



# Immobilization of heterogeneous polydiacetylene supramolecules on SiC substrate for cyclodextrin sensors

H. Choi<sup>1</sup>, C. W. Lee<sup>1</sup>, G. S. Lee<sup>1</sup>, M. K. Oh<sup>1</sup>, D. J. Ahn<sup>\*1</sup>, J. Kim<sup>\*1</sup>, J.-M. Kim<sup>2</sup>, F. Ren<sup>3</sup>, and S. J. Pearton<sup>4</sup>

<sup>1</sup> Department of Chemical & Biological Engineering, College of Engineering, Korea University, Seoul 136-701, South Korea

<sup>2</sup> Department of Chemical Engineering, Hanyang University, Seoul 133-791, South Korea

<sup>3</sup> Department of Chemical Engineering, University of Florida, Gainesville, 32611, USA

<sup>4</sup> Department of Materials Science and Engineering, University of Florida, Gainesville, 32611, USA

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\* Corresponding authors: e-mail ahn@korea.ac.kr, jhkim@prosys.korea.ac.kr

Self-assembled Polydiacetylenes (PDAs) with two different functional groups were successfully immobilized and chemisorbed on the surface of SiC substrates coated with thermally grown SiO<sub>2</sub>. Patterned PDAs on the surface of SiC with thermally grown SiO<sub>2</sub> have shown selective response only to

α-CDs (cyclodextrins) and not to γ-CDs through the manipulation of the outer structures of these PDAs. This shows the potential of integrating PDA-based chemosensors with high temperature SiC microelectronics and MEMS systems.

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**1 Introduction** SiC has shown tremendous promise in high power rectifiers, high frequency electronics and sensors in harsh environments such as toxic solutions, high temperature, space and nuclear energy reactors [1–6]. SiC is well-suited to these applications because of its exceptional chemical, wide-energy bandgap and excellent electrical transport properties such as higher breakdown field ( $3 \times 10^6$  V/cm), higher thermal conductivity (3.2–4.9 W/cm K), higher saturation velocity ( $2 \times 10^7$  cm/s) and higher Young's modulus (700 GPa) than silicon [7]. In addition, SiC is not etched by most acids. It can, however, be etched by alkaline hydroxide bases such as KOH over 600 °C [7]. These properties also make SiC very promising for applications in Micro Electro Mechanical System (MEMS) technology and in various sensors and actuators systems [8–11].

Polydiacetylenes (PDAs) are unique in terms of their output fluorescence emission signals, which range from no fluorescence emission to red fluorescence emission in response to environmental perturbations such as heating, pH or ligand-acceptor interactions [12–14]. After Charych et al. [15] first used PDAs to detect influenza virus, there have been intensive research efforts to develop PDA-based chemosensor systems. However, most efforts have focused

on developing solution-based chemo-sensor systems, which are less sensitive against smaller amount of analytes than PDA vesicle sensors immobilized on solid state substrates [16]. Recently, we have reported immobilization of PDAs on glass substrates [16], but the immobilization of PDAs on semiconductor substrates will be more advantageous because of their higher sensitivity for detection and they can be readily integrated with advanced microelectronics and MEMS for Lab-on-Chip applications. Since the immobilization requires a high quality oxide for the chemisorption of self-assembled monolayer (SAM), it was difficult to demonstrate the chemisorption of PDAs on semiconductor substrate. Unlike silicon, III–V compound semiconductors do not generally have high-quality native oxides. For example, gallium oxide grown by oxygen plasma exposure is very unstable in humid environments and generally not uniform. Therefore, a novel approach is necessary to functionalize the surface of III–V compound semiconductors. Baur et al. [17] successfully functionalized the surface of GaN and AlN using H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>. Another alternative is thermally grown SiO<sub>2</sub> which has higher quality than SiO<sub>2</sub> grown by the PECVD (plasma-enhanced chemical vapor deposition) technique. It is relatively straightforward to thermally grow SiO<sub>2</sub> on single-crystal

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SiC. In this paper, we report that heterogeneous PDA vesicles were successfully immobilized on SiO<sub>2</sub>/SiC substrates and used as chemosensors to detect  $\alpha$ -cyclodextrin (CD), which has similar structure but different pore size compared with  $\gamma$ -cyclodextrin (CD) [18]. The PDAs with various functional groups can be designed and synthesized to monitor ion, glucose, protein and *E. Coli* [18, 19]. The integration of PDAs with advanced SiC microelectronics and MEMS opens possibilities in the area of effective PDA-based SiC bio- and chemo-sensor systems.

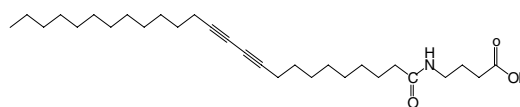
**2 Experiments** Single-crystal 4H-SiC hexagonal substrates with thickness 500  $\mu\text{m}$  and nominal n-type doping of  $5 \times 10^{16} \text{ cm}^{-3}$  were used in these experiments. After the thermal growth of 500  $\text{\AA}$  of SiO<sub>2</sub> on SiC at high temperature (1000  $^{\circ}\text{C}$ ) on the Si face direction, the SiC was cleaned with acetone and isopropanol, followed by ozone plasma exposure for 30 min. Then, the SiC was dipped in an amine solution for 4 h for amine coating. The surface contact angle measured with pure water at pH of 5.5 was 49.5 $^{\circ}$  (Fig. 1). After amine treatment, SiC was coated with biotin for 2 h and with avidin for another 2 h because biotin was critical to immobilize avidin, which was required to immobilize polydiacetylene supramolecules (vesicles).

To synthesize heterogeneous vesicles, PCDA-ABA and PCDA-Biotin were self-assembled (Fig. 2). PCDA-ABA (10,12-Pentacosadiynoic acid-aminobutyric acid): PCDA-Biotin (10,12-Pentacosadiynoic acid-2,2'-(ethylenedioxy)-bis-(ethylamide)-biotin) = 9:1 were mixed. PCDA was purchased from GFS Chemicals, Inc. The details about the PCDA-ABA and PCDA-Biotin can be found in previous papers [18, 20]. The PCDA-ABA was designed to detect  $\alpha$ -CD and the PCDA-Biotin was used for immobilization of self-assembled supramolecules on SiC substrate with thermally grown SiO<sub>2</sub>, where biotin was employed to work as an anchor for amine on the surface of SiO<sub>2</sub>. Cyclodextrins (CDs) were purchased from Aldrich. A nano-plotter microarrayer from Gesim was used to pattern supramolecules on thermally grown SiO<sub>2</sub> surface, which was coated with avidin/biotin/amine prior to use of the microarrayer. The heterogeneous supramolecules (self-assembled PCDA-Biotin:PCDA-ABA) were deposited on the SiO<sub>2</sub>/SiC surface, which was followed by rinsing

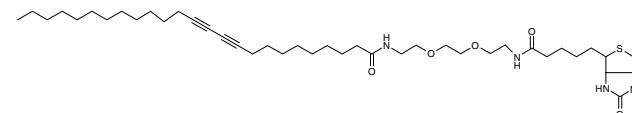


**Figure 1** (online colour at: [www.pss-rapid.com](http://www.pss-rapid.com)) Contact angle measurement against pure water at pH of 5.5 at room temperature after dipping in amine solution for 4 h.

PCDA-ABA (for analyte detection)



PCDA-Biotin (for immobilization on modified glass)

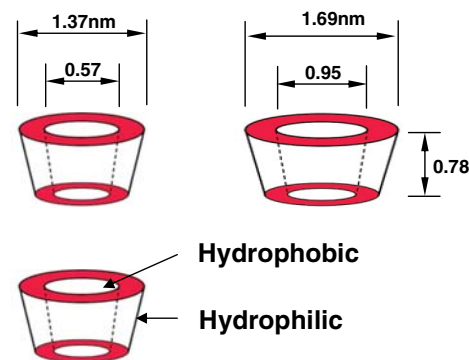


**Figure 2** Structure of diacetylenic monomers: PCDA-ABA (top) and PCDA-Biotin (bottom).

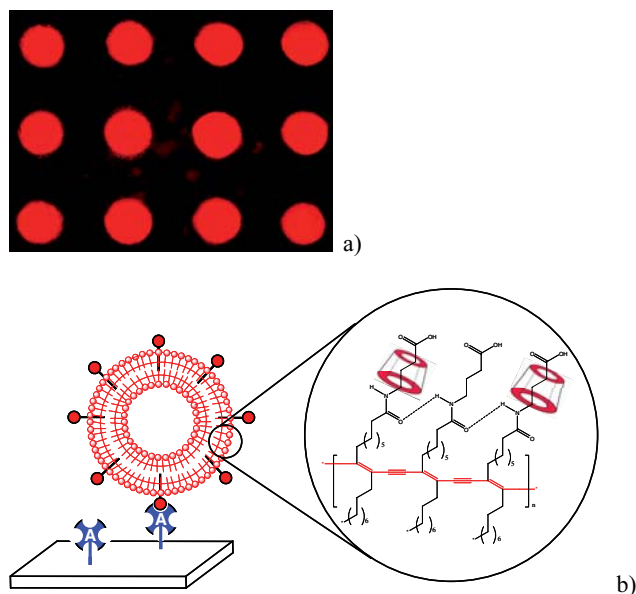
with deionized water. Then the supramolecules/SiC hybrid structure was exposed to UV light (254 nm) for 5 min at an intensity of 1 mW/cm<sup>2</sup> for polymerization. Finally, the supramolecules were immobilized and chemisorbed on SiO<sub>2</sub>/SiC surface.

**3 Results and discussion**  $\alpha$ -CD and  $\gamma$ -CD were employed to test the selectivity. Figure 3 shows the size of  $\alpha$ -CD and  $\gamma$ -CD. The top and bottom of CD are hydrophobic, while the side of CD is hydrophilic. The inner pore diameter of  $\alpha$ -CD is smaller than that of  $\gamma$ -CD, which results in higher steric hindrance upon binding to the supramolecules [18]. The structure of self-assembled hetero-supramolecules (Fig. 4b, enlarged circle) shows that the outside of the supramolecules expresses long biotin and relative short ABA terminals. As we described, biotin moiety works as an immobilization anchor for supramolecules. ABA moiety works as a detector for  $\alpha$ -CD. Due to the inter-chain distance in PCDA supramolecules, which is about 0.5 nm [21], it is more likely that  $\alpha$ -CD is more capable of perturbing the ordered structure of the supramolecules than  $\gamma$ -CD. Because of the larger outer diameters, it is much more difficult for  $\gamma$ -CD to penetrate the densely packed PDA layers.

Figure 4a shows the fluorescence image after the SiC substrate with immobilized supramolecules was dipped in  $\alpha$ -CD solution. The red fluorescent image was clearly evident. Figure 4b describes the mechanism for selectivity,



**Figure 3** (online colour at: [www.pss-rapid.com](http://www.pss-rapid.com)) Size of  $\alpha$ -CD (left) and  $\gamma$ -CD (right).



**Figure 4** (online colour at: [www.pss-rapid.com](http://www.pss-rapid.com)) (a) Fluorescence image showing selective detection of  $\alpha$ -CDs. (b) Immobilized PDAs which were stimulated by  $\alpha$ -CDs.

which results from the steric hindrance of densely packed ABA layer complexed with  $\alpha$ -CD. As expected from the size and structure, there was no effect from  $\gamma$ -CD. The fluorescent image after the SiC substrate was heated to 110 °C to intentionally stimulate PDAs, showed the red dots. This confirmed that the PDAs were successfully chemisorbed on SiO<sub>2</sub>/SiC surface.

While there have been a number of reports about liquid-phase PDA chemosensors, to our best knowledge, there has been no report about SiC-based PDA chemosensor, which have a huge potential when they are integrated with SiC microelectronics and SiC MEMS. In addition, SiC microelectronics technology is compatible with more advanced Si microelectronics technology, including high quality native SiO<sub>2</sub>, which is critical to make supramolecules chemisorbed on substrate surfaces.

**4 Conclusions** Self-assembled hetero-polydiacetylene supramolecules were successfully immobilized and chemisorbed on the surface of single-crystal SiC substrates with thermally grown SiO<sub>2</sub>. These PDAs were designed to sense only  $\alpha$ -CD by controlling the outer structure. Compared with solution-based PDA sensors, it was shown that PDA vesicle array patterns on SiO<sub>2</sub>/SiC substrates were sensitive enough to detect the effects of external stimuli, including CDs and temperature. There is a great potential for PDA-based sensor systems integrated with advanced SiC microelectronics and SiC MEMS.

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