ACCOUNTS
of chemical research

Wet-Chemical Passivation of InAs: Toward Surfaces with High Stability and Low Toxicity

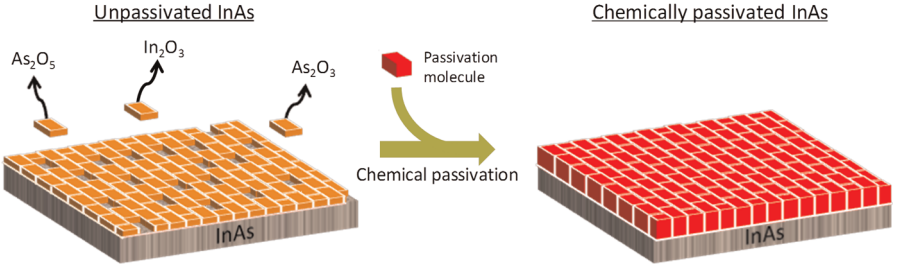
SCOTT A. JEWETT[†] AND ALBENA IVANISEVIC[*,‡]

[†]*Weldon School of Biomedical Engineering, Purdue University, West Lafayette, Indiana 47907, United States, and* [‡]*Department of Materials Science and Engineering, North Carolina State University, Joint Department of Biomedical Engineering NCSU/UNC-CH, Raleigh, North Carolina 27695, United States*

RECEIVED ON DECEMBER 1, 2011

CONSPECTUS

Chemical passivation helps prevent the dissolution of toxic components



In a variety of applications where the electronic and optical characteristics of traditional, siliconbased materials are inadequate, recently researchers have employed semiconductors made from combinations of group III and V elements such as InAs. InAs has a narrow band gap and very high electron mobility in the near-surface region, which makes it an attractive material for high performance transistors, optical applications, and chemical sensing. However, silicon-based materials remain the top semiconductors of choice for biological applications, in part because of their relatively low toxicity. In contrast to silicon, InAs forms an unstable oxide layer under ambient conditions, which can corrode over time and leach toxic indium and arsenic components. To make InAs more attractive for biological applications, researchers have investigated passivation, chemical and electronic stabilization, of the surface by adlayer adsorption. Because of the simplicity, low cost, and flexibility in the type of passivating molecule used, many researchers are currently exploring wet-chemical methods of passivation.

This Account summarizes much of the recent work on the chemical passivation of InAs with a particular focus on the chemical stability of the surface and prevention of oxide regrowth. We review the various methods of surface preparation and discuss how crystal orientation affects the chemical properties of the surface. The correct etching of InAs is critical as researchers prepare the surface for subsequent adlayer adsorption. HCl etchants combined with a postetch annealing step allow the tuning of the chemical properties in the near-surface region to either arsenic- or indium-rich environments. Bromine etchants create indium-rich surfaces and do not require annealing after etching; however, bromine etchants are harsh and potentially destructive to the surface. The simultaneous use of NH_4OH etchants with passivating molecules prevents contact with ambient air that can occur during sample transfer between solutions. The passivation of InAs is dominated by sulfur-based molecules, which form stable In—S bonds on the InAs surface. Both sulfides and alkanethiols form well-defined monolayers on InAs and are dominated by In—S interactions. Sulfur-passivated InAs surfaces prevent regrowth of the surface oxide layer and are more stable in air than unpassivated surfaces.

Although functionalization of InAs with sulfur-based molecules effectively passivates the surface, future sensing applications may require the adsorption of functional biomolecules onto the InAs surface. Current research in this area focuses on the passivation abilities of biomolecules such as collagen binding peptides and amino acids. These biomolecules can physically adsorb onto InAs, and they demonstrate some passivation ability but not to the extent of sulfur-based molecules. Because these adsorbents do not form covalent bonds with the InAs surface, they do not effectively block oxide regrowth. A mixed adlayer containing a biomolecule and a thiol on the InAs surface provides one possible solution: these hybrid surfaces enhance passivation but also maintain the presence of a biomolecule on the surface. Such surface functionalization strategies on InAs could provide long-term stability and make these surfaces suitable for biological applications.

Published on the Web 06/20/2012 www.pubs.acs.org/accounts
10.1021/ar200282f

Introduction

Because of their unique chemical, electronic, and material properties, group III−V semiconductors have emerged as vital components in a variety of applications. Among III−V semiconductors, InAs is unique with its low band gap (0.354 eV) and relatively high electron mobility. These properties make InAs attractive in high speed optoelectronic devices and field-effect transistors (FETs) or nanowire-based chemical sensors.[1] There is also interest in using InAs in biological applications such as cellular sensors[2] and Hall effect devices.[3,4] Furthermore, the dimensions and structure of InAs nanomaterials can be easily controlled,[5] which opens the door to InAs nanowire FETs and other nanoscale electronic applications.[6] Other III−V semiconductors such as GaN[7] and GaP[8] have demonstrated stability and biocompatibility under biological conditions, but in applications such as FET based sensors, the low band gap, high electron mobility, and nanoscale properties of InAs make it a very attractive material. However, under ambient or aqueous conditions, InAs forms an oxide layer that can disrupt the electronic properties of the device. Also, the oxide layer is physically unstable and can corrode over time.[9] When used in proximity to a biological environment, the leaching of toxic components from the oxide layer can cause damage to cells or surrounding tissue.[10] Therefore, creating a chemically stable surface without perturbing electronic properties is critical.

One common way of stabilizing semiconductor surfaces is through passivation. In the semiconductor literature, passivation can have a number of meanings, but in general, passivation refers to both the *chemical* and *electronic stabilization* of a surface. More specifically, chemical passivation of semiconductors generally denotes the stabilization of the surface to prevent corrosion or the buildup of contamination. Electronic passivation of semiconductors generally refers to the stabilization of the electronic properties of the semiconductor surface, such as the reduction of surface states. Both chemical and electronic passivation of semiconductor surfaces is critical for device function; however, this Account will focus primarily on chemical passivation of InAs.

One common method of passivating III−V semiconductors is through the attachment of molecules on the surface of the material. This adsorbed surface layer creates a protective barrier between the surface and the surrounding environment which electronically stabilizes the surface,[11] prevents corrosion,[9] and can improve the biocompatibility of a potentially toxic material.[12] A variety of methods exist to create this passivation layer, but the most common and inexpensive method is through molecular functionalization using wet-chemical methods. The goal of this Account is to summarize much of the recent work regarding the chemical passivation of InAs, with a particular focus on the chemical stability of the surface and prevention of oxide regrowth. We review the various methods of surface preparation and also discuss how crystal orientation affects the chemical properties of the surface.

Surface Preparation, Structure, and Orientation

Controlled preparation of InAs is critical for designing surfaces with the desired characteristics because slight changes in preparation parameters can cause drastic differences in surface properties. Planar InAs is generally cleaved along three crystal planes, InAs(001), (100), and (111). The (001) and (100) orientations are the most common and will be discussed herein. To further modify the InAs surfaces, specific etchants have been developed to reconstruct the surface structure of each individual orientation and give distinct chemical properties in the near-surface region. Furthermore, these surface etchants are used to remove the unwanted native oxide layer and prepare the surface for subsequent molecular functionalization. A variety of methods are used to prepare InAs surfaces, including photoelectrochemical etching,[13] reactive-ion etching,[14,15] and wet-chemical etching.[16] This section of the Account focuses on wet-chemical etchants to prepare both indium- and arsenic-rich InAs surfaces. The advantages of wet-chemical methods include low time and cost, and flexibility in creating the desired surface properties. We focus primarily on the resulting *surface chemistry* of the etched surfaces, and not on the physical and material properties of the surface reconstructions. For comprehensive review of the materials science of reconstructed surfaces, we direct the reader to a review by Schmidt.[17]

InAs(100). Several different wet-chemical etchants have been used on InAs(100) to create both indium- and arsenic-rich surfaces. One of the simplest wet etches consists of HCl diluted in isopropanol (IPA). As evidenced by X-ray photoelectron spectroscopy (XPS) analysis, treatment for short times (∼60 s) in an HCl/IPA solution completely removes the native oxide from the InAs surface. However, HCl/IPA treatments cause a physiadsorbed contamination layer of elemental arsenic to form on the surface immediately following etching.[18,19] This adsorbed contamination can be

removed through annealing the substrates at temperatures above 100 °C. Furthermore, by adjusting the annealing temperature, one can tune the chemical properties in the near-surface region. At annealing temperatures between ~100 and 300 °C, the majority of the weakly bound contaminants are removed, resulting in a relatively well-ordered surface with a thin layer of physiadsorbed elemental arsenic remaining. At 330 °C, all of the physiadsorbed elemental arsenic is removed, and the surface reorganizes to exhibit an arsenic-rich environment. Finally, at anneal temperatures above 410 °C, the surface again reorganizes and exhibits an indium-rich environment.[19] This flexibility of tuning the chemical properties in the near-surface region could allow for the selective functionalization of adsorbates onto InAs surfaces using either indium or arsenic interactions.

While the HCl/IPA etchant can create highly ordered InAs(100) surfaces, in all cases it requires a highly controlled post-etch anneal to generate the desired chemical properties in the near-surface region. If not performed in an ultrahigh vacuum (UHV), this extra step could leave the surface open to contamination or the regrowth of the oxide layer. Another halogen based wet-chemical etchant consists of a low (<1%) concentration of methanolic bromine. Methanolic bromine etchants have been used to produce oxide free InAs(100) surfaces without the need for a post-etch anneal.[11,18,20−22] The methanolic bromine etchant tends to form indium-rich surfaces, and unlike the case with the HCl/IPA etchant, there is currently no established way to tune the chemical properties in the near-surface region to an arsenic-rich reconstruction. Also, bromine is notoriously hazardous to work with and can be physically destructive to the InAs surfaces, at times forming extremely rough surfaces.[23−25] Low concentrations and short times in the methanolic bromine solution can help mitigate the formation of rough surfaces. Less commonly, the etchant and functionalization compound can be the same molecule. An example is the Na_2S treatment, which is strong enough to strip the native oxide without the need for an additional etchant.[26] Also, the etching and functionalization steps can occur simultaneously, as with NH_4OH and $(NH_4)_2S_x$.[27] The simultaneous etching and functionalization are more commonly seen with thiols, and the (001) orientation and will be discussed in more detail below.

InAs(001). For materials such as InAs that have zinc blende crystal structures, the (100) and (001) orientations are physically identical; therefore, similar results are seen post-etching. Surface oxides on InAs(001) are removed after a short incubation in HCl/IPA solution, and physiadsorbed contaminants are removed via annealing, with the majority of elemental arsenic and $InCl_3$ being removed at 200 °C. Arsenic-rich surface reconstructions are seen with anneal temperatures at 330 °C, and indium-rich reconstructions are seen with anneal temperatures above 410 °C.[28]

As mentioned above, another common wet-chemical etchant for InAs includes treatment with NH_4OH. The NH_4OH treatment is primarily used when a simultaneous etching and functionalization is desired. During simultaneous etching and passivation, compounds such as sulfides[29−31] and thiols,[32,33] which are readily soluble in NH_4OH, are diluted with a relatively low (~3%) concentration of NH_4OH. The NH_4OH is strong enough to strip the native oxide layer off of InAs, allowing for the adsorption of the thiol or sulfide passivation layer. Furthermore, for the assembly of thiols, the highly basic NH_4OH will deprotonate the thiol and allow for the easier formation of In−S bonds on the surface. The advantage to the simultaneous chemistry is the lack of contact with air between etching and functionalization steps, which lowers the chance of oxide regrowth and external contamination. As with (100) surfaces, for the assembly of some sulfides, the etchant agent and functionalization molecule can also be the same molecule (e.g., $(NH_4)_2S_x$).[34]

Methods of Passivation

To take full advantage of the electronic properties of InAs, the surface must be both chemically and electronically passivated. A variety of molecules have been used to passivate InAs surfaces using both wet and dry methods. In this Account, we focus on only wet-chemistry methods. Dry passivation techniques include atomic layer deposition[35] and vapor deposition.[36,37] The majority of the dry techniques must be performed under UHV conditions, resulting in a much higher cost and difficulty.

Planar Surfaces . Thiol-Based Molecules. The assembly of alkanethiol self-assembled monolayers (SAMs) on metals and semiconductors has been extensively studied.[38−40] The high affinity of the thiol group for many inorganic molecules allows for covalent X−S binding and results in very stable, well-defined monolayers. For InAs, a variety of different alkanethiol SAMs have been shown to form a stable monolayer that can effectively passivate the surface (Table 1). The general procedure for the stepwise assembly of alkanethiols begins with the removal of the oxide layer via a wet-chemical etchant and is followed by incubation in an ethanolic thiol solution

(Scheme 1). Importantly, for alkanethiol functionalization, it is important to use an etchant that gives an indium rich environment in the near-surface region, since In–S binding is thermodynamically favored over As–S binding. This is shown experimentally, as XPS analyses indicate that the binding occurs primarily through In–S bonds with no evidence of As–S binding.[32,41] It is important to note that there is some difficulty in explicitly demonstrating In–S bonding using XPS, as the In–S and In–oxide components differ by only a few tenths of an electronvolt in XPS spectra. Also, recent work by Losurdo et al. demonstrates the selective formation of In–S and As–S bonds, which are dependent on initial surface oxide composition, functionalization solvent, and concentration of adsorbate.[42] However, the lack of As–S bonds in most alkanethiol studies, along with thermodynamic data, indicates that In–S binding is the case.

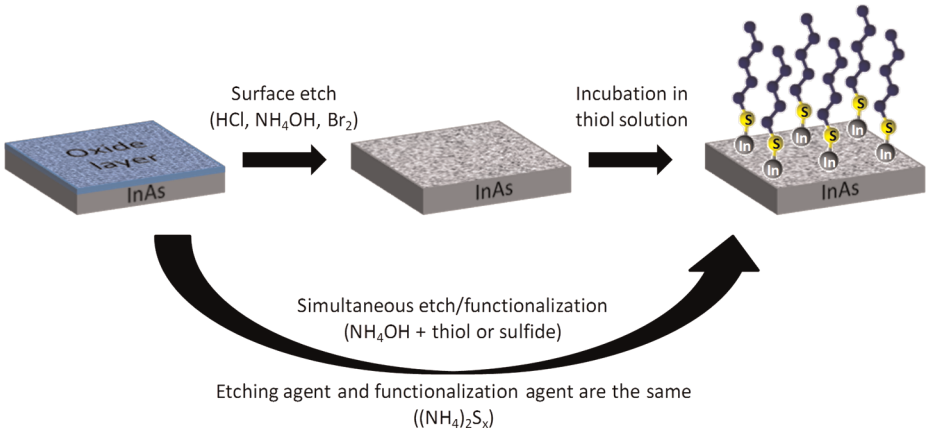
TABLE 1. Summary of Chemical Passivation on InAs

passivating molecule(s)	surface orientation/ structure	etchant	ref
alkanethiols			
ODT, hexanethiol, dodecanethiol	(100)	Br_2/methanol	11
ODT	(001)	NH_4OH	32
ODT	nanowires		57
ODT	(100)	HCl/IPA	41
cysteamine	(001)	NH_4OH	33
cysteamine	(100)	HF/methanol and NH_4OH	42
sulfides			
thioacetemide	(001)	NH_4OH	29–31
$(NH_4)_2S_x$	(001)		34, 59
$(NH_4)_2S_x$	(100)	H_2SO_4/H_2O_2	46
$(NH_4)_2S_x$	(001)	H_2SO_4/H_2O_2	44
$(NH_4)_2S_x$	nanowires		58
$(NH_4)_2S_x$	(100)	NH_4OH	27
$(NH_4)_2S_x$	(111)		45, 60
$(NH_4)_2S_x$	n/a	HF	61
Na_2S	(100)		26
amino acids	(100)	Br_2/methanol	20, 21
peptides	(100)	Br_2/methanol	18
mixed peptide/ thiol adlayer	(100)	Br_2/methanol	22

Aside from the stepwise functionalization (using a wet-chemical etchant followed by functionalization), another common method of functionalizing alkanethiols onto InAs is using a simultaneous etching and functionalization step. As discussed earlier, simultaneous etching and functionalization inhibits the formation of the oxide layer and the buildup of contamination by preventing contact with ambient air that can occur between etching and functionalization. The most common etchant used is NH_4OH, which is diluted with an ethanolic alkanethiol solution. The highly basic NH_4OH removes the oxide layer from the surface while simultaneously deprotonating the thiol, which allows for In–S bonds to form on the InAs surface. The concentrations of NH_4OH and temperature play a critical role in optimizing the quality of the alkanethiol monolayer. The functionalization is optimized at 55 °C with NH_4OH concentrations ranging from 2 to 10%.[32]

The stability of the SAM on the surface is an important parameter in the overall ability of the SAM to successfully passivate the surface. For biological applications, the semiconductor surface may come into contact with solutions of varying pH and salinity. Therefore, the ability of the surface passivating layer to resist oxidation or dissolution is paramount. Unfortunately, there are few comprehensive studies regarding the stability of surface adlayers on InAs. Some evidence suggests that alkanethiol functionalized InAs has relatively high stability due to the tight In–S binding. Exposure to ambient air shows arsenic oxide formation occurring after 1 h and reaching a maximum of one monolayer or less at ~19 h with little to no change in oxide up to two weeks (Figure 1a).[32,41] Sulfur oxides also form over time, as the adsorbed thiols oxidize in air (Figure 1c). In terms of

SCHEME 1. Formation of Sulfur-Based Passivation Layers on InAs



thermal stability, the alkanethiols were stable at temperatures up to ~140 °C, after which the thiol molecules desorbed from the InAs, leaving the surface open to oxidation (Figure 2).[41] More studies such as these are necessary to fully explore the ability of thiol passivated InAs surfaces to be used under aqueous or ambient conditions.

Sulfide-Based Molecules. Along with alkanethiols, sulfides are also commonly used to passivate InAs surfaces. Similar to thiols, sulfides are highly reactive toward a number of inorganic compounds and tend to form highly stable covalent bonds with these inorganic surfaces. In the case of InAs, Table 1 shows that $(NH_4)_2S_x$ is most commonly used to obtain sulfide molecules for use in surface functionalization. In general, the crystal structure and etching method do not seem to affect the resulting surface chemistry of $(NH_4)_2S_x$ passivated InAs, with the (001), (111), (100), and several different etchants showing similar results. One advantage to $(NH_4)_2S_x$ is that a prior etch is not necessarily required to remove any native oxide, as the concentrated $(NH_4)_2S_x$ solution is strong enough to completely remove the native oxide. Regardless, initial adsorption of $(NH_4)_2S_x$ on etched InAs indicates the presence of mostly In−S bonds along with small amounts of As−S bonds.[34,43] These As−S bonds could then be easily removed through annealing at temperatures above ~300 °C,[27,44−46] resulting in well-ordered sulfide layers characterized by In−S bonds. This structure is known as the "layer-cake" structure, as put forth by Petrovykh et al.,[34] in which the indium and arsenic atoms are stacked layers and the sulfur atoms are covalently bound to the terminal indium atoms.

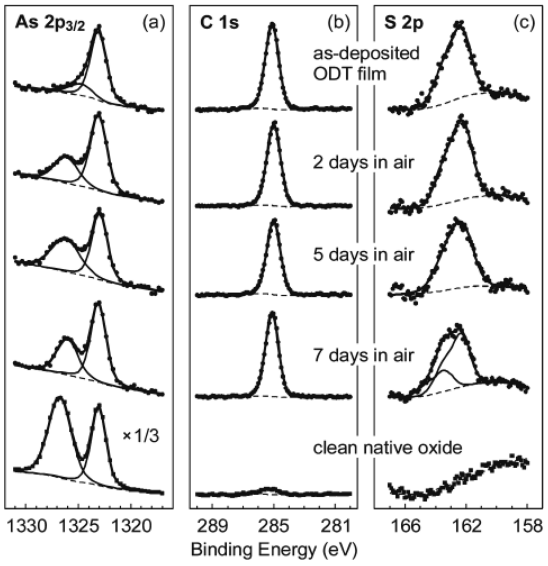


FIGURE 1. XPS analysis of the reoxidation of octadecanethiol (ODT) functionalized InAs. Initial arsenic and sulfur oxides on as-deposited ODT are negligible. The approximate binding energy for the reoxidation of arsenic oxide is 1324.8 eV, and that of sulfur oxide is 163.5 eV. Reprinted with permission from ref 32. Copyright 2009 American Chemical Society.

Another sulfide that has been adsorbed on InAs is thioacetemide (TAM), a simple thioamide. As with other sulfides, TAM forms stable In−S bonds with the InAs surface.[31] Time-lapse analysis of the reoxidation pathways of TAM functionalized InAs shows much slower reoxidation when compared to the cases of unpassivated surfaces and slower reoxidation when compared with the cases of $(NH_4)_2S_x$ functionalized samples.[30] Interestingly, the surface chemistry of the passivated TAM can be modified simply by modulating the pH of the passivating solution. In a basic TAM solution, In−S interactions are found exclusively. With an acidic TAM solution, an appreciable amount of As−S interactions are observed. The As−S binding tends to be less stable than In−S, and oxidizes faster in ambient air.[29]

Biomolecules. Due to its high electron mobility and high sensitivity to surface adsorbates, there has been interest in using InAs as a sensing platform for biomolecules or cells.[2,32] However, there are limitations in using InAs in biological applications because of the inherent toxicity of indium and arsenic components.[47,48] The oxide layer that forms on the

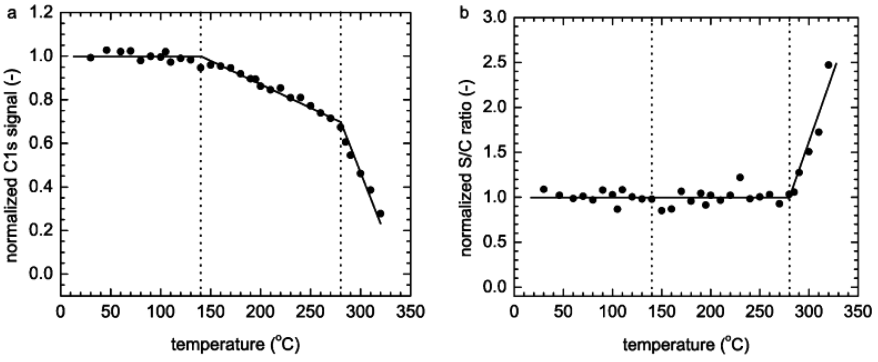


FIGURE 2. ODT monolayer quality as a function of temperature. Reprinted with permission from ref 41. Copyright 2009 American Chemical Society.

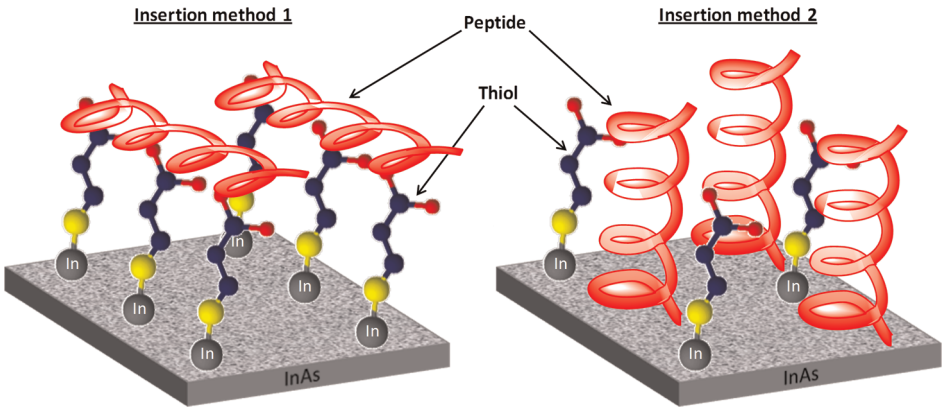


FIGURE 3. Proposed surface structure of mixed peptide/thiol adlayers formed by two separate functionalization strategies[22] (yellow = sulfur, blue = carbon, red = oxygen).

InAs surface is unstable and can leech into the surrounding environment, potentially harming any cell or tissue in the vicinity. Chemical passivation of InAs using the methods described above is one way of stabilizing surfaces for use in biological applications. However, there is also interest in the direct adsorption and passivation abilities of biomolecules on InAs. Specifically, biomolecules could be used as ligands for chemical sensing or as templates for nanocrystal growth or assembly.[49] In general, the interactions among various biomolecules and semiconductors have been of interest for the past decade, but much of the focus has been on silicon and GaAs.[50−52] Regarding InAs, our primary focus has been on assessing the adsorption and passivation abilities of biomolecules on InAs to further its utility in biological applications.

As the most basic building block of proteins, initial reports focused on the adsorption and passivation abilities of a set of amino acids onto InAs. Amino acids were shown to have some ability to prevent the oxide regrowth, with cysteine displaying the highest prevention of oxide regrowth on InAs(100).[20,21] Interestingly, cysteine is the only amino acid to contain a sulfur group, suggesting that sulfur could play a role in the adsorption of cysteine onto InAs and the blocking of the oxide growth, as seen above with alkanethiols and sulfides. No evidence of In−S binding was seen using XPS, suggesting that there was no covalent binding occurring during cysteine passivation. However, because of the close proximity of the In−S and In−oxide components in the In 3d spectrum, it can be difficult to definitively show the presence, or lack, of In−S binding using the In 3d spectrum. Passivation was also higher for the basic, nitrogen containing amino acids lysine and arginine; however, again no covalent binding was detected.[20] This lack of tight, covalent binding would negatively affect the ability of the passivating layer to prevent oxide regrowth over time. The relationship between semiconductor binding and basic amino acids has been shown previously in studies involving histidine residues in peptides on GaAs.[50,51] Peptides containing histidine bound to GaAs to a high degree. When nonpolar alanine residues were substituted for histidine, the binding decreased dramatically.

More recent work has focused on the adsorption of larger biomolecules onto InAs, including collagen binding peptides on InAs(100).[18] The binding of such peptides is of interest because of their potential use as templates for nanocrystal growth[49] or as ligands for further addition of collagen-based adlayers. On the basis of the XPS data, peptides are able to adsorb onto InAs; however, it is difficult to determine the exact binding mechanism of the peptides onto InAs. No evidence of In−S or As−S binding was seen, and on the basis of previous results, it seems unlikely that nitrogen groups were responsible for binding.[33] Overall, on the basis of relatively high oxide layer thicknesses, it is apparent that the amino acids and peptides used do not passivate InAs nearly as well as the sulfur-based molecules discussed in previous sections. Most likely, the biomolecules discussed are not able to form stable, covalent bonds with the InAs surface, as opposed to the In−S bonds formed with sulfur-based molecules. More likely, weaker, electrostatic interactions could drive the assembly of these molecules on InAs. This poses a problem for biological applications, as regrowth of the oxide layer could be detrimental to device function and could induce the leaching of toxic components. It could be advantageous to combine the passivating properties of a sulfur based molecule with the functionality of a biomolecule, such as a collagen binding peptide.

Mixed adlayers are a versatile and robust method of creating surfaces with various functional groups.[53] Mixed

adlayers can combine the properties of different molecules to create a surface with the desired properties. In the case of InAs, (100) surfaces were functionalized with mixed peptide/thiol adlayers using several different functionalization schemes (Figure 3) which were varied by the order of molecular assembly.[22] Short chain thiols with carboxylic acid functional groups were used because of their solubility in water, and the collagen binding peptide was used because of its potential as a functional ligand in the addition of further collagen-based adlayers. For insertion method 1, the thiol was adsorbed first and was followed by adsorption of the peptide. The thiol formed a relatively good monolayer characterized by In−S binding. The peptide adsorbed on top of the thiol, creating a layered thiol/peptide structure. For insertion method 2, the peptide was adsorbed first and was followed by adsorption of the thiol. The peptide most likely adsorbed in clusters, as seen previously on InAs and other semiconductors,[18,50,51] and the thiol then adsorbed on the surface where the peptide was not present. Both mixed adlayer surfaces showed a greater degree of passivation in terms of oxide regrowth when compared with peptide-only or thiol-only surfaces. The increase in passivation ability was attributed to the addition of the thiol, which bound via In−S binding and was able to block the oxide regrowth.

Nanomaterials. One of the most promising applications of InAs is its use in nanoscale applications. In particular, InAs nanowires and nanocrystals have generated much interest due to the potential use in nanoscale FET devices.[6] InAs nanowires can be synthesized to precise dimensions using both solution and vapor-phase growth routes.[5,54] Additionally, InAs can be doped to tune the chemical, optical, and magnetic properties of the nanostructures.[55,56] However, the problems seen with oxide growth on planar InAs are still present, even exacerbated, on the nanoscale. Therefore, it is of interest to explore the passivation of InAs nanostructures.

As with planar surfaces, the primary mode of passivating InAs nanomaterials is through sulfur-based molecules. Thiols have been found to prevent the oxide regrowth on InAs nanowires when compared to unpassivated nanowires. The thiol/InAs interface is similar in structure to that of the planar surfaces discussed earlier, with In−S binding dominating the surface structure. The electronic properties of thiol passivated InAs nanowires show improved capabilities in terms of subthreshold slope and field-effect mobility when compared with bulk nanowires.[57] Similar results were shown using a passivating solution consisting of dilute $(NH_4)_2S_x$.[58] While not a wet-chemical method, passivation of InAs has also been shown through the addition of cadmium dopant atoms into InAs nanowires. XPS indicated that the dopant cadmium atoms accumulated near the nanowire surface, forming a passivated nanowire with similar electronic characteristics to those of thiol-passivated InAs nanowires.[56]

Conclusion and Outlook

Wet-chemistry methods can provide low cost and effective ways to passivate InAs materials as opposed to costly and difficult UHV-based techniques. To prepare InAs surfaces for passivation, a variety of wet etching techniques exist including HCl/IPA, Br_2/methanol, and NH_4OH. Sulfur-based molecules are the most common and effective methods of passivating InAs, as they form relatively stable In−S bonds in the near-surface region and prevent the regrowth of the oxide layer. Most of the research has dealt with sulfide functionalization including $(NH_4)_2S_x$ and TAM. Thiol-based molecules have also been extensively studied, with alkanethiols showing promising passivation abilities. Overall, these wet-chemical passivation methods are able to make chemically and electronically stable InAs surfaces.

Recently, there has been much interest in employing III−V semiconductor FETs as chemical and biological sensors.[62] The electronic properties of III−V semiconductors make them more attractive than other traditional materials such as silicon. However, silicon has one major advantage over InAs and other III−V semiconductors: incontrovertible biocompatibility. This problem with InAs biocompatibility could potentially be rectified through proper surface passivation. Unfortunately, while much research has gone into understanding the chemical, electronic, and material properties of passivated InAs, there are few examples of rigorous studies dealing with the stability of these materials in biological solutions. Due to heavy metals such as gallium and indium, along with the metalloid arsenic, many devices using III−V semiconductors are considered toxic. For InAs, the toxicity of both indium and arsenic has been demonstrated in cells,[63,64] mammals,[65,66] and aquatic organisms.[47,48] This inherent toxicity may not be a concern for *ex-vivo* analyte sensors that do not come into contact with cells or tissue, but toxicity for cellular or *in vivo* biosensors is of major concern. For such sensors, the leaching of toxic semiconductor materials into the surrounding environment is an obvious problem. Aside from direct toxicity, the use of products containing III−V semiconductor materials is also an environmental concern. Over time, the leaching of these materials from products can cause a buildup of toxic materials

in the environment, causing irreparable damage to ecosystems and either direct or indirect harm to public health. For these reasons, it is imperative that future studies look at the stability of chemically passivated surfaces in biological conditions to better employ InAs in biological applications.

BIOGRAPHICAL INFORMATION

Scott A. Jewett is a Ph.D. candidate in Biomedical Engineering at Purdue University. He received his B.S. in Biomedical Engineering in 2008 from Louisiana Tech University. His research interests include surface modifications on semiconductors, with a focus on the toxicity and stability of modified surfaces.

Albena Ivanisevic is an associate professor appointed in the Department of Material Science and Engineering at North Carolina State University and the Joint Department of Biomedical Engineering at NCSU/UNC-CH. Her research lab focuses on using surface science techniques to study biomaterials, sensors, and optoelectronic platforms.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: ivanisevic@ncsu.edu.
The authors declare no competing financial interest.

REFERENCES

1 Offermans, P.; Crego-Calama, M.; Brongersma, S. H. Gas Detection with Vertical InAs Nanowire Arrays. *Nano Lett.* **2010**, *10*, 2412–2415.

2 Berthing, T.; Bonde, S.; Sorensen, C. B.; Utko, P.; Nygard, J.; Martinez, K. L. Intact Mammalian Cell Function on Semiconductor Nanowire Arrays: New Perspectives for Cell-Based Biosensing. *Small* **2011**, *7*, 640–647.

3 Sandhu, A.; Handa, H.; Abe, M. Synthesis and Applications of Magnetic Nanoparticles for Biorecognition and Point of Care Medical Diagnostics. *Nanotechnology* **2010**, *21*, 442001.

4 Lee, W.; Joo, S.; Kim, S. U.; Rhie, K.; Hong, J.; Shin, K. H.; Kim, K. H. Magnetic Bead Counter Using a Micro-Hall Sensor for Biological Applications. *Appl. Phys. Lett.* **2009**, *94*, 153903.

5 Dayeh, S. A.; Soci, C.; Bao, X. Y.; Wang, D. L. Advances in the Synthesis of InAs and GaAs Nanowires for Electronic Applications. *Nano Today* **2009**, *4*, 347–358.

6 Dayeh, S. A. Electron Transport in Indium Arsenide Nanowires. *Semicond. Sci. Technol.* **2010**, *25*, 1–20.

7 Jewett, S. A.; Makowski, M. S.; Andrews, B.; Manfra, M. J.; Ivanisevic, A. Gallium Nitride is Biocompatible and Non-Toxic Before and After Functionalization with Peptides. *Acta Biomater.* **2012**, *8*, 728–733.

8 Richards, D.; Zemlyanov, D.; Ivanisevic, A. Assessment of the Passivation Capabilities of Two Different Covalent Chemical Modifications on GaP(100). *Langmuir* **2010**, *26*, 8141–8146.

9 Kirchner, C.; George, M.; Stein, B.; Parak, W. J.; Gaub, H. E.; Seitz, M. Corrosion Protection and Long-Term Chemical Functionalization of Gallium Arsenide in an Aqueous Environment. *Adv. Funct. Mater.* **2002**, *12*, 266–276.

10 Wang, A. F.; McAllister, J. P.; Finlayson, P.; Li, J.; Brabant, K.; Tang, H. Y.; Black, C.; Cao, T.; Liang, X. M.; Salley, S. O.; Auner, G. W.; Ng, K. Y. S. Short-and Long-Term Neural Biocompatibility of Heparin Coated Sapphire Implants. *Mater. Sci. Eng., C* **2007**, *27*, 237–243.

11 Tanzer, T. A.; Bohn, P. W.; Roshchin, I. V.; Greene, L. H.; Klem, J. F. Near-Surface Electronic Structure on InAs(100) Modified with Self-Assembled Monolayers of Alkanethiols. *Appl. Phys. Lett.* **1999**, *75*, 2794–2796.

12 Cho, Y.; Ivanisevic, A. In Vitro Assessment of the Biocompatibility of Chemically Modified GaAs Surfaces. *NanoBiotechnology* **2006**, *2*, 51–59.

13 Harris, D.; Kohl, P. A.; Winnick, J. Photoelectrochemical Etching of InAs. *J. Electrochem. Soc.* **1994**, *141*, 1274–1277.

14 Pearton, S. J. Reactive Ion Etching of III-V Semiconductors. *Int. J. Mod. Phys. B* **1994**, *8*, 1781–1786.

15 Frost, F.; Schindler, A.; Bigl, F. Reactive Ion Beam Etching of InSb and InAs with Ultrasmooth Surfaces. *Semicond. Sci. Technol.* **1998**, *13*, 523–527.

16 Sharma, B. L. Chemical Etchants for InAs. *Solid-State Electron.* **1966**, *9*, 728–729.

17 Schmidt, W. G. III–V Compound Semiconductor (001) Surfaces. *Appl. Phys. A: Mater. Sci. Process.* **2002**, *75*, 89–99.

18 Jewett, S.; Zemlyanov, D.; Ivanisevic, A. Characterization of Peptide Adsorption on InAs Using X-ray Photoelectron Spectroscopy. *Langmuir* **2011**, *27*, 3774–3782.

19 Tereshchenko, O. E.; Placidi, E.; Paget, D.; Chiaradia, P.; Balzarotti, A. Well-Ordered (100) InAs Surfaces Using Wet Chemical Treatments. *Surf. Sci.* **2004**, *570*, 237–244.

20 Slavin, J. W. J.; Jarori, U.; Zemlyanov, D.; Ivanisevic, A. Characterization of Amino Acid Adlayers on InAs Surfaces Using X-ray Photoelectron Spectroscopy. *J. Electron Spectrosc. Relat. Phenom.* **2009**, *172*, 47–53.

21 Slavin, J. W. J.; Zemlyanov, D.; Ivanisevic, A. Adsorption of Amino Acids on Indium Arsenide (1 0 0) Surfaces: Assessment of Passivation Capabilities. *Surf. Sci.* **2009**, *603*, 907–911.

22 Jewett, S.; Ivanisevic, A.; Zemlyanov, D. Adsorption of Mixed Peptide/Thiol Adlayers on InAs: Assessment of Different Functionalization Strategies Using X-ray Photoelectron Spectroscopy. *J. Phys. Chem. C* **2011**, *115*, 14244–14252.

23 Wagner, G.; Dreilich, A.; Butter, E. Chemical Thinning of III–V Compound Semiconductors for Transmission Electron Microscopy. *J. Mater. Sci.* **1988**, *23*, 2761–2767.

24 Millea, M.; McColl, M.; Silver, A. Electrical Characterization of Metal/InAs Contacts. *J. Electron. Mater.* **1976**, *5*, 321–340.

25 Seker, F.; Meeker, K.; Kuech, T. F.; Ellis, A. B. Surface Chemistry of Prototypical Bulk II–VI and III–V Semiconductors and Implications for Chemical Sensing. *Chem. Rev.* **2000**, *100*, 2505–2536.

26 L'vova, T. V.; Sedova, I. V.; Dunaevskii, M. S.; Karpenko, A. N.; Ulin, V. P.; Ivanov, S. V.; Berkovits, V. L. Sulfide Passivation of InAs(100) Substrates in Na_2S Solutions. *Phys. Solid State* **2009**, *51*, 1114–1120.

27 Kirk, A. P.; Milojevic, M.; Kim, J.; Wallace, R. M. An In Situ Examination of Atomic Layer Deposited Alumina/InAs(100) Interfaces. *Appl. Phys. Lett.* **2010**, *96*, 202905.

28 Tereshchenko, O. E.; Paget, D.; Chiaradia, P.; Bonnet, J. E.; Wiame, F.; Taleb-Ibrahimi, A. Preparation of Clean Reconstructed InAs(001) Surfaces Using HCl/Isopropanol Wet Treatments. *Appl. Phys. Lett.* **2003**, *82*, 4280–4282.

29 Stine, R.; Aifer, E. H.; Whitman, L. J.; Petrovykh, D. Y. Passivation of GaSb and InAs by pH-Activated Thioacetamide. *Appl. Surf. Sci.* **2009**, *255*, 7121–7125.

30 Petrovykh, D. Y.; Long, J. P.; Whitman, L. J. Surface Passivation of InAs(001) with Thioacetamide. *Appl. Phys. Lett.* **2005**, *86*, 242105.

31 Petrovykh, D. Y.; Sullivan, J. M.; Whitman, L. J. Quantification of Discrete Oxide and Sulfur Layers on Sulfur-Passivated InAs by XPS. *Surf. Interface Anal.* **2005**, *37*, 989–997.

32 Petrovykh, D. Y.; Smith, J. C.; Clark, T. D.; Stine, R.; Baker, L. A.; Whitman, L. J. Self-Assembled Monolayers of Alkanethiols on InAs. *Langmuir* **2009**, *25*, 12185–12194.

33 Stine, R.; Petrovykh, D. Y. Oriented Self-Assembled Monolayers of Bifunctional Molecules on InAs. *J. Electron Spectrosc. Relat. Phenom.* **2009**, *172*, 42–46.

34 Petrovykh, D. Y.; Yang, M. J.; Whitman, L. J. Chemical and Electronic Properties of Sulfur-Passivated InAs Surfaces. *Surf. Sci.* **2003**, *523*, 231–240.

35 Timm, R.; Fian, A.; Hjort, M.; Thelander, C.; Lind, E.; Andersen, J. N.; Wernersson, L. E.; Mikkelsen, A. Reduction of Native Oxides on InAs by Atomic Layer Deposited Al_2O_3 and HfO_2. *Appl. Phys. Lett.* **2010**, 97.

36 Lowe, M. J.; Veal, T. D.; McConville, C. F.; Bell, G. R.; Tsukamoto, S.; Koguchi, N. Passivation and Reconstruction-Dependent Electron Accumulation at Sulphur Treated InAs(001) Surfaces. *Surf. Sci.* **2003**, *523*, 179–188.

37 Bezryadin, N. N.; Tatokhin, E. A.; Budanov, A. V.; Linnik, A. V.; Arsent'ev, I. N. Position of the Fermi Level on an Indium Arsenide Surface Treated in Sulfur Vapor. *Semiconductors* **1999**, *33*, 1301–1303.

38 Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1170.

39 Schreiber, F. Structure and Growth of Self-Assembling Monolayers. *Prog. Surf. Sci.* **2000**, *65*, 151–257.

40 Sheen, C. W.; Shi, J. X.; Maartensson, J.; Parikh, A. N.; Allara, D. L. A New Class of Organized Self-Assembled Monolayers: Alkane Thiols on Gallium Arsenide(100). *J. Am. Chem. Soc.* **1992**, *114*, 1514–1515.

41 Knoben, W.; Brongersma, S. H.; Crego-Calama, M. Preparation and Characterization of Octadecanethiol Self-Assembled Monolayers on Indium Arsenide (100). *J. Phys. Chem. C* **2009**, *113*, 18331–18340.

42 Losurdo, M.; Wu, P. C.; Kim, T.-H.; Bruno, G.; Brown, A. S. Cysteamine-Based Functionalization of InAs Surfaces: Revealing the Critical Role of Oxide Interactions in Biasing Attachment. *Langmuir* **2012**, *28*, 1235–1245.

43 Fukuda, Y.; Ichikawa, S.; Shimomura, M.; Sanada, N.; Suzuki, Y. Structures and Electronic States of InAs (001) and (111)B Surfaces Passivated with Sulfur Studied by AES, LEED, UPS, XPS, and IPES. *Vacuum* **2002**, *67*, 37–41.

44 Fukuda, Y.; Suzuki, Y.; Sanada, N.; Shimomura, M.; Masuda, S. $(NH_4)_2S_x$-Treated InAs(001) Surface Studied by X-ray Photoelectron Spectroscopy and Low-Energy Electron Diffraction. *Phys. Rev. B* **1997**, *56*, 1084–1086.

45 Ichikawa, S.; Sanada, N.; Utsumi, N.; Fukuda, Y. Surface Structures and Electronic States of Clean and $(NH_4)_2S_x$-Treated InAs(111)A and (111)B. *J. Appl. Phys.* **1998**, *84*, 3658–3663.

46 Oigawa, H.; Fan, J. F.; Nannichi, Y.; Sugahara, H.; Oshima, M. Universal Passivation Effect of $(NH_4)_2S_x$ Treatment on the Surface of III−V Compound Semiconductors. *Jpn. J. Appl. Phys., Part 2* **1991**, *30*, L322–L325.

47 Sharma, V. K.; Sohn, M. Aquatic Arsenic: Toxicity, Speciation, Transformations, and Remediation. *Environ. Int.* **2009**, *35*, 743–759.

48 Lin, H. C.; Hwang, P. P. Acute and Chronic Effects of Indium Chloride ($InCl_3$) on Tilapia (Oreochromis mossambicus) Larvae. *Bull. Environ. Contam. Toxicol.* **1998**, *61*, 123–128.

49 Bai, H. Y.; Xu, F.; Anjia, L.; Matsui, H. Low Temperature Synthesis of ZnO Nanowires by Using a Genetically-Modified Collagen-Like Triple Helix as a Catalytic Template. *Soft Matter* **2009**, *5*, 966–969.

50 Goede, K.; Busch, P.; Grundmann, M. Binding Specificity of a Peptide on Semiconductor Surfaces. *Nano Lett.* **2004**, *4*, 2115–2120.

51 Goede, K.; Grundmann, M.; Holland-Nell, K.; Beck-Sickinger, A. G. Cluster Properties of Peptides on (100) Semiconductor Surfaces. *Langmuir* **2006**, *22*, 8104–8108.

52 Whaley, S. R.; English, D. S.; Hu, E. L.; Barbara, P. F.; Belcher, A. M. Selection of Peptides with Semiconductor Binding Specificity for Directed Nanocrystal Assembly. *Nature* **2000**, *405*, 665–668.

53 Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. Insertion, Conductivity, and Structures of Conjugated Organic Oligomers in Self-Assembled Alkanethiol Monolayers on Au{111}. *J. Am. Chem. Soc.* **1998**, *120*, 2721–2732.

54 Wang, F.; Dong, A.; Sun, J.; Tang, R.; Yu, H.; Buhro, W. E. Solution-Liquid-Solid Growth of Semiconductor Nanowires. *Inorg. Chem.* **2006**, *45*, 7511–7521.

55 Stowell, C. A.; Wiacek, R. J.; Saunders, A. E.; Korgel, B. A. Synthesis and Characterization of Dilute Magnetic Semiconductor Manganese-Doped Indium Arsenide Nanocrystals. *Nano Lett.* **2003**, *3*, 1441–1447.

56 Hang, Q. L.; Wang, F. D.; Buhro, W. E.; Janes, D. B. Ambipolar Conduction in Transistors Using Solution Grown InAs Nanowires with Cd Doping. *Appl. Phys. Lett.* **2007**, *90*, 062108.

57 Hang, Q. L.; Wang, F. D.; Carpenter, P. D.; Zemlyanov, D.; Zakharov, D.; Stach, E. A.; Buhro, W. E.; Janes, D. B. Role of Molecular Surface Passivation in Electrical Transport Properties of InAs Nanowires. *Nano Lett.* **2008**, *8*, 49–55.

58 Suyatin, D. B.; Thelander, C.; Bjork, M. T.; Maximov, I.; Samuelson, L. Sulfur Passivation for Ohmic Contact Formation to InAs Nanowires. *Nanotechnology* **2007**, *18*, 105307.

59 Ho, J. C.; Ford, A. C.; Chueh, Y. L.; Leu, P. W.; Ergen, O.; Takei, K.; Smith, G.; Majhi, P.; Bennett, J.; Javey, A. Nanoscale Doping of InAs Via Sulfur Monolayers. *Appl. Phys. Lett.* **2009**, *95*, 072108.

60 Ichikawa, S.; Sanada, N.; Mochizuki, S.; Esaki, Y.; Fukuda, Y.; Shimomura, M.; Abukawa, T.; Kono, S. Structure of an InAs(111)A-(2×2)S Surface Studied by Scanning Tunneling Microscopy, Photoelectron Spectroscopy, and X-ray Photoelectron Diffraction. *Phys. Rev. B* **2000**, *61*, 12982–12987.

61 Kim, H. S.; Ok, I.; Zhang, M.; Zhu, F.; Park, S.; Yum, J.; Zhao, H.; Lee, J. C.; Majhi, P.; Goel, N.; Tsai, W.; Gaspe, C. K.; Santos, M. B. A Study of Metal-Oxide-Semiconductor Capacitors on GaAs, $In_{0.53}Ga_{0.47}As$, InAs, and InSb Substrates Using a Germanium Interfacial Passivation Layer. *Appl. Phys. Lett.* **2008**, *93*, 062111.

62 Makowski, M. S.; Ivanisevic, A. Molecular Analysis of Blood with Micro-/Nanoscale Field-Effect-Transistor Biosensors. *Small* **2011**, *7*, 1863–1875.

63 Bustamante, J.; Dock, L.; Vahter, M.; Fowler, B.; Orrenius, S. The Semiconductor Elements Arsenic and Indium Induce Apoptosis in Rat Thymocytes. *Toxicology* **1997**, *118*, 129–136.

64 Aoki, Y.; Lipsky, M. M.; Fowler, B. A. Altered Protein Synthesis in Rat Kidney Cells Exposed to Semiconductor Materials. *Appl. Organomet. Chem.* **1994**, *8*, 253–258.

65 Yamazaki, K.; Tanaka, A.; Hirata, M.; Omura, M.; Makita, Y.; Inoue, N.; Sugio, K.; Sugimachi, K. Long Term Pulmonary Toxicity of Indium Arsenide and Indium Phosphide Instilled Intratracheally in Hamsters. *J. Occup. Health* **2000**, *42*, 169–178.

66 Tanaka, A. Toxicity of Indium Arsenide, Gallium Arsenide, and Aluminium Gallium Arsenide. *Toxicol. Appl. Pharmacol.* **2004**, *198*, 405–411.