following 2 main reactions



A detailed examination of the Gibbs free energy of formation of the various decomposition pathways indicates that the above net reactions are mediated by the rapid initial decomposition of SiC [16]



, followed by the slower removal of the free elemental silicon via the following 2 reactions (Fig. 3)



Clearly, the second reaction, having a much lower Gibbs free energy change, ΔG will

dominate, giving rise to faster removal of Si, speeding up graphene growth by as much as 100x, as has been observed in our lab (Fig. 5). In other words, the Si-removal species changes from atomic Silicon to gaseous SiF₂. Furthermore, this process appears to break the growth rate/material quality tradeoff in the traditional EG growth process, as discussed in 2.1, although it is not clear whether this is due to ease of in-diffusion of SiF₄ or out-diffusion of SiF₂ (Fig. 1),

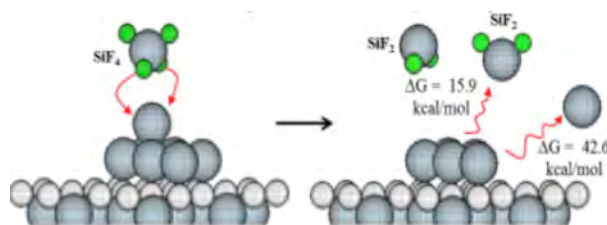


Fig. 4: Si-removal pathways from SiC i.e. SiF₂ (new process) and Si-evaporation (traditional EG growth), with SiF₂ loss leading to lower ΔG at 1900K and faster growth rate.

or some combination thereof. With this process, layers >100ML have been demonstrated at the PI's lab, with defect densities controllable by temperature. Further details are provided in section 2.5-6. **Another key difference from the traditional EG process is that only turbostratically stacked HAG can be grown, whereas, with EG both Bernal & turbostratic can be grown for defect engineering.** Since layers >100ML can be grown. The results of this detailed investigating are shown in the Figure below.

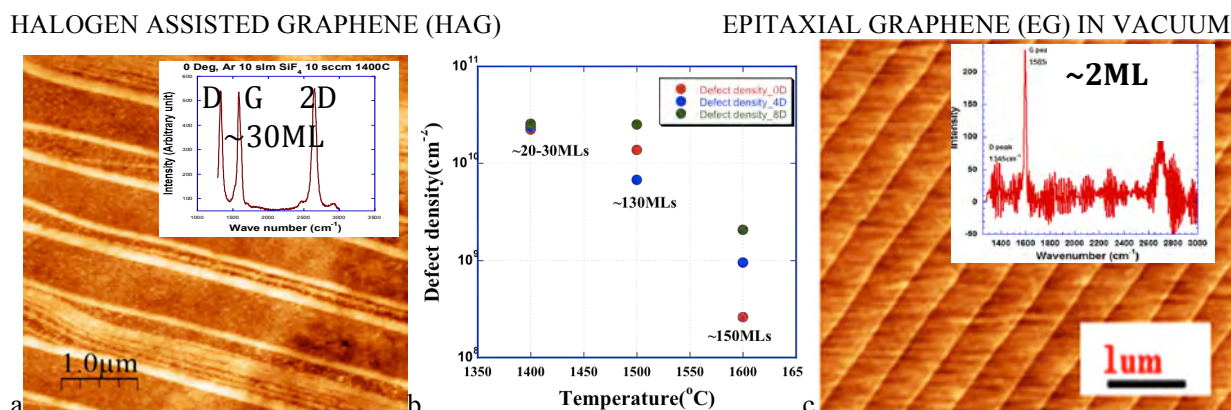


Fig 5 : Atomic force micrographs (AFM) of a) halogen assisted graphene (HAG)[10] and c) vacuum grown epitaxial graphene (EG) [6] at 1400°C growth temperature on Si-face SiC. The insets are Raman spectra of the respective films. b) Defect density of HAG extracted by Raman, as described in section 4.1 showing how defect engineering is achieved by changing temperature and SiC orientation (0-8°). Increasing the growth temperature decreases the defect density, as there is more energy available for the formation of C-C bonds. Growing on on-axis (0°) SiC generally gives lower defect densities. HAG shows turbostratic stacking, while EG shows Bernal stacking. The best EG layers show Raman D/G ratio < 0.05 [5], corresponding to defect densities < 10⁸ cm⁻², similar to the best HAG layers here and at the state of the art in the field [5].

Here, the defect density is controlled primarily by changing the temperature, with further control by changing substrate orientation. **Increasing the growth temperature decreases the defect density, as there is more energy available for the formation of C-C bonds. Growing on on-axis (0° orientation) SiC substrates generally gives lower defect densities, as determined by Raman.** Nitrogen doped chemo-mechanical polished (CMP) 4H-SiC substrates with various off cuts (~0°, 4° and 8°) were used. Graphene epitaxial growths were performed in the vertical hotwall CVD reactor (Fig. 9). Ultra high purity (99.9999%) Ar gas was used as the carrier gas at 300Torr. Ultra high purity SiF₄ ~0.1% was used as the Si-removal agent (Fig. 3) to perform the growth at temperatures from 1300-1600°C for each offcut. The advantage is that this process is compatible with the new SiC growth process shown in 1.1, enabling high performance devices to be achieved.

1.3 Developed neutron sensitization technologies using hydrogenation of epitaxial graphene for proton recoil detection of neutrons

Electrochemistry offers the most controlled route to systematic functionalization, as the extent of the hydrogenation of graphene (EG) can be precisely controlled by changing the current level (or voltage) and time. Furthermore, through electrochemistry, reactions can be conducted at ambient conditions, opposed to *in situ* as in other techniques. The convenience and controllability of electrochemical hydrogenation of graphene provides a realistic approach for a tunable bandgap in graphene, though an observed dependence on the underlying SiC substrate using this technique has been shown previously. In this work, we show that electrochemical

reactivity appears to be instead dependent on point defects present in the EG. Material dependence was investigated and observed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Raman to study the mechanisms of electrochemical hydrogenation of graphene.

To determine the material dependence on electrochemical functionalization three different EG samples (Si-face EG [$\sim 2\text{ML}$], C-face EG [$\sim 10\text{ML}$] and defective Si-face EG [$>50\text{ML}$]) and a smooth graphite disk [$>1000\text{ML}$] were characterized using a homebuilt electrochemical setup, Ag/AgCl reference electrode (0.198V vs. NHE) and dilute HClO_4 as source of hydrogen as shown in Figure 1. A 99.6% Pt wire and exposed EG (approximately a 4mm diameter circular area) were used as the anode and cathode respectively. A potentiostat (Series GTM 300, Gamry Instruments, Warminster, PA, USA) was used for CV and EIS measurements.

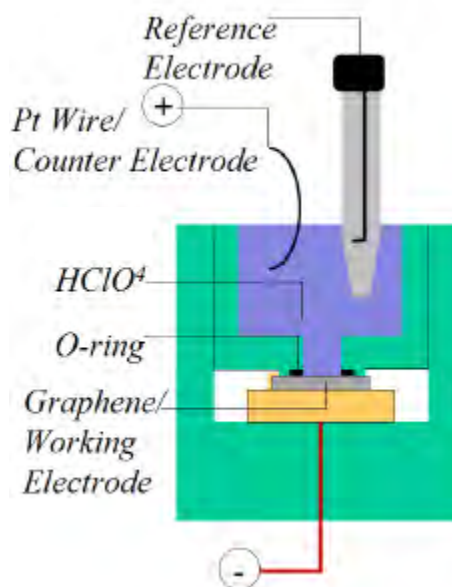


Figure 6. Schematic of home-build electrochemical cell for hydrogenation of epitaxial graphene

Raman spectroscopy was performed using a micro-Raman setup with laser excitation wavelength of 632nm . All spectra obtained were difference Raman spectra; blank SiC substrate was scaled and subtracted from EG/SiC spectra leaving behind the remaining graphene peaks. CV was performed to determine oxidation and reduction potentials at a scan rate of 25mV s^{-1} . EIS recorded the impedance spectrum of the carbon electrodes between 100 kHz and $.1\text{ Hz}$ with a perturbation signal of 10mV . Raman spectra of the electrodes were taken to compare electrode reactivity with material properties.

The material with the lowest starting $I(\text{D})/I(\text{G})$ ratio, a measure of defect sites in the material C-face EG, showed an absence of hydrogenation peak in the CV as shown in Figure 7. This is most likely attributed to the lack of point defects in the material with an $I(\text{D})/I(\text{G})$ ratio of ~ 0 . The EIS shows an almost linear trend in the high frequency regime, which suggests that the reaction is limited by the number of sites hydrogen can occupy on the electrode. In contrast, the Si-face EG with $I(\text{D})/I(\text{G})$ ratio of ~ 0.08 showed a sharp hydrogenation peak, though the system was shown to still be kinetically slow.

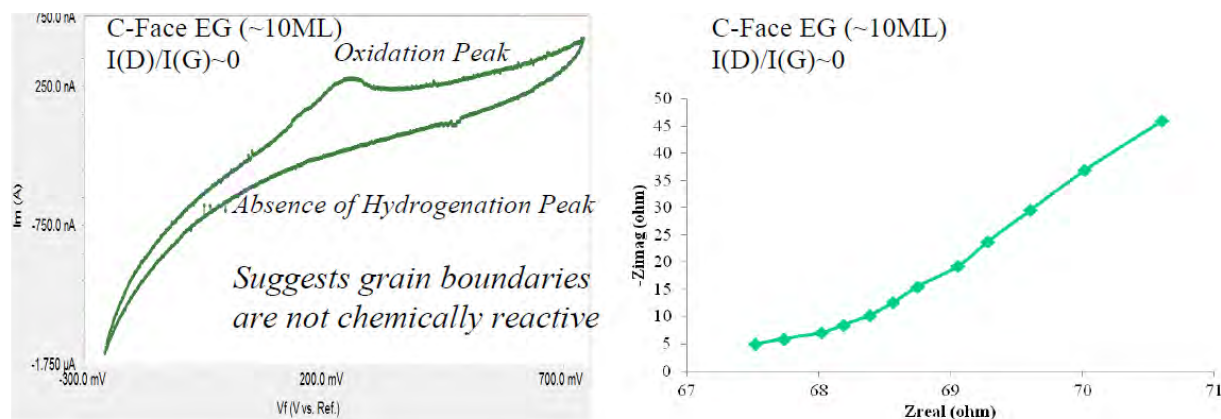


Figure 7. CV and EIS data of C-face EG showing an absence of hydrogenation peak in the CV. EIS shows the system is mass transfer controlled, or reaction is limited by the number of sites available on the electrode.

The material with the highest I(D)/I(G) ratio, highly defective Si-face EG, revealed a semicircle in the high frequency regime using EIS along with the emergence of the hydrogenation peak in CV. In the EIS, the small diameter of the semicircle revealed that the system is kinetically fast, with ample sites for hydrogen adsorption through the presence of point defects. The dependence on defects in electrochemically functionalizing EG suggests that similar kinetics could be observed with other carbon based materials, enabling the electrochemical fabrication of very thick hydrocarbon layers for neutron detection using

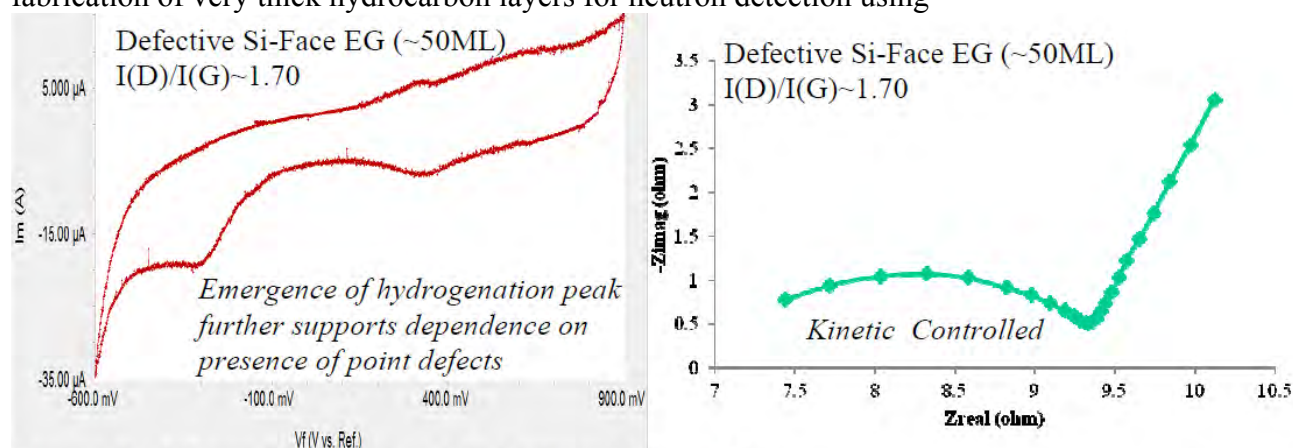


Figure 8. CV and EIS data of highly defective Si-face EG revealing the emergence of the hydrogenation peak in CV. EIS shows the system is kinetic controlled in the high frequency regime, with ample sites, most likely defects, for hydrogen to adsorb.

1.4 Developed a new device architecture based on a SiC bipolar phototransistor (SBPT) with a thin, radiation transparent graphene window as an electrode.

Most radiation detectors do not contain built-in readout gain. In this project, we developed a new way of building in additional gain using a bipolar phototransistor based on SiC, with a transparent graphene window (Fig. 9a). By using UV light as an exciter for the device, the expected performance and gain under neutron exposure may be predicted.

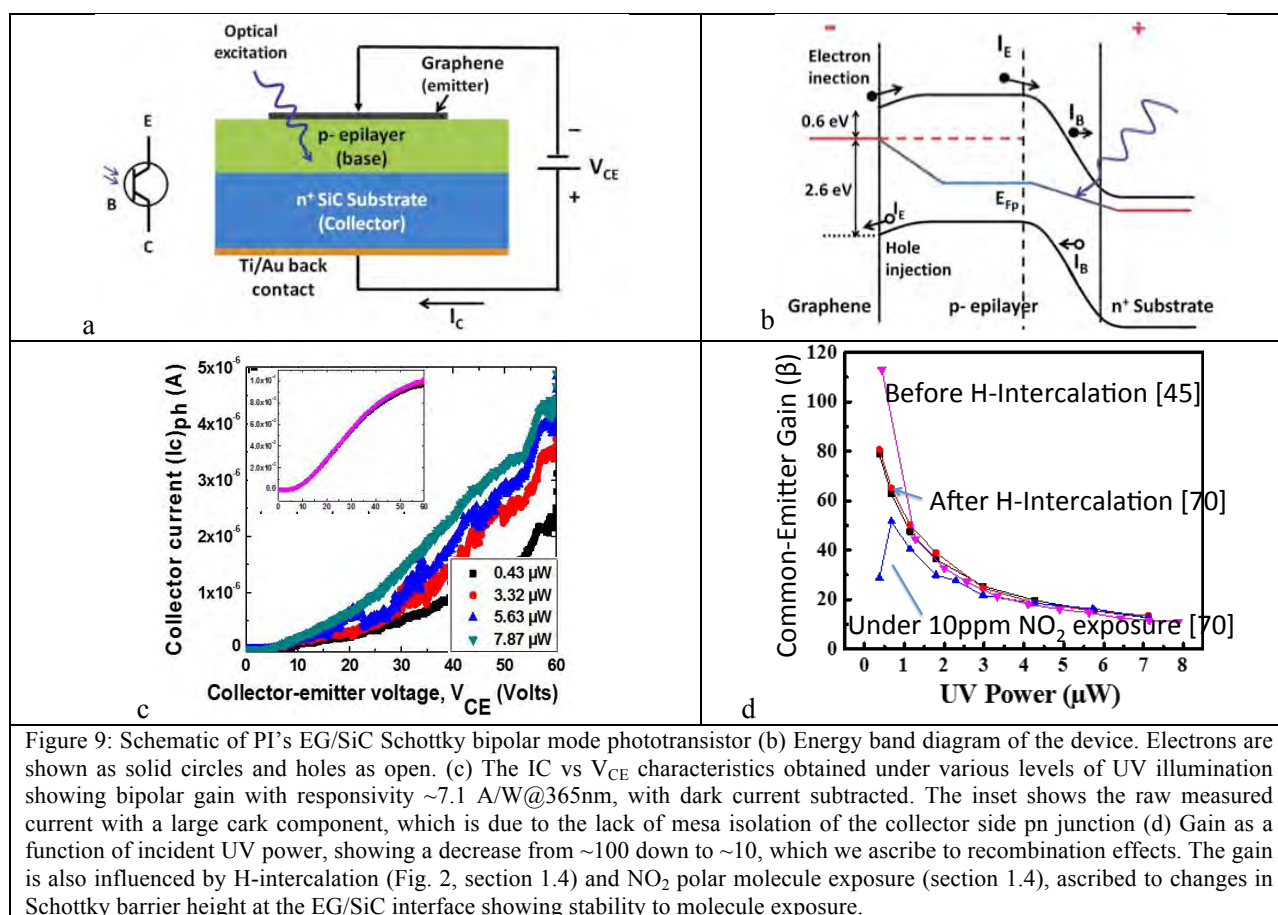
The epitaxial p-SiC layer was grown by chemical vapor deposition (CVD) on a commercial n+ doped SiC (0001) substrate with an offcut angle of 4° using techniques described above. The p-doping was achieved by maintaining a low C/Si ratio in the source gas for CVD growth. The

resulting site competition epitaxy produced p-doped epilayers with carrier concentrations of $\sim 3 \times 10^{14} \text{ cm}^{-3}$, as determined by mercury probe C-V. The epilayer thicknesses was $\sim 30 \text{ }\mu\text{m}$. The epitaxial graphene (EG) was grown by thermal sublimation of the p-SiC epilayer surface at 1350°C . XPS results showed EG thicknesses of 2-3 monolayer in similar growth conditions. The graphene mesa was defined using a O_2 plasma etch through a photoresist mask. A plasma sputtered Ti/Au film was used to form a large area ohmic contact on the back of the SiC substrate.

For phototransistor operation, the graphene emitter was held at a negative bias with respect to the n+ SiC emitter layer by directly contacting the graphene layer using a tungsten probe. The base current was provided by optical excitation from an Omnicure S1000 Hg-vapor lamp with variable intensity. The lamp spectrum provided three sub-bandgap (for SiC) excitation lines at 312, 334 and 365 nm wavelengths. The optical power was measured using a Karl Suss i-line (365 nm) photo-detector, and the power in the other two lines were estimated by their relative intensities with the i-line in the lamp spectrum. Fig-9b shows the typical collector current (I_C) vs collector-emitter voltage (V_{CE}) characteristics for the graphene/SiC HBPT under different levels of illumination.

For the estimation of gain, the base photocurrent was determined by taking into consideration the generation rate from the incident photons over the base thickness as well as the absorption lengths for each of the three excitation lines. Nevertheless, the numbers obtained were only a rough estimate of the base current, I_B . The collector current corresponding to the photocurrent was obtained from the flat part of the dark current subtracted characteristics (inset of Fig 1c). For the $30 \text{ }\mu\text{m}$ epitaxial layer, a gain of ~ 300 was observed. The gain showed slight decrease with increasing light intensity, which is consistent with the expected increase in the recombination rates within the base region. The overall current level measured is $\sim 1 \text{ A/cm}^2$, well above those anticipated in current pulses for radiation detection.

As an added advantage of using a universally transparent EG layer as the emitter, a zero-bias responsivity of $\sim 0.1 \text{ A/W}$ to a 365 nm illumination, as compared to $\sim 10^{-4} \text{ A/W}$ for SiC p-n diodes and often used in radiation detection. The responsivity was estimated by dividing the dark current subtracted collector current (I_C) by the total incident optical power (P_{opt}). As the device bias was increased, and bipolar gain was achieved, the responsivity increased up to $\sim 15 \text{ A/W}$ at 15 V. We developed a physical understanding of this process, which was published in Appl. Phys. Lett., and led to a provisional patent application. The dark current, which sets the scale on the noise and sensitivity of our detectors for these initial studies was very high $\sim 100 \text{ }\mu\text{A}$. We were able to reduce this significantly to $< 1 \text{ }\mu\text{A}$ (Fig. 10) by optimizing the device fabrication, and we believe this can be reduced further by mesa-isolating the thick base.



1.5 2 Undergraduates Accepted to Nationally Recognized PhD Programs in Energy Fields

At the time of initial award of this proposal, our group had just hired 2 undergraduate students into research assistant positions. Since they were still in their early sophomore years at that time, there was a significant incubation time before they became productive, requiring extensive training by the PI and his PhD students. Their promise was realized when they both won the prestigious Magellan scholarship for undergraduate research (funded by the Vice Provost for Research) in their Junior years, both in the development of graphene materials and devices.

Hani Gomez, Latina American-Hani has been working on the characterization of epitaxial graphene grown on SiC, and its use in sensing applications, including gases, as well as radiation. She has been extensively involved in performing Raman, atomic force microscopy (AFM), Fourier Transform Infrared (FTIR) spectroscopy. More recently, she has been developing her analytical skills, and is currently developing an analytical model to understand surface contamination of a graphene surface. She will be co-author on at least 2 papers before graduation. She has just been awarded the prestigious National Science Foundation (NSF) graduate fellowship, and will begin her PhD in the ECE department at University of California at Berkeley. We anticipate that she will continue her research in energy-related applications of semiconductor materials.

Joseph Andrews- Joseph, or Joey as he is known informally in our group, has been working on the growth and characterization of epitaxial graphene on SiC for applications in energy, including microbial fuel cells, and in detection. This is remarkable, particularly given the fact that even graduate students often struggle to master epitaxial growth. In addition to scientific acumen, crystal growth requires a level of maturity, attention to detail and overall organization that is often seen in senior researchers with years of experience. The PI has had the privilege of mentoring Joey to this level, and his graduation is a loss to the group. PhD student Ifat Jahangir will take over the crystal growth responsibilities in this lab from Joey. Joey has received a full research assistantship to Duke University's Electrical Engineering department, where he will begin his PhD this fall, focusing on energy-related applications of semiconductor materials.

1.6 3 PhD graduates with 1 more funded to graduate in 2017 under another project

3 PhD graduates, Sabih U. Omar, Shamaita Shithi (female) and Kevin Daniels, were funded directly under this work. Dr. Kevin Daniels (African American) has accepted a prestigious postdoctoral position at the Naval Research Laboratory under the direction of Dr. Rachel Myers-Ward, working on detection technologies using SiC and graphene technologies. Drs. Omar and Shithi are currently device engineers at Intel (Hillsboro, OR). One more, Ms. Anusha Balachandran is expected to graduate in 2017, although her continued funding will be through an NSF grant. This meets the diversity and workforce mandate of NEUP.

1.7 15 Journal articles in print, 3 patent applications, and over 10 conference presentations

Published 15 journal articles in high impact journals such as Appl. Phys. Lett., J. Appl. Phys., IEEE Trans. Elec. Dev. as a direct consequence of this funding (see products below). This was accompanied by >10 conference presentations at the Electronic Materials Conference (2015 plenary talk was given by Dr. S. Nakamura, the 2014 Physics Nobel Laureate), ANS, and IEEE conferences. Some key talks are highlighted below. This work also led to 3 provisional patent applications, which will eventually be converted to full applications through the University of South Carolina, which the Federal government, as always, will have the first right of refusal to.

2. Plans for follow-on studies

2.1 Develop electrical measurement infrastructure for neutron measurements

The following year, we wish to develop measurement infrastructure for neutron detection at no further cost, as our team has a repository of devices ready for testing. With the loss of Co-PI Dr. Mendez-Torres, we are left without a partner at Savannah River to do this work. One possibility is for us to purchase a Cf-252 source at USC to do this work, although this would have put us over the budget for the project. If DOE can help with this, that would be helpful. Another possibility is to use another DOE lab, although the logistics to developing new partnerships can be prohibitive. We have identified a potential partner at ORNL, although we need the program managers support in developing the appropriate work-scope and protocols for making this work happen. We also appreciate suggestions on any other potential partners. The PI requests a meeting with the program manager, and is happy to travel for a one-on-one meeting. If these experiments are successful, DOE would benefit in the long run with a new low-cost technology for neutron detection.

2.2 Reduce dark leakage current of SBPT detector from nA regime to <1pA by mesa-isolation of the buried collector junction

As seen in Fig. 9 above, the SBPT device has 2 junctions: the graphene/p-SiC schottky emitter-base junction, and the SiC p-n junction base-collector that is buried. The leakage is from the large area buried p-n junction collector, since the top emitter junction is isolated to minimize the number of defects in it statistically. The UV detection characteristics below clearly show that dark current has been brought down from ~100uA, to 400nA simply by improving the quality of the material and overall device. However, the final decrease must occur through mesa-isolation of the thick 10-30um thick base region without causing damage. This requires a deep-etch process, similar to [Cho et. al, Appl. Phys. Lett., 76, 739 (2000)] to be developed, although our group has previously not performed such development. This is currently underway for future work, and we anticipate the active area of the collector junction to decrease from ~1cm² down to 1x10⁻⁴cm², with dark current decreasing by at least a corresponding amount. The actual decrease will likely be better, as more defects will be excluded from the active device region, enabling dark currents <1pA, for high sensitivity detection.

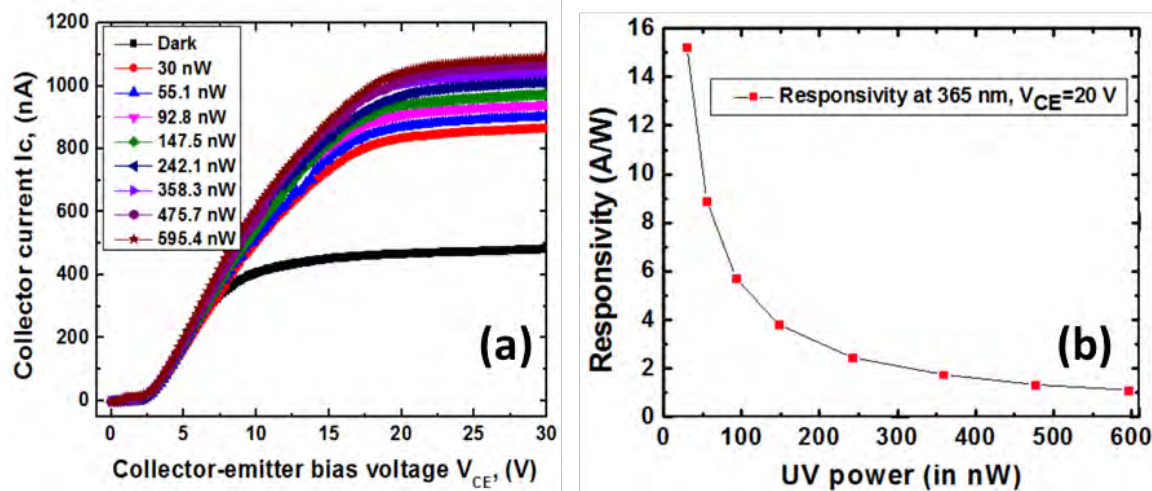


Figure 10: Sensing characteristic of new non-isolated SBPT detectors tested with 365nm light. Responsivity of 15A/W corresponds to current gain >450x. The dark current is seen to be ~400nA.

3 Personnel and Management issues

In addition to the undergraduates described above, this project led to the award of 2 PhD's, including one African American, Kevin Daniels, who has accepted a position at the Naval Research Laboratory, fulfilling DOE's mandate for workforce development. Other issues and relevant personnel are discussed below.

Personnel

Dr. Adrian Mendez-Torres, Co-PI, has left his position at SRNL to become a nuclear inspector at the IAEA in Vienna, Austria. This has removed our capability for neutron testing at SRNL facilities. Therefore, we have identified a new beam-line collaborator at ORNL. The PI will consult the program manager to deal with this issue further. We appreciate any help the program manager can offer.

Mr. Surya Chava, a recent MS graduate of the Indian Institute of Technology (IIT-Mumbai) has joined our research group. He was funded under this proposal, and will continue work on the bipolar phototransistor devices as he progresses.

Mr. Ifat Jahangir joined my group to replace Mr. Gabriel Brown, who left the NEUP program (see above). He will be responsible for the fabrication and characterization of the bipolar devices detector devices in this proposal. He is being supported under a separate grant. We are also looking into diodes fabricated using unique process developed at USC. Specifically, B-diffused SiC diodes are expected to be superior to the other devices in this proposal owing to the quality of the junction. This process is available only at USC.

Mr. Omar Sabih finished his PhD work at USC this December, and will be a product of this project. He has been instrumental in developing the application of SiC diodes and transistors to radiation detector applications, and is being supported under this proposal. Omar's experience has helped jump-start the work, as can be seen in the outputs in the sections following. These SiC diode devices are the key to this proposal.

Ms. Anusha Balachandran has started as a PhD student in Fall 2013. She has been working on SiC materials growth to produce the devices in this proposal. She will be continuing this work on designing, fabricating and testing the transistor structures in the proposal. Her work is consonant with a recently funded NSF proposal in the PI's group that uses a subthreshold SiC MESFET for sensing applications, the same architecture proposed in Tasks 2 and 4.

Mr. Kevin Daniels is an African American PhD student in my group who graduated Summer 2015 and has started a postdoctoral position at the Naval Research Laboratory (NRL). He spearheaded the electrochemical hydrogenation work described in previous years.

We will also continue to engage our most promising senior undergraduate students through the ELCT403/404 mechanism to recruit excellent graduate students, as we have done with Gabriel Brown. This will also help to train qualified students for employment into nuclear energy fields.

4. REFERENCES: Cumulative Major Outputs-Papers, Presentations, Patents

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3. T. Rana, MVS Chandrashekhar, T.S. Sudarshan, J. Cryst. Gr., 380, 61-67 (2013), **“Vapor phase surface preparation (etching) of 4 H-SiC substrates using tetrafluorosilane (SiF₄) in a hydrogen ambient for SiC epitaxy”**
3. Gabriel Brown, Jameson Shull, Rahmi Pak, Sabih Omar, T.S. Sudarshan, C.I. Thomas, Adrian Mendez-Torres, MVS Chandrashekhar, presented at Electronic Materials Conference 2013, Notre Dame University, IN, **“Multi-Channel Spectroscopy of 4H-SiC pin Diodes for Selective Electromagnetic and Ionizing Radiation Detection: Towards Neutrons”**
4. Kevin M. Daniels, A. Obe, B. K. Daas, J. Weidner, C. Williams, T.S. Sudarshan, MVS Chandrashekhar, manuscript accepted, J. Elec. Soc. (2015), **“Metal Catalyzed Electrochemical Formation of Graphane”**
5. Kevin M. Daniels, S. Shetu, J. Staser, J. Weidner, C. Williams, T.S. Sudarshan, MVS Chandrashekhar, presented at Electronic Materials Conference 2013, Notre Dame University, IN, **“History Dependence of Reversible Electrochemical Hydrogenation of Epitaxial Graphene/SiC”**,
6. Sabih U. Omar, Haizheng Song, Tawhid A. Rana, Tangali S. Sudarshan, MVS Chandrashekhar, presented at Electronic Materials Conference 2013, Notre Dame University, IN, **“Effect of structural defects on the reverse I-V characteristics of Ni/4H-SiC schottky diodes: establishment of defect-dependent performance metrics”**
7. Invention Disclosure: **“Solid-state cladding layers for neutron absorption and γ -ray attenuators for enhanced radiation detector performance”** MVS Chandrashekhar, Gabriel Brown, Adrian Mendez-Torres, Jameson Shull, submitted to University of South Carolina Office of Technology Commercialization.
8. Gabriel Brown, J. Shull, R. Pak, Adrian Mendez-Torres, MVS Chandrashekhar, accepted for presentation at IEEE Sensors 2013 Conference. **“Modeling of neutron absorption for detection in SiC diodes”**, journal article in preparation
9. C. Coletti, S. Forti, A. Principi, K.V. Emtsev, A.A. Zakharov, K.M. Daniels, B.K. Daas, M.V.S. Chandrashekhar, T. Ouisse, D. Chaussende, A. H. MacDonald, M. Polini, U. Starke, **“Revealing the electronic band structure of trilayer graphene on SiC”** Phys. Rev. B., 88, 155439 (2013) **(EDITOR’S CHOICE FEATURED ON HOMEPAGE)**
10. Shamaita Shetu, Sabih. U. Omar, K.M. Daniels, Joseph Andrews, B.K. Daas, T.S. Sudarshan, MVS Chandrashekhar, J. Appl. Phys., 114, 164903 (2013) **“Si-atom kinetics in defect mediated growth of multilayer epitaxial graphene films on 6H-SiC”**
11. K. M. Daniels, S. Shetu, J. Staser, J. Weidner, C. Williams, T.S. Sudarshan, MVS Chandrashekhar, ECS Trans., 58, 439-445 (2013), **“Electrochemical Hydrogenation of Dimensional Carbon”**

12. Sabih U. Omar, T.S. Sudarshan, H. Song, T. Rana, **MVS Chandrashekhar**, J. Phys. D, (2014), 47, 295102 ” **Large barrier, highly uniform and reproducible Ni-Si/4H-SiC forward Schottky diode characteristics: testing the limits of Tung's model**”
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16. Sabih U Omar, Gabriel J Brown, Shamaita S Shetu, Tangali S Sudarshan, MVS Chandrashekhar, submitted Phys. Rev. Lett., (2014) “**Efficient minority carrier injection in a Graphene/SiC Schottky junction**”
17. Provisional Patent: MVS Chandrashekhar, T.S. Sudarshan, S.U. Omar, Gabriel Brown, S. Shetu, “**Optically switched graphene/4H-SiC junction bipolar transistor (G-SiC BJT)**”, provisional patent filed USPTO 15/049,743.)
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19. Sabih U. Omar (GS), Tangali S. Sudarshan (CC), Tawhid A. Rana (GS/CC), Haizheng Song (CC), **MVS Chandrashekhar** *accepted*, IEEE Trans. Elec. Dev. (2014), doi: 10.1109/TED.2014.2383386 “**Interface trap induced non-ideality in as-deposited Ni/4H-SiC Schottky barrier diodes**”
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21. Haizheng Song (CC), **MVS Chandrashekhar**, T.S. Sudarshan (CC), Electrochemical Soc. JSS, 4, P71-P76 (2015) “**Study of Surface Morphology, Impurity Incorporation and Defect Generation during Homoepitaxial Growth of 4H-SiC Using Dichlorosilane**”
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23. Anusha Balachandran, Hai Zheng Song, Tangali S Sudarshan, Shamaita S Shetu, **MVS Chandrashekhar**, Mat. Sci. For., 821, 137-140 (2015), “**Study of SiC Epitaxial Growth Using Tetrafluorosilane and Dichlorosilane in Vertical Hotwall CVD Furnace**”

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25. Invention Disclosure: A. Balachandran, **MVS Chandrashekhara**, TS Sudarshan, “**Basal Plane Dislocations elimination and conversion below the epilayer interface**” USC IP office, under review.