Decomposition of Thimerosal and Dynamics of Thiosalicylic Acid Attachment on GaAs(001) Surface Observed with in Situ Photoluminescence

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The decomposition dynamics of thimerosal in phosphate-buffered saline (PBS) solution was monitored using in situ measurements of photoluminescence (PL) from GaAs(001) substrate. The intensity of the GaAs PL peak is modulated by the presence of thimerosal, resulting in a characteristic PL maximum observed after ~5 h from the onset of the experiment. We interpret this result as a competition between the formation of PBS-related nonradiative recombination centers on the surface of GaAs and passivation of the GaAs surface by thiosalicylic acid (TSA) reacting with As and Ga atoms of the substrate. The amplitude of the TSA PL maximum was found to depend on the concentration of thimerosal in PBS. The decomposition of thimerosal was also verified with UV−vis optical absorption measurements. The presence of the decomposition products, TSA and ethyl mercuric chloride, on the GaAs(001) substrate was demonstrated with X-ray photoelectron spectroscopy measurements. The results indicate that the investigated method has the potential to provide a practical means for rapid detection of thimerosal in some pharmaceutical products.

Introduction

To avoid microbiological spoilage in aqueous products, pharmaceutical products are stored in the presence of antimicrobial preservatives that reduce the likelihood of microbial growth. Thimerosal (TMS) is widely used as an antiseptic agent and as a preservative in topical medications, cleaning solutions for eye lenses, cosmetics, and vaccines.[1−3] Analytical methods previously developed for the detection of TMS are spectrometry,[4] polarography,[5] atomic absorption spectroscopy,[6] colorimetry,[7] cyclic voltametry,[8] and high performance liquid chromatography (HPLC).[7,9−12] With respect to stability specifications, HPLC is probably the only method suitable for analyzing thimerosal in the presence of its degradation products. Pilar da Silva et al.[13] investigated thimerosal decomposition by ligand exchange with tetramethylenedithiocarbomate using liquid chromatography in combination with electrochemical methods. Caraballo et al.[14] reported that TMS decomposes into thiosalicylic acid (TSA) and ethyl mercuric chloride (C_2H_5HgCl) in the presence of chloride anions. Tan and Parkin[15] observed that the TMS decomposition reaction in water is much slower when compared to sodium chloride. Tleugabulova and Perez[16] and Costa et al.[17] studied the stability of TMS in Cuban recombinant hepatitis B vaccine samples stored at different temperatures using reverse-phase liquid chromatography.

It is well-known that photoluminescence (PL) could provide information on the quality of semiconductor surfaces and interfaces.[18,19] This nondestructive technique requires very little manipulation because the sample is excited optically; thus, electrical contacts and junctions are unnecessary, and high-resistivity materials pose no practical difficulty. The PL measurements have been used to assay organic compounds interfaced with GaAs.[20−24]

The PL method is particularly promising for detection and analysis of traces of some organic compounds in aqueous solutions. For instance, the highly covalent nature of thiol-GaAs bonding that allows electron sharing with the surface of GaAs and the related reduction of surface trap density leads to increased PL efficiency.[23,25−27] In addition, the electric dipole moment of surface adsorbates could increase/decrease the intensity of PL emission, depending on the sense of polarization of their electric field vector.[28] The effect of increased PL intensity of GaAs has often been related to the reduced concentration of nonradiative recombination centers achieved by adsorbates, such as sulfur, donating electrons to the surface defects or As or Ga atoms.[26,27] Indeed, the attachment of different thiols via sulfur atoms to the GaAs surface has been known to lead to the increased PL signal from this material.[21−24,29] Similarly, an increase of the GaAs PL signal has also been observed following the surface physisorption of SO_2[19] and oxygen.[20] We have reported recently that PL measurements provide a useful means to investigate in situ dynamics of hexadecanethiol attachment to the surface of GaAs(001).[30] The thiol group of TSA should also provide a link suitable for chemisorption on the GaAs surface. Here, we report on the application of the PL technique for monitoring in situ adsorption of TSA produced by the TMS decomposion in a phosphate buffered saline (PBS) solution.

Experimental Section

Reagents. TMS, TSA, and PBS solutions were obtained from Sigma-Aldrich, Canada. The water used for all the experiments was purified with a Milli-Q system. Semiconductor grade Optic-clear (National Diagnostics, Atlanta, GA), acetone (ACP Chemicals, Canada), isopropyl alcohol (Anachemia), and NH_4OH (Anachemia) were used without further purification.

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Degassed PBS solution (typically 250 mL) was prepared by flushing it with N_2 (944 mL/min) under sonication for 4 h. A nominally undoped GaAs/AlGaAs multilayer structure grown by molecular beam epitaxial on a semi-insulating GaAs(001) substrate was designed to monitor the decomposition dynamics of thimerosal at a low excitation power (<150 mW/cm^2) of the 532 nm laser used for the generation of the PL signal.[30] A 20 mL Teflon reaction chamber equipped with a 3.2-mm-thick fused-silica window was used for holding studied samples. Topping the chamber with liquid solution and sliding the silica window sideways provided a bubble-free environment. The samples were irradiated at normal incidence through the 16-mm-thick layer of liquid, and the PL emission was measured at 870 nm.

Sample Preparation. In all cases, the GaAs(001) samples were cleaned in an ultrasonic bath for 5 min in each of the following chemicals: Optic-clear, acetone, and isopropyl alcohol. After cleaning, the sample was then dried with nitrogen and etched in NH_4OH (28%) solution for 2 min. Etched samples were immediately exposed to the degassed PBS solution and kept in the reaction chamber without exposing to air.

PL measurements were carried out using a custom-designed Hyperspectral Imaging PL Mapper (HI-PLM). The HI-PLM instrument allowed collection of PL maps of up to 7 mm × 7 mm samples with a spatial resolution of 5 μm. The acquisition time to obtain a PL map in the spectral region of interest was ~70 s. With the computer interface, HI-PLM maps were collected for up to 24 h at, typically, 10 min intervals. For the purpose of this experiment, the PL signal was averaged over the entire sample surface.

The absorbance spectra of PBS and TMS diluted in PBS were recorded using Ultraspec 2100 pro UV/Visible spectrophotometer.

X-ray photoelectron spectroscopy (XPS) spectra were recorded in UHV (<10^{-9} Torr) with an Axis Ultra DLD (Kratos Analytical Ltd.) utilizing a monochromatic Al Kα source (1486.6 eV) and an analyzer having pass energy of 20 eV. The analysis area (700 μm × 300 μm) was defined by an aperture in the transfer lens column. The data were collected for a takeoff angle of 60° with respect to the surface normal. Binding energy reference to untreated GaAs wafer positioned the As 3d5/2 peak at 41.37 eV, which was subsequently used as a nominal calibration. No charge neutralization current was applied. Peak fitting and quantification analysis were performed using the software package Casa XPS to deconvolute the spectral envelopes into their constituent chemical states. An etched GaAs reference wafer kept in PBS was used to calibrate the background parameters.

Results and Discussion

The initial experiment was carried out to investigate the effect of exposure of the GaAs(001) surface to PBS and TSA solution in ethanol. Figure 1 shows temporal behavior of the PL peak intensity from the GaAs(001) substrate exposed to 10 mM PBS solution in water at pH = 7.4. A rapid decay of the PL signal to <60% of the initial intensity is observed within 10−12 min. This is followed by the appearance of a maximum at ~45 min from the onset of the PL experiment. Subsequently, the PL signal decreases at 500 min to ~50% of its initial value. The decay of the PL signal from freshly etched or partially neutralized (passivated) GaAs is a well-known phenomenon.[24] It is related to the formation of surface state defects responsible for nonradiative electron−hole recombination. Conversely, if the GaAs surface is passivated with sulfur atoms, such as those provided by different thiols, the formation of surface states is reduced, and a stable

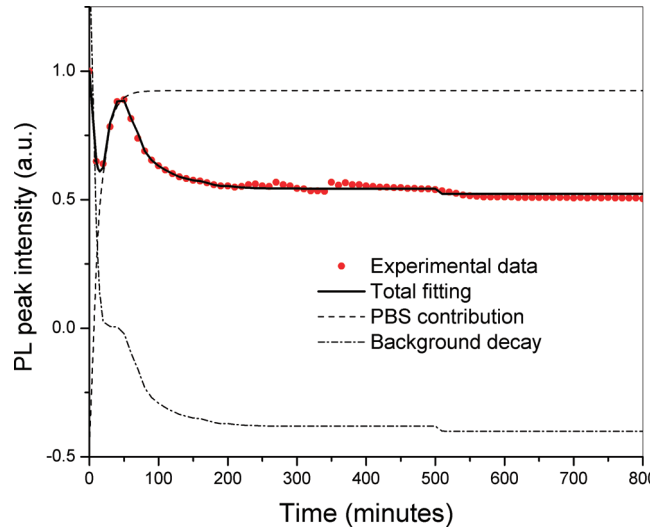

Figure 1. Intensity of the in situ PL peak emission from GaAs(001) exposed to PBS solution at pH = 7.4. Experimental points (•) have been fitted with a solid-line curve (—) that takes into account the contribution from PBS (dashed) and background decay (dashed−dotted).

or even increased PL signal is expected.[21−24,29,30] The class of molecular adsorbates known as Lewis bases, including sulfur, are electron donors in their bonds with GaAs. This can, for example, lead to reduced occupation of the surface states, resulting in a contraction of the surface depletion region and PL enhancement by the dead-layer effect.[18,19] It is reasonable to expect that some of these effects contribute to the behavior observed in Figure 1. In particular, formation of the PL maximum at 45 min appears to be a result of the interaction between negatively charged phosphate anions in the PBS solution and the GaAs surface. In aqueous environments, phosphates exist in four possible states, depending upon the pH of the solution. At pH = 7.4, the dominant ionic forms are HPO_4^{2-} and $H_2PO_4^-$. It is possible to attach these species to the GaAs surface through the phosphate group with the high polarity of the P−O bond.[31]

We also observed formation of a 45-min-PL maximum in an experiment involving the TMS decomposition in deionized water solution. This suggests that the OH^- species present in water could also contribute to the formation of such a peak, in agreement with the results reported earlier.[32] Assuming that the contribution from $HPO_4^{2-}/H_2PO_4^-$ or OH^- to the PL signal can be described by an increasing and quickly saturating signal shown by a dashed curve in Figure 1, while the background PL signal decays as described by a dashed-dotted curve in Figure 1, we could fit the experimental data with a solid-line curve shown in that figure. The nonmonotonic decay of the background PL (dash-dotted line) observed between 30 and 50 min suggests the presence of an additional source enhancing the overall PL signal not included in this analysis. For the PBS solution used in this experiment, the surface density of molecules is at ~3.3×10^{12} cm^{-2}. This compares to ~10^{15} cm^{-2} of GaAs surface atoms available for the reaction. Thus, it is reasonable to expect that the saturation of the PL component indicated by the dashed line in Figure 1 is related to the limited concentration of PL-enhancing molecules available in the vicinity of the GaAs surface.

We employed in situ PL measurements to investigate TSA chemisorption on the GaAs surface from a 0.779 mg/mL (2 mM) solution in ethanol. As shown in Figure 2, the overall PL signal (squares) reaches a maximum at 100 min from the onset of the

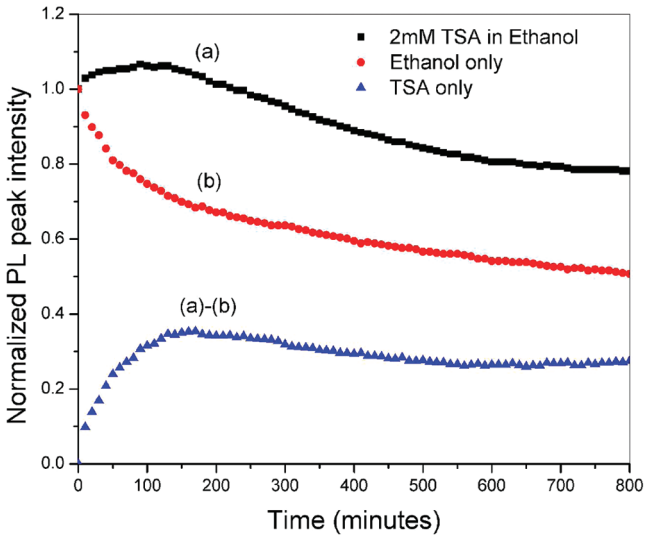

Figure 2. Intensity of the in situ PL peak emission of GaAs(001) exposed to an ethanol solution of TSA (2 mM) showing TSA attachment dynamics on the GaAs surface.

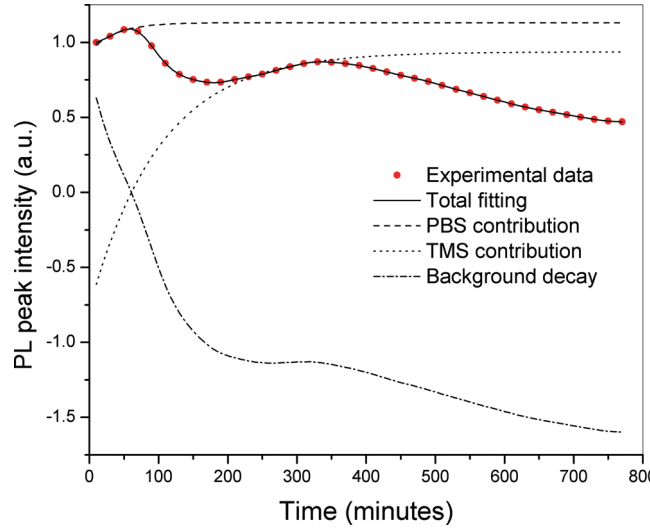

Figure 3. Intensity of the in situ PL peak emission of GaAs(001) exposed to 0.1 mg/mL solution of TMS in PBS at pH = 7.4. Experimental points (•) have been fitted with a solid-line curve (—) that takes into account the contribution from PBS (dashed), TSA (dotted) and background decay (dashed−dotted). For the clarity of the figure, only half of the experimental points have been shown.

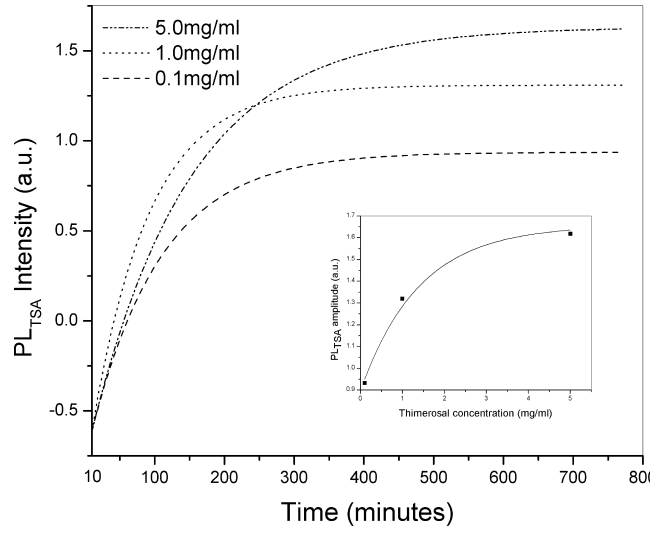

Figure 4. Intensity of the TSA related PL peak emission of GaAs(001) surface exposed to 0.1 (dashed), 1.0 (dotted) and 5.0 (dashed−dotted) mg/mL thimerosal in PBS solution at pH = 7.4. Dependence of the TSA PL peak amplitude on the TMS concentration shown in the inset (the solid line is a guide for the eye).

experiment. In a separate run, a decay of the PL signal from a GaAs(001) sample exposed to ethanol only (circles) was monitored for the same period of time. The subtraction of the ethanol component from the overall PL signal gives the net contribution from TSA (triangles). It can be seen that the TSA PL reaches maximum at near 150 min, and then, it slowly decreases to reach a stable level at $t \geq 8$ h. Such a behavior likely indicates the exhaustion with time of TSA available for the attachment with GaAs, whereas desorption of some of the TSA molecules that initially weakly reacted with Ga or As atoms could be responsible for some reduction of the PL signal. It is relevant to mention that we have observed qualitatively a similar effect of PL increase and saturation during thiol attachment from a solution of hexadecanethiol in ethanol.[30] However, the PL signal in that case, after the rapid initial increase (~150 min), was still observed increasing up to 10 h from the onset of the experiment, likely indicating the slow process of thiol SAM formation.

The time-dependent PL peak emission of GaAs(001) exposed to a 0.1 mg/mL solution of TMS in PBS at pH = 7.4 is presented in Figure 3. Two maxima of the PL signal have been observed at near 40 and 320 min from the onset of the experiment. Although the origin of the 40-min maximum can be traced to the presence of phosphate anions and/or OH^- in PBS, as observed in Figure 1, we argue that the second peak is related to the presence of TMS in the investigated solution. Additional information that supports this idea was provided by in situ measurements of the PL peak emission from GaAs(001) exposed to a solution of TMS in degassed ethanol. This solvent is known to maintain the integrity of TMS;[33] therefore, no PL enhancement was expected to take place. Indeed, this experiment revealed only a decaying PL signal, similar to the result illustrated in Figure 2b or reported elsewhere.[30] The absence of the first peak is consistent with the lack of free anions in the ethanol solution. Assuming that the background PL decay follows a dependence shown in Figure 3 by the broken-dotted curve and the contribution to the two PL peaks comes from the source-limited reactions of GaAs with phosphate ions (broken curve) and TSA (dotted curve), we were able to fit the experimental data with the solid-line curve shown in that figure. Qualitatively, similar sets of data were obtained for 1.0 and 5.0 mg/mL TMS solutions.

Figure 4 shows time-dependent plots of the TSA PL components (PL_{TSA}) obtained from the fitting procedure for the 0.1 mg/mL of TMS (as discussed in Figure 3) and, additionally, for 1.0 and 5.0 mg/mL TMS solutions. It can be seen that PL_{TSA} amplitudes saturate after 300 min for the 0.1 and 1.0 mg/mL solutions, and after 600 min for the 5.0 mg/mL solution. Our optical absorption study (discussed in the next paragraph) has indicated that it takes ~300 min for TMS to decompose in the 0.05 mg/mL solution. Thus, the observed in Figure 4 saturation of the PL_{TSA} amplitude at $t \geq 300$ min suggests the presence of a source-limited mechanism. Clearly, the TSA−GaAs reaction time must be much faster than the rate of breaking TSA in the investigated TMS solutions. The inset in Figure 4 shows the dependence of the TSA PL saturation amplitude on the concentration of TMS in PBS. Although this amplitude is less sensitive to the variation of TMS concentrations exceeding 1

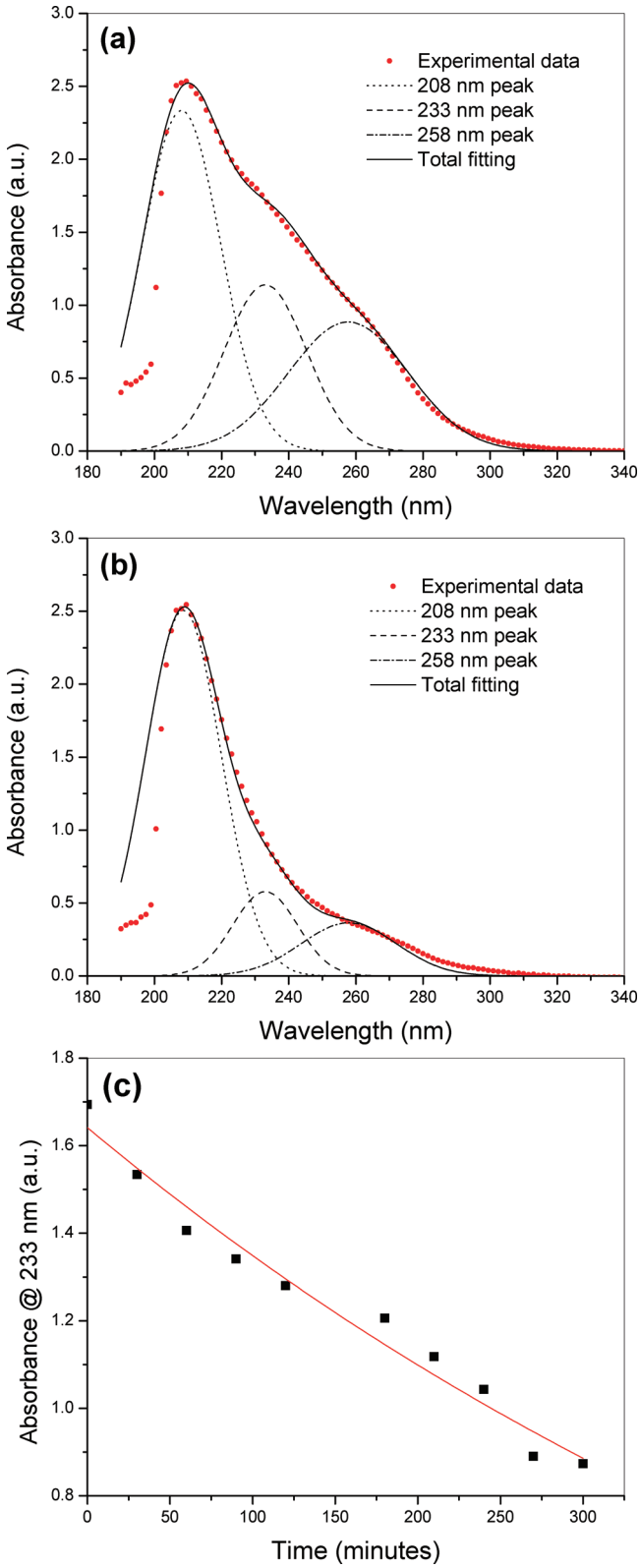

Figure 5. The initial UV−vis spectrum of thimerosal (0.05 mg/mL) in PBS buffer at pH = 7.4 (a), and after 300 min (b). The decrease in the 233 nm absorption peak shows the dynamics of breaking the Hg−S bond (c).

mg/mL, the results suggest the potential of the approach for detecting lower concentrations of TMS.

The decomposition of a 0.05 mg/mL TMS solution in PBS was investigated using UV−vis spectrometry by measuring its absorption every 30 min, up to 540 min exposure. Figure 5 compares the initial UV−vis spectrum of the investigated TMS solution (Figure 5a) with that observed after 300 min (Figure 5b). We were able to deconvolute each spectrum with a set of three peaks at 208, 233, and 258 nm, as shown by dotted, dashed, and dotted−dashed lines, respectively. The high-energy peak (208 nm) is related to benzene (ε = 8000) absorption,[34] and the 233 nm peak is due to Hg−S bonding in TMS. For instance, it has been reported that the $HgSO_3$ complex has a characteristic UV absorption peak at 233 nm.[33] The peak at 258 nm is usually called a secondary band for benzene derivatives.[34] As shown in Figure 5c, we could monitor the formation of TSA and ethylmercury ($C_2H_5Hg^+$), as suggested by the decaying intensity of the 233 nm peak. No significant change in the amplitude of this peak was observed for $t > 300$ min. The exact mechanism of such a behavior is not clear, but it is possible that it is related to the increased rate of the Hg−S recombination in the TSA and ethylmercury-rich environment. Note that the PL maximum related to the adsorption of TSA on the GaAs surface occurs at ~300 min, that is, it coincides with saturation of the investigated solution with TSA available for binding with GaAs. Some increase of the 208 nm peak has also been observed (compare Figure 5a and b). The likely reason for this behavior is the increased concentration of ethylmercury that is known to absorb at 206 nm.[35] This peak is not resolvable from the 208 nm peak with the current experimental setup.

The Ga 3s region of the XPS spectra from GaAs(001) following 20 h exposure to PBS and to a 0.1 mg/mL solution of TMS in PBS are shown in Figure 6. The background for these spectra was determined by using an etched GaAs as a reference sample. Analogously to the previously reported procedure,[28] the difference with respect to the spectrum envelope has been filled by artificially assigned components associated with inelastic scattering in the bulk material (broken line). These features, known as As plasmon loss peaks, are due to the interaction between photoelectron and other electrons in the surface region of the same sample.The GaO_x peak in Figure 6a indicates that oxidation of the sample surface takes place in the PBS environment. In contrast, the sample exposed to TMS (Figure 6b) shows the S 2p doublet, with 162.84 and 163.90 eV peaks assigned to S 2p3/2 and S 2p1/2, respectively.[36] This illustrates that the formation of GaO_x is suppressed by the reaction of TSA with GaAs as TSA binds to GaAs through sulfur atom. The covalent binding of S with GaAs is a well-known phenomenon.[27,28] The analysis in the Ga 3d region (see the Supporting Information) confirmed the presence of GaOx peak in the PBS treated sample. No GaO_x peak could be detected in the sample exposed to TMS, suggesting, as expected, that the reaction of GaAs with sulfur compound (TSA) protects its surface from rapid oxidation.

Additional XPS peaks have been observed at 100.90 and 105.05 eV for the samples exposed to TMS in PBS, as shown in Figure 6c. These peaks, identified as Hg 4f 5/2 and Hg 4f 7/2, suggest that ethylmercury binds to GaAs probably via ionic interaction of Hg with GaAs.[37] The absence of a peak at 99.2 eV, which is responsible for Hg(0), supports the hypothesis that the Hg−S bond breaking indeed took place in the investigated TMS−PBS solution.

Conclusion

We have demonstrated that the decomposition of TMS in PBS and attachment dynamics of TSA on GaAs(001) surface can be monitored in situ by using PL measurements. Both PL and UV−vis absorption measurements suggest that TMS decomposes almost entirely within 300 min and provides TSA

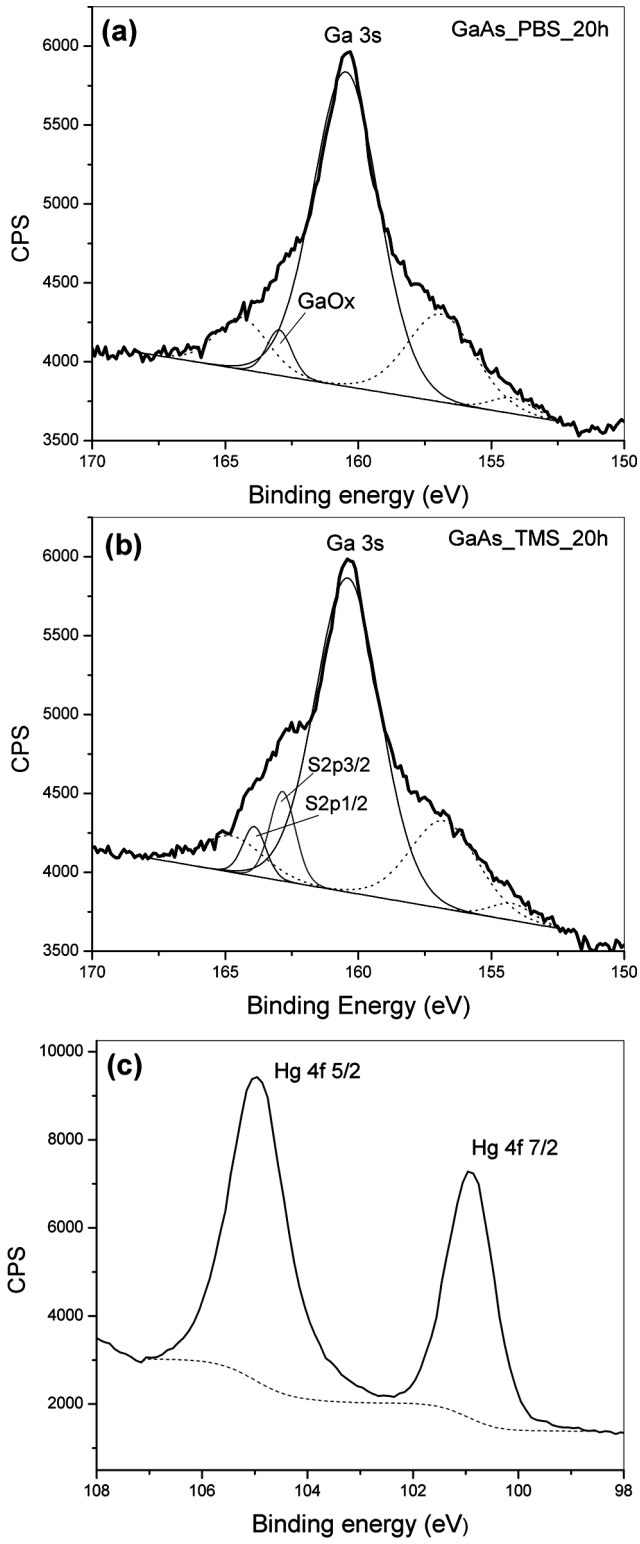

Figure 6. Angle-resolved XPS data of the Ga 3s peak region for GaAs(001) surface treated with PBS only (a) and with thimerosal (0.1 mg/mL) in PBS buffer at pH = 7.4 (b). The inelastic scattering is shown by the broken line. The S 2p doublet indicates TSA chemisorbed on the surface of GaAs. Part c shows the Hg 4f doublet, indicating that Hg has been adsorbed on the GaAs(001) surface (the dashed line is an XPS background signal from etched GaAs with subtracted Ga 3p peak).

for binding with the GaAs surface. The XPS results show the presence of chemisorbed TSA as well as that of ethylmercury on the GaAs(001) surface exposed to TSA−PBS solution for 20 h. The PL method allows detection of 0.1 mg/mL of TMS in PBS; however, experiments with lower concentrations of TMS have to be carried out, and the ultimate sensitivity of the method has yet to be determined.

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Note Added after ASAP Publication. This article was published ASAP on July 19, 2010. Figure 6c has been modified. The correct version was published on July 26, 2010.

Supporting Information Available: Angle-resolved XPS data of the Ga 3d peak region for GaAs(001) surface exposed to PBS and TMS. This information is available free of charge via the Internet at http://pubs.acs.org.

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