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Consequence of Galvanic Displacement Reaction on Digital Photocorrosion of GaAs/Al_{0.35}Ga_{0.65}As Nanoheterostructures

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consequence of the electron transfer from GaAs toward Au^{3+} is a significantly increased rate of DIP. At the same time, the formation of neutralized gold nanoparticles and Au–Ga alloy takes place on the surface of photocorroding nanoheterostructures. In the presence of 2.8% solution of ammonia and 0.1 mM gold chloride, a significantly reduced rate of deposition of gold nanoparticles is observed. This allows achieving layer-by-layer removal of the investigated material, which is sensitive to perturbations induced by surface immobilized electrically charged molecules. We have elaborated various factors stimulating photocorrosion of the GaAs/ $Al_{0.35}Ga_{0.65}As$ nanoheterostructures and we demonstrate the biosensing potential of an innovative GD-based DIP sensor.

1. INTRODUCTION

Metal ions with a redox potential more positive than that of some semiconductors could spontaneously accept electrons from semiconductors through the galvanic displacement (GD) process, leading to the formation of a reduced metal film on the surface of a semiconductor surface.^{1–10} The assimilation of metals with the semiconductor surface significantly alters the electrical conductivity, optoelectronic, and electromagnetic properties of semiconductors; ^{11–13} therefore, it became a viable approach for manufacturing sensors, ^{14–16} catalysts, ^{17–22} as well as optoelectronic^{23,24} and nanoelectronic devices. ^{25,26} Among the semiconductors, GaAs has been intensively studied because of its attractive optoelectronic properties related to the direct band gap, high electron mobility, and near-infrared photoluminescence (PL) that falls within the range of wavelengths where most biological materials, such as bacteria have minimal optical absorption.^{27,28} Numerous electrochemical sensors were developed based on the GD-based process.^{29,30} Crooks and co-workers had established a method for the electrochemical detection of silver nanoparticles by recording the anodic stripping voltammograms during the galvanic exchange between Ag nanoparticles and the carbon/ Au electrode.^{31,32} In another work, by using a similar method, they had configured a fluidic device for the detection of biomolecules labeled with silver nanoparticles.³² The concentration of biomolecules was determined by calibrating the GD process between biomolecules labeled with Ag^0 and Au^{3+} ions.

The photophysical properties of gold nanoparticles related to the surface plasmon resonance effect and surface-enhanced Raman scattering can be altered by changing the size, shape, and stoichiometry of materials.³³ Yi Lu et al. have developed a GaAs biosensor for the detection of specific DNA sequences through the surface plasmonic resonance enhanced fluorescence of gold nanoparticles.³⁴ Sayed and co-workers have fully characterized the stoichiometry, size, and shape of nanoparticles developed on the surface of a GaAs substrate through the GD process.^{35,36} They characterized the formation of Ga– Au alloy at the interface between gold nanoparticles and a GaAs substrate, also observing that surface functionalization of GaAs significantly altered the size and shape of gold nanoparticles developed through the GD displacement reaction.

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Figure 1. Graphical illustration of the GD mechanism involved in DIP of GaAs/AlGaAs nanoheterostructures.

Recently, we have reported that the GD process could be used for decorating bacteria with gold nanoparticles while contacting a semiconductor surface.³⁷ In this case, the bacterial cell was functionalized with ionic gold and, subsequently, exposed to an antibody-coated GaAs substrate. The luminescent gold nanoparticles were developed in situ through the spontaneous electron transfer process between GaAs and Au³⁺ ions surrounding the bacterial surface. This allowed us to generate high contrast imaging without the need for employing image enhancing procedures, such as green fluorescent protein conjugation. Since GaAs, and especially GaAs/AlGaAs nanoheterostructures, have been employed for the development of the so-called digital photocorrosion (DIP) biosensors, 27,38-44 it is highly relevant to investigate the potential role of the GD process in the functioning of DIP biosensors. Earlier, we have standardized the DIP effect in terms of duty cycle (DC) corresponding to the ratio of the excitation time to the total duration of a cycle,⁴⁵ power of the PL-exciting laser source^{39,46} and $\ensuremath{pH^{47}}$ on the time-dependent photocorrosion process of GaAs/AlGaAs nanoheterostructures. Because of the high solubility of photocorrosion byproducts such as As₂O₃ and Ga₂O₃ in ammonium hydroxide solution, the faster etch rates are achievable in basic media than normal pH. In the present work, we have analyzed the effect of the presence of gold ions in a 2.8% ammonium hydroxide solution on the photocorrosion rates of GaAs/AlGaAs nanoheterostructures. The results, in addition to shedding some light on the fundamental effects concerning the role of GD on the photocorrosion of GaAs and some other III-V semiconductors, allowed us to conclude about the potential of employing galvanic exchange for achieving enhanced performance of GaAs/AlGaAs nanoheterostructure-based DIP biosensors.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Hexadecanethiol (HDT) and phosphate buffered saline were purchased from Sigma-Aldrich. Deionized water was used throughout the experiments. Biotinylated polyethylene glycol (PEG) thiols were purchased from Prochimia Surfaces (Sopot, Poland). Acetonitrile and deuterated solvents were purchased from Merck and Sigma-Aldrich, respectively. Semiconductor grade OptiClear (National Diagnostics), acetone (ACP Chemicals, Canada),

isopropyl alcohol, and 28% ammonium hydroxide (Anachemia, Canada) were used without further purification.

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2.2. GaAs/Al_{0.35}Ga_{0.65}As Nanoheterostructures. The nanoheterostructures (Wafer D3422) were grown by metal organic chemical vapor deposition (CPFC, National Research Council of Canada, Ottawa) on a semi-insulating GaAs (001) substrate. They consist of a 20-pair AlAs/GaAs (2.4 nm/2.4 nm) superlattice and a 500 nm GaAs buffer layer followed by a 100 nm thick $Al_{0.35}Ga_{0.65}As$ layer. Six pairs of 12 nm thick GaAs and 10 nm thick $Al_{0.35}Ga_{0.65}As$ were grown on top of this microstructure and capped with a 12 nm thick GaAs layer.

2.3. X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements were conducted in the Au 4f and Ga 3d regions to investigate the chemical composition of the GaAs substrate after the GD reaction. The measurements were carried out with a Kratos Analytical AXIS Ultra DLD XPS spectrometer equipped with an Al K α source operating at 150 W. For each measurement, the data were collected for a takeoff angle of 60° with respect to the surface normal.

2.4. Atomic Force Microscopy. The surface morphology of processed samples was studied using an atomic force microscopy (AFM) technique (Digital Instrument, Nanoscope III). The AFM instrument was operated in tapping mode. All images were collected over a 2.0 μ m × 2.0 μ m surface area, using a tip velocity of 12 μ m/s and at a scan rate of 0.598 Hz.

2.5. Optical Microscopy. The samples were analyzed with a ZEISS optical microscope with a total magnification of 500X.

2.6. PL Measurements. The time-dependent PL was measured using a custom designed quantum semiconductor photonic biosensor reader.³⁸ Unless indicated otherwise, the samples were irradiated with 1.8 s pulses in every 25 s (DC = 1.8/25) using a homogenized beam of the light emitting diode (LED) operating at 660 nm and a delivery power of 15 mW/ cm² to the sample surface. The PL spectra of GaAs/AlGaAs nanoheterostructures were excited with a homogenized beam of the 532 nm laser and collected with a custom designed hyperspectral imaging PL mapper (HI-PLM).^{27,49}

3. RESULTS AND DISCUSSION

The structure of the GaAs/Al_{0.35}Ga_{0.65}As nanoheterostructure (wafer D3422) consists of seven layers of 12 nm thick GaAs and six layers of 10 nm thick $Al_{0.35}Ga_{0.65}As$ (Figure S1a). The



Figure 2. (A) Temporal behavior of PL intensity from D3422 samples DIP in different solvents (DC = 1.8 s/25 s). Data were normalized to the initial values in each case. (B) Linear regression curves showing variation of the PL peak positions with respect to time. The position of peaks determined with +/- 1.5 min.

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PL spectrum of the wafer was recorded with HI-PLM exciting samples with a 532 nm source and generating emission that peaked at 870 nm originating from GaAs epitaxial layers (Figure S1b). During photocorrosion, whenever a 12 nm thick GaAs layer is exposed to a water-based environment, some oxides, dominated by Ga_2O_3 , form at the surface and lead to the increased PL intensity observed at 870 nm. In contrast, whenever a 10 nm thick $Al_{0.35}Ga_{0.65}As$ layer is exposed to the oxidizing solution, the PL intensity is drastically reduced due to the significantly stronger surface recombination process of photoholes on AlGaAs in comparison to that on GaAs. Therefore, the formation of seven PL intensity maxima is expected during DIP of this particular nanoheterostructure.

A schematic illustration of the reaction involving GD in DIP of GaAs/AlGaAs nanoheterostructures is shown in Figure 1. The AuCl₃ compound coordinates with ammonia ions that are stronger field ligands compared to H₂O.⁴⁸ Upon interaction with the GaAs substrate, a spontaneous electron transfer between GaAs and Au³⁺ ion (GD reaction) takes place. This results in reduction of Au³⁺ ions to Au⁰ and oxidation of GaAs to Ga₂O₃. Because of the high solubility of Ga₂O₃ in ammonium hydroxide compared to aqueous solution, such an oxide layer is continuously removed under a flow of 0.1 mM gold solution in 2.8% ammonium hydroxide (Figure S2). Because of the large gap in the reduction potentials of gold and gallium ions, the reaction taking place in the GaAs-ionic solution results in the reduction of gold ions to gold nanoparticles and oxidation of GaAs with Ga2O3 dissolved by the presence of ammonia (notice that As oxides are dissolvable in the presence of water). Thus, the photocorrosion process leads to a dramatic change in the PL signal while the GaAs/AlGaAs nanoheterostructure is etched with an atomic laver resolution.

To further analyze the effect of GD on the photocorrosion of the GaAs D3422 sample, the PL spectra were recorded for the process carried out in solutions of deionized (DI) water, 2.8% ammonium hydroxide, and 0.1 mM Au³⁺ in 2.8% ammonium hydroxide. Figure 2A is a comparison of timedependent positions of PL maxima corresponding to GaAs-AlGaAs interfaces revealed in different solvent systems (all



Figure 3. (A) Time-dependent PL plots for the D3422 sample with different surface functionalization values, and photocorroding at a DC of 1.8/25 under continuous flow of 0.1 mM AuCl₃ in 2.8% ammonium hydroxide solution. (B) Time-dependent PL plots of the D3422 sample in the presence of 0.1 mM AuCl₃ solution in DI water and 2.8% ammonium hydroxide. Data were normalized to the initial values in each case.





Figure 4. High-resolution XPS scans of the GaAs/AlGaAs nanoheterostructure after DIP under continuous flow of 0.1 mM Au³⁺ in DI water (DC = 1.8/25, 144 cycles) corresponding to the Au 4f peak (A) and Ga 3d peak (B). High-resolution XPS scans of the GaAs/AlGaAs nanoheterostructure after DIP under a continuous flow of 0.1 mM Au³⁺ in 2.8% ammonium hydroxide (DC = 1.8/25, 144 cycles) corresponding to the Au 4f peak (C) and the Ga 3d peak (D).

these experiments were carried out with DC = 1.8 s/25 s and an LED power of 16 mW/cm²). The positions of the first PL maximum were revealed at ~ 23 and ~ 20 min in DI water and 2.8% of NH₄OH, respectively. Furthermore, a noticeable delay of the higher order PL maxima was observed in DI water, which must be related to the reduced photocorrosion rate in the presence of Ga₂O₃ accumulating under these conditions. In contrast, a significantly faster photocorrosion rate, even compared to ammonia solution alone, was observed in the ammonia solution with 0.1 mM Au³⁺. Under these conditions, the first PL maximum was revealed at ~5 min and it took less than 120 min to reveal all other PL maxima, compared to the required 250 and 330 min in NH₄OH and DI H₂O solutions, respectively. Figure 2B shows that the time to reveal each PL maximum increases linearly with respect to the peak number. Furthermore, the difference in the position of respective maxima increases with the peak number.

3.1. Effect of Surface Functionalization on the Photocorrosion Rate. The surface of the GaAs substrate

was functionalized with thiols and antibodies using an already established procedure by our group.^{27,37–39,43,44,49,50} The photocorrosion profile was recorded with the continuous flow of 0.1 mM Au³⁺ ion in 2.8% ammonium hydroxide. The PL plots of samples functionalized with biotinylated thiols (HDT/PEG biotin) and antibodies (HDT/PEG biotin + *E. coli*-specific antibody) are compared as shown in Figure 3A with the plot of an unfunctionalized nanoheterostructure. Only one weak PL maximum is observed at ~12 min for the HDT/ PEG biotin-functionalized sample. The intensity of this PL signal diminishes rapidly to an almost unmeasurable level at ~140 min. Consistent with the XPS results discussed later in this report, the attenuation of the 870 nm emission from GaAs is related to the presence of the growing concentration of gold nanoparticles developed on the surface of investigated samples through the GD reaction.

It is relevant to mention that the byproducts of the GD reaction between GaAs and Au³⁺ are highly soluble in 2.8% ammonium hydroxide compared to DI water. Therefore, in the



Figure 5. AFM images of the $Al_{0.35}Ga_{0.65}As$ surface revealed after DIP of GaAs/AlGaAs nanoheterostructures under a continuous flow of 0.1 mM Au^{3+} (DC = 1.8/25, 144 cycles) in DI water (A) and in 0.1 mM Au^{3+} in 2.8% ammonia (B). Optical images of the unfunctionalized GaAs surface revealed after DIP of GaAs/Al_{0.35}Ga_{0.65}As nanoheterostructures under continuous flow of 0.1 mM Au^{3+} (DC = 1.8/25, 144 cycles) in DI water (magnification 500X) (C) and in 2.8% ammonium hydroxide solution (magnification 500X) (D).

presence of 2.8% ammonium hydroxide the byproducts which include gallium oxide and gallium—gold alloy are removed from the surface and, consequently, the layer-by-layer etching of GaAs/AlGaAs nanoheterostructure can be achieved. Whereas in DI water, because of the insolubility of metal oxides, the nonluminescent materials deposit on the semiconductor surface, which results in a diminishing PL signal (Figure 3B).

The XPS survey spectra of GaAs/AlGaAs nanoheterostructure DIP under continuous flows of 0.1 mM Au³⁺ in DI water (Figure S3) and 2.8% ammonium hydroxide (Figure S4) revealed qualitative differences related to electronic transitions originating from Au, Ga, As, and O. High-resolution XPS scans of the material formed on unfunctionalized GaAs/AlGaAs nanoheterostructures for a flow 0.1 mM Au³⁺ in DI water is shown in Figure 4A,B (DC = 1.8/25, 144 cycles) and for a flow of 0.1 mM Au3+ in 2.8% ammonium hydroxide is shown in Figure 4C,D. These results revealed that the photocorrosion in a DI water environment supports the formation of gold nanoparticles and Au₉Ga₄ alloy on the surface of the semiconductor (Figure 4A,B). The binding energy peaks at 84.01 and 84.84 eV correspond to $4f_{7/2}$ electronic transitions in Au⁰ and Au₉Ga₄, respectively, reported by us previously³⁷ in agreement with the literature data.^{2,35} In contrast, the photocorrosion carried out in a continuous flow of ammonium hydroxide (Figure 4C) supported the formation of only one type of gold nanoparticle characterized by a binding energy of 83.9 eV that corresponds to the $4f_{7/2}$ electronic transition in Au⁰ nanoparticles. The slightly lower binding energy in this case might be due to the absorption of ammonia by the gold nanoparticles. Similarly, the slightly lower binding energy of the 19.12 eV XPS peak related to the Ga $3d_{5/2}$ electronic transition in GaAs is observed in this case compared to the 20.20 and 20.70 eV XPS peaks associated with Ga₂O₃ and Au₉Ga₄. The composition of material developed after DIP with a continuous flow of Au³⁺ ions and 2.8% ammonium hydroxide was examined using XPS spectra and revealed only two types of Ga present on the surface. The peaks at 19.00 and 20.14 eV represent the Ga $3d_{5/2}$ electron of GaAs and Ga₂O₃, respectively. Here, the weaker intensity of Ga₂O₃ suggests that the oxide layer has been removed almost entirely because of its high solubility in ammonium hydroxide (Figure 4D).

The surface morphology after DIP of the D3422 sample in the presence of gold ions at different conditions (DI water or 2.8% ammonium hydroxide) was investigated with AFM and optical microscopy measurements. The surface roughness calculated from AFM images revealed the higher values of $\sigma_{\rm rms}$ whenever samples were photocorroded under a continuous flow of 0.1 mM Au³⁺ in DI water compared to photocorrosion in an ammonium hydroxide solution under nominally same conditions. This trend is possible due to the significant formation of Ga oxides and Au–Ga alloy on the surface of this semiconductor photocorroding in DI water. In contrast, ammonium hydroxide removes quite efficiently Ga oxides and Au nanoparticles from the semiconductor surface (Figure 5A), which has also been validated by the XPS results (Figures S3–S6).

The optical microscopy images recorded after DIP of GaAs/ AlGaAs nanoheterostructures under a continuous flow of 0.1 mM Au^{3+} in DI water revealed, consistently with the AFM images, the presence of metallic nanoparticles, while the



Figure 6. (A) Photocorrosion profile of the GaAs/AlGaAs nanoheterostructure after photocorrosion under a continuous flow of 0.1 mM Au³⁺ and 2.8% ammonia for different DCs: (A) DC = 1.8/25, (B) DC = 1.8/30, and (C) DC = 1.8/40. (D) Linear regression of peak positions for different DCs. Data in (A–C) were normalized to the initial values in each case.

smoother surface was observed for photocorrosion in 0.1 mM Au^{3+} in 2.8% ammonia (Figure 5C,D).

3.2. Effect of Duty Cycle on the Rate of Digital Photocorrosion. The effect of DC on the DIP process of GaAs/Al_{0.35}Ga_{0.65}As nanoheterostructures in the presence of Au³⁺ ions diluted in ammonium hydroxide is illustrated in Figure 6. The PL photocorrosion scans were recorded in this case for the excitation power 10 mW/cm^2 and a continuous flow of 2.8% ammonium hydroxide with 0.1 mM Au³⁺ ions at 0.04 mL/min. The results reveal that the photocorrosion proceeds at faster rates with reduced DCs (increased time-off between the excitation pulses). At the same time, the PL maxima corresponding to GaAs/AlGaAs interfaces became broader and weakly defined in proportion to the distance at which these interfaces are located below the surface. These results are consistent with the growing contribution of GDassisted dark corrosion to the process of material removal. On the other hand, a significantly increased DC is expected to lead to the conventional photoetching process. Therefore, it is of interest to estimate the precision of the investigated DIP

process in material removal. The upper axes in Figure 6A–C show the number of cycles applied to complete each experiment. It can be seen that it took 180 cycles to reveal six PL maxima with DC = 1.8/25, compared to 130 cycles required to reveal the same with DC = 1.8/40. The results, summarized in Figure 6D, allow us to conclude that the average removal rate achieved with DC = 1.8/25 is at 0.59 nm/ cycle, which corresponds to two monolayers of the GaAs/Al_{0.35}Ga_{0.65}As (001) system.⁵⁰ It is reasonable to expect, also consistent with our preliminary results, that decomposition of GaAs/Al_{0.35}Ga_{0.65}As nanoheterostructures at such a weak rate should be sensitive to small perturbations induced by the attachment of electrically charged molecules to their surface.

4. CONCLUSIONS

We have investigated DIP on GaAs/Al_{0.35}Ga_{0.65}As nanoheterostructures in the presence of Au nanoparticles formed by the process of GD. The loss of PL signal from GaAs because of the excessive formation of the nonluminescent oxidized

product could be controlled by employing a 2.8% of ammonium hydroxide solution. The conditions have been optimized for layer-by-layer etching of the material through the GD reaction. While the DIP process of GaAs/AlGaAs nanoheterostructures offers conditions attractive for the detection of bacteria, as reported before, the GD-assisted formation of Au nanoparticles on the surface of the investigated material has the potential to facilitate the development of an innovative biosensing platform taking advantage of the strong affinity of gold to some molecules, or plasmonic properties of Au nanoparticles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c08346.

Functionalization procedure; schematic cross-section view and PL spectrum of $GaAs/Al_{0.35}Ga_{0.65}As$ nanoheterostructures (Figure S1); temporal behavior of PL intensity (Figure S2); XPS overview scans of GaAs/AlGaAs nanoheterostructure (Figures S3 and S4); and high-resolution XPS core level O 1 s spectra (Figures S5 and S6) (PDF)

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Notes

The authors declare no competing financial interest.

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