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Quantitative Analysis of the Functionalization of Gallium Phosphide With Organic Azides

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Summary: Gallium phosphide (GaP) surfaces were functionalized with two different molecules that contain an azide moiety at their terminus. Compound 4-azidophenacyl bromide (4AB) is an aryl azide with a bromine group at its opposite terminus that provides easy identification of the molecule’s presence on the surface with x-ray photoelectron spectroscopy (XPS). O-(2-aminoethyl)-O′-(2-azidoethyl)pentaethylene glycol (AAP) is a small poly(ethylene glycol) molecule with an amine group at its opposite terminus. Atomic force microscopy was used to identify the uniformity of the clean and functionalized GaP surfaces. Water contact angle revealed a more hydrophobic surface with AAP functionalization (33°) and even more hydrophobic (53°) with the 4AB functionalized surface compared to a clean surface (16°). XPS confirmed the presence of each of the organic azides on the surface. XPS was further used to calculate the adlayer thickness of each functionalization. This analysis revealed an adlayer thickness of about 8 Å for the 4AB functionalized surfaces compared to 1 Å for the AAP adlayer, which led to the conclusion that AAP functionalization only provided partial coverage. A stability study using 4AB-functionalized surfaces showed good stability in saline solutions with varying concentrations of hydrogen peroxide. Finally, inductively coupled plasma mass spectrometry was used to evaluate the gallium concentration in the stability solutions. While the functionalization with the organic azides did not provide complete suppression of gallium leaching, both of the azides decreased the leaching by 10–50%. SCANNING 34: 332–340, 2012. © 2012 Wiley Periodicals, Inc.

Key words: gallium phosphide, azide, functionalization, XPS, toxicity

Introduction

A considerable amount of effort in the past decades has been devoted to developing implantable devices for specific purposes, especially biosensing. There are many considerations for the advancement of implantable devices, including the optimization of sensitivity and selectivity; however, the most important is most likely biocompatibility. Much research has been dedicated to tailoring inorganic surfaces with organic molecules so as to minimize toxicity.

One of the most common classes of materials used in biosensing is semiconductors. Indeed, silicon has been experimented with extensively for biosensors due to its broad physical and electrical characterization (Cui et al., 2001; Kim et al., 2007). In addition, III-V semiconductors have also been used in sensing applications. Gallium arsenide is the most commonly used III-V semiconductor, again owing to its maturity development (Lee et al., 2008). Gallium phosphide (GaP) is a III-V semiconductor that is commonly used in optoelectronic and high-temperature devices. It is an excellent candidate for future biosensor devices because its unmodified surface has shown favorable biocompatibility in previous studies (Hallstrom et al., 2007).
Like many semiconductors, GaP is susceptible to corrosion and degradation. This process can lead to the leaching of toxic surface ions into the surrounding solution. Obviously, this poses a problem when it comes to materials such as GaP being used in implantable devices. Therefore, our group has used organic adsorbates to covalently bind to the surface of GaP to reduce the amount of the toxic and leachable oxide layer (Flores-Perez et al., 2008; Richards et al., 2010). In this article, we propose a new method to covalently functionalize a GaP surface using azide chemistry. Azides, which are commonly used in click chemistry, have the ability to form a highly reactive nitrene intermediate when irradiated with ultraviolet (UV) light (Ziani-Cherif et al., 1999). Azides have been used to link various organic molecules to polystyrene (Nahar et al., 2001), poly(ethylene terephthalate) (Ziani-Cherif, Imachi et al., 1999), glass cover slips (Chen et al., 2009), quartz (Harmer, 1991), and silicon (Harmer, 1991).

Due to its successful functionalization of a broad range of materials, it is proposed that azides can provide a new stable route to covalently link organic molecules and biomolecules to a GaP surface. We used 4-azidophenacyl bromide (4AB) and O-(2-aminoethyl)-O′-(2-azidoethyl)pentaethylene glycol (AAP) as the azide reactants (see Fig. 1). Specifically, 4AB was used to allow for easy identification of its presence on a GaP surface. Its bromine group generates a distinct peak in an x-ray photoelectron spectroscopy (XPS) spectrum that provides evidence that the molecule is indeed attached to the GaP surface. In addition, the bromine group is not capable of bonding to both the GaP surface and the azide molecule. AAP was chosen because of the antibiofouling capabilities poly(ethylene glycol) (PEG) like molecules can confer on a surface.

Photochemistry on a GaP surface is not uncommon. In our past study, GaP was reacted with a terminal alkene under UV light resulting in the formation of a dense adlayer (Ivanisevic et al., 2008). To our knowledge, functionalization with azides on a GaP surface has not been studied before.

Besides XPS, other surface sensitive techniques including atomic force microscopy (AFM) and water contact angle were used to analyze the functionalized surfaces. A stability study was performed using water, various pH solutions, and saline with varying concentrations of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}). Finally inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify the amount of gallium leaching from the functionalized surfaces in the stability solutions.

**Materials and Methods**

**Surface Cleaning and Functionalization**

GaP (100) wafers were purchased from University Wafer (South Boston, MA). The (100) plane of GaP was chosen because of its ability to accommodate a wide range of adlayers including UV-reactive adlayers (Ivanisevic et al., 2008; Richards et al., 2010). Compounds 4AB and AAP were purchased from Sigma-Aldrich (St. Louis, MO). The GaP wafers were cut into 5 mm × 5 mm pieces. Before functionalization, all wafers were degreased. The

Fig 1. The functionalization schemes of the two different azide adsorbates.
degreasing process consisted of ultrasonication in water for 20 min and ethanol for 20 min followed by drying with N₂. The wafers were then exposed to NH₄OH for 30 s in order to remove the oxide layer (Morota and Adachi, 2006). The wafers were then rinsed with water and ethanol and dried with N₂. Finally, the wafers were exposed to either a 1-mM solution of 4AB in toluene or a 1% solution of AAP in ethanol. The reaction vials were exposed to UV light (302 nm) for 3 h. After the functionalization was complete, the wafers that were exposed to 4AB were rinsed with copious amounts of toluene, water, and ethanol and dried with N₂ after each rinse. The wafers exposed to AAP were rinsed with copious water and ethanol with subsequent N₂ drying after each rinse. All wafers were stored in a vacuum desiccator for an average of four days until subsequent analysis unless otherwise noted.

Stability Experiments

One milliliter solutions of water; saline; saline with 0.1%, 1%, and 10% H₂O₂; and phosphate-buffered saline (PBS) solutions of pH 5, 7, and 9 were created and placed in 1-mL plastic vials. One GaP sample functionalized with 4AB was placed in each vial. After one and five days of incubation in their respective solutions, the wafers were removed and rinsed with ethanol and dried with N₂. Water contact angle was performed on each sample. The reported contact angles are the average of at least three measurements taken in multiple locations on the sample. Each GaP wafer was rinsed with ethanol, dried with N₂, and then placed back in the respective solution. After seven days, all of the GaP wafers were removed from their solution. Water contact angle was performed for the last time and the wafers were not placed back in solution. The solutions of water, saline, saline with 1% H₂O₂, and PBS buffer solutions of pH 5, 7, and 9 were analyzed to determine how much gallium ion was present using ICP-MS. AAP-functionalized samples were exposed to water, saline, saline with 1% H₂O₂, and PBS buffer solutions of pH 5, 7, and 9. These solutions were also analyzed with ICP-MS to determine the amount of gallium ion present.

Surface Characterization

Water contact angle measurements were performed on a Tantac, Inc. (Acquired by Chemsultants International, Inc., Mentor, OH) contact angle meter, model CAM-PLUS, using the half-angle method.

AFM images were collected using the tapping mode setting on a Multi-Mode Nanoscope IIIa atomic force microscope (Veeco, Plainview, NY). A scan size of 1 μm × 1 μm at a rate of 1 Hz was used on each sample. Single-beam cantilevers were purchased from Asylum Research (Santa Barbara, CA). Data analysis was performed using the Nanoscope III 5.12r3 software (Veeco, Plainview, NY).

XPS data were obtained with a Kratos Ultra DLD spectrometer (Shimadzu, Nakagyo-ku, Kyoto, Japan) using monochromatic Al Kα radiation (hν = 1486.6 eV). Survey and high-resolution spectra were collected at a fixed analyzer pass energy of 160 and 20 eV, respectively, and acquisition was performed at photon emission angles of 0°, 45°, and 60° measured with respect to the surface normal. Binding energy values were referenced to the Fermi edge, and charge correction was done using the Carbon 1s peak set at 284.80 eV. Curve fitting was performed after linear or Shirley-type background subtraction assuming a Gaussian/Lorentzian peak shape.

ICP-MS data were obtained with an Element2 ICP mass spectrometer (ThermoFisher, Bremen, Germany) equipped with an Aridus desolvating introduction system (with a T1Hnebulizer) to enhance sensitivity and reduce oxide and hydride interferences (Cetac Technologies, Omaha, NE). The argon sweep gas and nitrogen of the Aridus were adjusted for maximum peak height and stability using 7Li, 115In, and 238U peaks obtained from a Merck multielement standard (1 ng/mL, Merck & Co., Whitehouse station, NJ). After tuning and calibration of the ICP instrument, medium resolution analyses were carried out on the Ga69 and Ga71 peaks.

Results and Discussion

Before the GaP wafers were exposed to the azide reactants, the cleaned GaP wafers were subject to water contact angle in order to identify that the wafers were indeed clean and ready for functionalization. A clean GaP surface revealed a water contact angle of about 16°, which is consistent with previous reports (Flores-Perez et al., 2008; Mukherjee et al., 2010). After functionalization with AAP and 4AB, the contact angle increased to about 33 ± 5° and 53 ± 5°, respectively (Table I). The contact angle for AAP correlates with the literature related to PEG on various surfaces (Schlapak et al., 2006; Alibeik et al., 2010). This is a fair assessment since AAP is essentially a low molecular weight PEG molecule. The contact angle for GaP functionalized with 4AB is higher due to the mostly hydrophobic structure of the 4AB molecule.

<table>
<thead>
<tr>
<th>Functionalization</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean GaP</td>
<td>16 ± 6</td>
</tr>
<tr>
<td>GaP with AAP</td>
<td>33 ± 5</td>
</tr>
<tr>
<td>GaP with 4AB</td>
<td>53 ± 5</td>
</tr>
</tbody>
</table>
Fig 2. AFM surface topography images after AAP-functionalization (A), clean GaP (B), and after 4AB-functionalization (C). (Scale bar corresponds to 250 nm).

In order to analyze the surface topography of the clean GaP sample and the functionalized samples, we used AFM. A surface topography image allows us to identify a uniformly functionalized surface that lacks any large pits or mounds of debris or excess reactant and solvent. A clean, etched GaP wafer, as seen in Figure 2(B), was shown to be very smooth, with a root mean square (RMS) roughness of 0.21 nm. After functionalization with AAP and 4AB, the roughness increases slightly to 0.48 nm and 0.37 nm, respectively. The corresponding topography images can be seen in the Figure 2(A) and (C). We can conclude from these images and measurements that both functionalizations result in slight nonuniformity. Indeed, the roughness most likely plays a role in the relatively large error in the contact angle measurements. The increased RMS roughness values compared to the clean GaP RMS roughness value are consistent with the chemisorption of up to a monolayer of the respective reactant.

XPS Characterization

Further analysis of the clean and functionalized GaP surfaces was carried out with XPS. XPS is a powerful surface sensitive tool that allows qualitative as well as quantitative characterization of the surface. The 4AB molecule was chosen specifically because of the presence of its bromine group. Halogens, such as bromine, are easily detectable using XPS, therefore the presence of the bromine signature in the XPS spectra would provide a quick and easy identification of the successful functionalization of 4AB (Basu et al., 2006). Figure 3 depicts the Br 3d spectra of the clean GaP surface along with a 4AB functionalized GaP surface. An obvious peak at around 69 eV indeed indicates the presence of bromine and the 4AB adsorbate. The clean GaP Br 3d spectrum is lacking the signature peak.

More important information can be garnered from the XPS carbon 1s spectra (Fig. 4). First, the freshly cleaned GaP spectrum shows the typical signatures of a clean, etched surface. The peak at 284.8 eV corresponds to C-H bonding. We can conclude indirectly that the relatively large size of this peak compared to the functionalized samples is most likely the result of atmospheric contamination from the lab air. The clean GaP sample was exposed to lab air for several minutes while the sample was being loaded into the XPS chamber. This is likely a result of the
Fig. 4. XPS carbon 1s spectra of a clean GaP surface and two of each azide functionalizations.

electrostatically charged oxide-free GaP surface that attracts oppositely charged contamination (Reinhardt et al., 2008). Moreover, the greater exposure of the functionalized samples to the solvents (ethanol and toluene) and UV light likely removed some of the atmospheric contaminants. Loading the samples into the XPS chamber also resulted in lab air exposure. The other carbon components at higher binding energies are negligible since their area represents an order of magnitude less than the C-H peak area.

Figure 4 also depicts two separate samples of each type of functionalization. The GaP functionalized with 4AB revealed components that are to be expected. The peak at 284.8 eV again corresponds to the C-H bonding from the 4AB molecule. Indeed, this peak may also represent carbon contamination from the atmosphere. Shifted to a higher binding energy of about 286.5 eV lies a shoulder peak that is a result of the C-N bonding of the 4AB molecule covalently bonded to the surface. At an even higher binding energy of 289 eV, we observe the peak corresponding to C = O, which is relatively similar in area as the C-N peak. This finding correlates well with the 4AB structure since there is exactly one of each type of bond.

The spectra corresponding to the AAP-functionalized GaP again showed peaks that were expected. The most noticeable aspect of the spectra is the relatively higher shoulder peaks corresponding to C-O. The AAP is essentially a short PEG molecule and therefore has a large amount of C-O bonds compared to the other types of carbon bonds.

In the case of both functionalization schemes, the nitrene intermediate formed by UV irradiation is reactive enough to covalently bond to the atoms on the GaP surface. Specifically, the azides are most likely bound to the gallium atoms on the surface. This is not easily distinguishable using the XPS spectra, but other studies have reported that organic thiolated molecules preferentially bond to the gallium atoms on a GaP surface compared to the phosphorus atoms forming Ga-S bonds (Zerulla and Chasse, 2009). Therefore, based on this previous study, it is hypothesized that the azide molecules predominantly develop Ga-N bonds at the surface (see Fig. 1).

XPS was further used to determine the thickness of the adlayer on the GaP surface using the following equation adapted from Fadley, which assumes complete and homogeneous coverage (Fadley, ’78):

\[
N_{Ga2p}(P2p) = N_{Ga2p}^0 (P2p) \left( 1 - \frac{-t}{e^{\Lambda_{Ga2p}(P2p) \cos(\theta)}} \right),
\]

where \(N_{Ga2p}(P2p)\) and \(N_{Ga2p}^0(P2p)\) are peak intensities from the Ga 2p (P 2p) spectra before and after functionalization, respectively. \(\Lambda_{Ga2p}(P2p)\) is the electron attenuation length of Ga 2p or P 2p photoelectrons through the AAP and 4AB adlayers, \(\theta\) is the photoemission angle, and \(t\) is the thickness of the adlayer in Å. The electron attenuation length was estimated using an equation developed by Cumpson (Cumpson, 2001). The average thickness, \(t\), was calculated by plotting \(\ln(N/N^0)\) versus \(1/\cos(\theta)\). The slope of the resulting line corresponded to the value for \(-t\).

The thickness of the AAP adlayer on the GaP surface was determined to be 2 Å using the Ga 2p high-resolution spectrum and 1 Å using the P 2p high-resolution spectrum (Table II). Since the thickness of the adlayer must be at least the thickness of an AAP molecule lying on its side (~2 Å), we can say that the complete coverage assumption does not hold. Therefore, the AAP functionalization results in partial coverage of the GaP surface. In contrast, the thickness of the 4AB adlayer was calculated to be 8 Å with the Ga 2p high-resolution spectrum and 11 Å with the P 2p high-resolution spectrum. The results of these calculations demonstrate that the 4AB adsorbates are standing in a more perpendicular fashion with respect to the surface than the AAP adsorbates, especially considering the fact that the length of the 4AB molecule is approximately 9 Å, whereas the AAP molecule is approximately 27 Å. There are a variety of explanations for these findings, each of which may contribute partly. First, it is possible that the

<table>
<thead>
<tr>
<th>Functionalization</th>
<th>Calculated thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP with AAP</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>GaP with 4AB</td>
<td>8 ± 3</td>
</tr>
<tr>
<td>GaP</td>
<td>1 ± 2</td>
</tr>
<tr>
<td>GaP</td>
<td>11 ± 2</td>
</tr>
</tbody>
</table>
Water Contact Angle Stability Study

Since the 4AB adlayer has the potential for future functionalization by replacing the bromine with a reactive carboxylic acid, one is concerned with its stability in various solutions. In order to demonstrate the stability of the adlayer on the GaP surface, one 4AB-functionalized surface was exposed to each of the following solutions in 1 mL vials: water; PBS at pH 5, 7, and 9; saline; and saline with 0.1, 1, and 10% H$_2$O$_2$. After, one, five, and seven days, the 4AB-functionalized samples were removed and subject to contact angle analysis. A summary of the results can be found in Table III. With respect to the water solution, there is a decrease after one day to a contact angle of around 25° that remains stable until the seventh day. A similar trend is seen when the functionalized surface is exposed to a pH 5 solution. Samples exposed to the pH 7 and pH 9 solutions showed total wetting after just one day in solution. These trends indicate that the adlayer is degraded to a considerable extent in the water and pH 5 solutions since the contact angles are approaching the contact angle of clean GaP (16°). This trend was observed in our previous study and analysis by XPS after exposure to pH solutions indicated that there was indeed a depletion of the organic adlayer (data not shown). In the pH 7 and pH 9 solutions, the adlayers are not only completely degraded, but the GaP surface becomes more hydrophilic. This can most likely be attributed to the chemicals in the pH 7 and pH 9 PBS buffers, specifically hydrogen phosphate (HPO$_4^{2-}$) that react with the GaP surface atoms and form a hydrophilic oxide layer. Total wetting is not observed in the pH 5 PBS buffer because there is a lower concentration of HPO$_4^{2-}$ and a higher concentration of less reactive H$_2$PO$_4^-$.

Exposing the functionalized samples to physiological conditions is important in testing for future development of implantable devices. Saline with varying concentrations of H$_2$O$_2$ were used to simulate macrophage recruitment at implant sites (Linsmeier et al., 2008). The samples exposed to saline with varying concentrations of H$_2$O$_2$ showed a different trend compared to the water and pH solutions. There is a leveling off of the contact angle after just one day and continues at that level throughout the study. The contact angle values for the samples in plain saline seem to be a little higher than the values garnered from the water and pH 5 solutions suggesting that the adlayer is more resistant to degradation. Remarkably, the addition of H$_2$O$_2$ has little effect on the contact angles, which means that the H$_2$O$_2$ is not reacting with the adlayer. Instead, the H$_2$O$_2$ is most likely reacting with the bare GaP on the surface, which is confirmed by the increased gallium leaching from these samples as discussed in the following section. Similar trends were observed in our previous report, in which GaP surfaces were functionalized with thiols and terminal alkene molecules (Richards, Zemlyanov et al., 2010).

**Toxicity Analysis**

Toxicity of the 4AB- and AAP-functionalized surfaces was investigated by determining the amount of gallium leaching into various solutions. One sample of each functionalization was placed in each of the following solutions in 1 mL vials: water; saline; saline

<table>
<thead>
<tr>
<th>Table III</th>
<th>The contact angle of 4AB-functionalized GaP surfaces after one, five, and seven days incubation in water and various pH solutions and saline with varying concentrations of H$_2$O$_2$. (All measurements have an error of ±5°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water contact angle (°)</strong></td>
<td>Water</td>
</tr>
<tr>
<td>Begin</td>
<td>53</td>
</tr>
<tr>
<td>One day</td>
<td>29</td>
</tr>
<tr>
<td>Five days</td>
<td>21</td>
</tr>
<tr>
<td>Seven days</td>
<td>23</td>
</tr>
</tbody>
</table>
with 1% \( \text{H}_2\text{O}_2 \); PBS buffers of pH 5, 7, and 9. After seven days in solution, the samples were removed and the remaining solution was analyzed for the amount of gallium within it. Table IV summarizes the gallium concentration within the water samples for a 4AB-functionalized surface, an AAP-functionalized surface, and a clean GaP wafer as a control. There was approximately 80 ppb of gallium in the water that was exposed to a clean GaP wafer compared to 70 ppb and 60 ppb for the 4AB- and AAP-functionalized surface, respectively. The slight reduction can be explained by the azide molecules covalently bonding to the surface atoms that prevent the gallium from forming an unstable oxide that can dissolve into the surrounding solution. The lesser amount of leaching demonstrated by the AAP-functionalized surface compared to the 4AB-functionalized surface seems contradictory since the AAP demonstrated significantly less coverage. However, this finding can be attributed to the inherent nature of the AAP molecule compared to the 4AB molecule. As suggested earlier, the AAP is likely lying more parallel (or in a more “mushroom-like” configuration) to the surface, which allows for interaction of the oxygen atoms within each AAP molecule and the underlying gallium atoms. This significant amount of coordination of the oxygen with the gallium most likely prevents the formation of gallium oxide.

With respect to the low reduction in leaching (only about 10 or 20 ppb) compared to the clean GaP sample, we can conclude that the water must be having a large effect on the adlayers. The water from the in-house purification system is slightly acidic, therefore, the water is most likely etching the adlayer to an extent and leading to surface degradation.

The gallium concentration in the saline solutions shows a similar trend to the water solutions (Table V).

### Table IV Gallium concentration in water solutions exposed to clean and 4AB- and AAP-functionalized GaP surfaces

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ga concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean GaP in water</td>
<td>80 ± 5</td>
</tr>
<tr>
<td>AAP on GaP in water</td>
<td>60 ± 5</td>
</tr>
<tr>
<td>4AB on GaP in water</td>
<td>70 ± 5</td>
</tr>
</tbody>
</table>

The highest concentration (330 ppb) again occurred when the solution was exposed to a nonfunctionalized surface. Functionalized surfaces in saline showed significantly lower concentrations of 80 ppb and 140 ppb for 4AB and AAP, respectively. This is a large decrease in the amount of gallium leaching suggesting that the adlayers are protecting the underlying surface from the harsh conditions of the buffer ions without being heavily degraded by the acidity of the in-house water. In this case, the AAP-functionalized surface leached more, indicating that the AAP molecule is more susceptible to damage from the buffer conditions. Samples that were exposed to a 1% solution of \( \text{H}_2\text{O}_2 \) in saline had higher concentrations of gallium, however, they were still lower than the pure saline solution. As previously discussed, it is obvious that \( \text{H}_2\text{O}_2 \) has a significant effect on the amount of gallium leaching from the surface and it is irrespective of the functionalization.

Notably, the amount of gallium leaching from the 4AB surfaces in the saline/\( \text{H}_2\text{O}_2 \) solutions is considerably higher than that of the water solution. This finding seems somewhat contrary to the results obtained in the stability study in Table III. We would expect to see about the same or lower amount of gallium leaching from the samples exposed to saline solutions since the contact angles remained stable and relatively high until the seventh day. As mentioned previously, this would mean that the adlayer remained mostly intact throughout the seven days, thus preventing gallium leaching. Therefore, we can conclude that the 4AB adsorbates must not be forming a complete monolayer on the GaP surface exposing large areas of nonfunctionalized GaP. This allows the ions and \( \text{H}_2\text{O}_2 \) in the saline to attack at the open areas and release gallium into solution. The lack of complete coverage by 4AB is most likely the result of its large bulky structure that prohibits it from forming a densely packed adlayer.

The gallium leaching in the pH solutions (Table VI) shows a trend that coincides with the water contact angle stability study (Table III). The lowest amount of leaching is seen with the pH 5 and 7 solutions indicating that the adlayer is stable and remaining intact. This prevents gallium leaching from the surface. The greatest leaching occurs when the samples are exposed

### Table V Gallium concentration in various saline solutions exposed to clean and 4AB- and AAP-functionalized GaP surfaces

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ga concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean Gap in saline</td>
<td>330 ± 30</td>
</tr>
<tr>
<td>AAP on GaP in saline</td>
<td>140 ± 20</td>
</tr>
<tr>
<td>AAP on GaP in 1% ( \text{H}_2\text{O}_2 )</td>
<td>270 ± 30</td>
</tr>
<tr>
<td>4AB on GaP in saline</td>
<td>80 ± 10</td>
</tr>
<tr>
<td>4AB on GaP in 1% ( \text{H}_2\text{O}_2 )</td>
<td>270 ± 30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ga Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAP on GaP in pH 5</td>
<td>5 ± 2</td>
</tr>
<tr>
<td>AAP on GaP in pH 7</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>AAP on GaP in pH 9</td>
<td>150 ± 15</td>
</tr>
<tr>
<td>4AB on GaP in pH 5</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>4AB on GaP in pH 7</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>4AB on GaP in pH 9</td>
<td>40 ± 5</td>
</tr>
</tbody>
</table>

### Table VI Gallium concentration in various pH solutions exposed to 4AB- and AAP-functionalized GaP surfaces

to pH 9, which is consistent with the total wetting observed after one day of exposure. The adlayers are degrading quickly allowing the gallium to form oxide and dissolve into solution. The 4AB-functionalized samples leached less gallium compared to the AAP-functionalized samples, which attests to the more incomplete adlayer formed by AAP and its susceptibility to the buffer conditions.

The toxicity of gallium has been studied in previous reports due to gallium’s usefulness in treating conditions such as hypercalcemia (Warrell et al., ’88). This usefulness even prompted the FDA to approve a drug known as Ganite™ (gallium nitrate) for the treatment of this condition. Gallium has also demonstrated anticancer properties especially against lymphomas (Warrell et al., ’83; Weick et al., ’83). In a study by Hart et al., gallium, along with aluminum, indium, and thallium were evaluated for their antitumor properties as well as their in vivo toxicity. Gallium demonstrated a high effectiveness in its tumor suppression along with being the least toxic (Hart and Adamson, ’71). The normal gallium levels in human blood and human urine is roughly 0.5 ppb and 0.15 ppb, respectively (Liao et al., 2004). The gallium concentrations reported in Tables IV, V, and VI were the result of 5 mm × 5 mm GaP wafers in 1 mL of solution. Future implantable devices will require considerably less GaP and will obviously be exposed to more than 1 mL of solution, further alluding to the potential of this material.

Conclusions

In this report, GaP was functionalized with two organic molecules bearing an azide moiety. The first adsorbate was an aryl azide containing a bromine group at its opposite end (4AB) for easy XPS identification. The other was a small PEG azide with an amine group at its opposite end (AAP). AFM, XPS, and water contact angle were used to characterize the surface. AFM topography scans indicated a mostly smooth surface after functionalization with 4AB and a slightly more nonuniform surface after functionalization with AAP. XPS confirmed the presence of both azides on the surface. XPS was also used to determine the thickness of each adlayer. From this data, it was suggested that the 4AB formed a more ordered adlayer compared to the AAP adsorbates whose coverage was significantly less. A stability study performed on 4AB functionalized surfaces revealed that the adlayer had an excellent resistance to degradation in saline solutions with varying concentrations of H₂O₂. ICP-MS was used to evaluate the amount of gallium leaching into the surrounding stability solutions. In general, the 4AB functionalized surfaces decreased the amount of gallium in solution to a larger extent, which was expected considering the XPS calculations, however both functionalizations still had considerable gallium leaching. The lack of complete uniform coverage of the surfaces could be the result of a number of factors including the molecular structures of the organic azides. Furthermore, the strength and wavelength of the UV irradiation, the reaction time, and the solvents could play a role in the amount of coverage. While the results obtained here are beneficial, there must be considerable work done on increasing the adlayer coverage and decreasing leaching before the implementation of azide functionalization on GaP for implantable devices.

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References


