



**HAL**  
open science

## Selective Area Nd:YAG Laser Functionalization of Digital Photocorrosion GaAs/AlGaAs Biosensor

Grib Hakim, Khalid Moumanis, Walid M Hassen, Jan J Dubowski

► **To cite this version:**

Grib Hakim, Khalid Moumanis, Walid M Hassen, Jan J Dubowski. Selective Area Nd:YAG Laser Functionalization of Digital Photocorrosion GaAs/AlGaAs Biosensor. *Journal of Laser Micro/Nanoengineering*, 2020, 15 (2), pp.77-84. 10.2961/jlmn.2020.02.2001 . hal-03341371

**HAL Id: hal-03341371**

**<https://hal.science/hal-03341371v1>**

Submitted on 10 Sep 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/343323411>

# Selective Area Nd:YAG Laser Functionalization of Digital Photocorrosion GaAs/AlGaAs Biosensor

Article in *Journal of Laser Micro / Nanoengineering* · July 2020

DOI: 10.2961/jlmm.2020.02.2001

CITATION

1

READS

97

4 authors:



**Grib Hakim**

Université de Sherbrooke

1 PUBLICATION 1 CITATION

SEE PROFILE



**Khalid Moumanis**

Université de Sherbrooke

51 PUBLICATIONS 458 CITATIONS

SEE PROFILE



**Walid M Hassen**

Université de Sherbrooke

37 PUBLICATIONS 571 CITATIONS

SEE PROFILE



**Jan J. Dubowski**

Université de Sherbrooke

301 PUBLICATIONS 2,434 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



Pulsed Laser Deposition (PLD) [View project](#)



Selective area functionalisation of GaAs/AlGaAs biochips by IR Laser [View project](#)

# Selective Area Nd:YAG Laser Functionalization of Digital Photocorrosion GaAs/AlGaAs Biosensor

Hakim Grib<sup>1,2</sup>, Khalid Moumanis<sup>1,2</sup>, Walid Mohamed Hassen<sup>1,2</sup> and Jan J. Dubowski<sup>1,2</sup>

<sup>1</sup>Laboratory of Quantum Semiconductor and Photon-based BioNanotechnology, Department of Electrical and Computer Engineering, Interdisciplinary Institute for Technological Innovation (3IT), Université de Sherbrooke, 3000 boul. de l'Université, Sherbrooke, J1K0A5 Québec, Canada

<sup>2</sup>Laboratory of Nano-technologies and Nano-characterization (LN2) - CNRS UMI-3463, Interdisciplinary Institute for Technological Innovation (3IT), Université de Sherbrooke, 3000 boul. de l'Université, Sherbrooke, J1K0A5 Québec, Canada

E-mail: [jan.j.dubowski@usherbrooke.ca](mailto:jan.j.dubowski@usherbrooke.ca)

Digital photocorrosion (DIP) of GaAs/AlGaAs nanoheterostructures has been found sensitive to semiconductor surface states and, thus, attractive for rapid detection of negatively charged bacteria in aqueous environment. However, calibration of DIP biosensors depends on the reproducibility of chip-to-chip surface properties that are related to the chip fabrication process. To reduce the error related to this characteristics and provide a reference signal, we have examined the fabrication of biochips with a selective area removed biofunctionalization layer. The GaAs/AlGaAs biochips were coated with 1mM 16-mercaptohexadecanoic acid (MHTDA) self-assembled monolayers (SAM) designed for interfacing antibodies suitable for immobilization of bacteria. Selective area thermal desorption of SAM was investigated with an Nd:YAG laser emitting at 1064 nm in a continuous wave mode. The exposure of a biofunctionalized and laser-processed chips to bacterial solution resulted in a selected area capture of bacteria. With a low-cost light emitting diode, this approach should allow the realization of an advanced DIP biosensor with a small surface area designed for referencing the photocorrosion process of a biosensor.

DOI: 10.2961/jlmn.2020.02.2001

**Keywords:** digital photocorrosion biosensor, GaAs/AlGaAs nanoheterostructures, self-assembled monolayers, thermal desorption, internal referencing, Nd:YAG laser, bacteria biosensor

## 1. Introduction

Digital photocorrosion (DIP) biosensors have been investigated for rapid detection of *Escherichia coli* [1, 2] and *Legionella pneumophila* [3, 4] bacteria. The simplicity of this approach, the low cost of an optical reader and the potential to reuse the biochips make the DIP technology potentially attractive for a variety of biosensing applications. The DIP process could be monitored by measuring the open circuit potential of etched GaAs/AlGaAs biochips [5], however, more conveniently it is monitored with the photoluminescence (PL) effect induced in GaAs/AlGaAs nanoheterostructures [6, 7]. The photocorrosion rate undergoes a drastic change when the photocorrosion front passes through a GaAs/AlGaAs interface, resulting in the formation of a PL intensity maximum. This effect is modified by the interaction with negatively charged bacteria, which could result in a delayed position of PL maximum. The photocorrosion rate depends also on the concentration and nature of surface states that vary from sample-to-sample and results in fluctuations of the position of PL maxima. This affects the calibration error of a DIP biosensor.

The formation of an internal reference would require the removal of a biosensing architecture, typically employing alkanethiol self-assembled monolayers (SAM), from the selected area of a GaAs/AlGaAs biochip. This could be achieved by chemical etching in HCl [8] and H<sub>2</sub>O<sub>2</sub> [9] solutions, or UV-assisted chemical etching [10] and selective area atomic layer deposition [11]. However, selective area

microfabrication technique is a complicated processes requiring the application of photoresist-based lithography [12] that would not be acceptable for the realization of a low-cost biosensor. It has been demonstrated that hexadecanethiol (HDT) SAM desorb in vacuum from the GaAs surface at 180 °C [13]. Selected area heating of semiconductors to high temperatures could be achieved easily with IR lasers. For instance, it has been reported that a thermally isolated 10 mm x 10 mm GaAs/Al<sub>0.31</sub>Ga<sub>0.69</sub>As chip, coated with a 270 nm thick layer of SiO<sub>2</sub>, could be heated to ~ 800 °C within 15 sec if irradiated with a continuous wave (CW) Nd:YAG laser delivering power of 1 W/mm<sup>2</sup> to a 3-mm diameter spot [14]. Thus, this approach appears attractive for selective area desorption of SAM from the surface of biofunctionalized biochips. It is expected that the portion of a biochip with the laser created SAM-free zone would photocorrode at a significantly faster rate, typical of as-fabricated GaAs/AlGaAs nanoheterostructures.

The internal referencing concept has been investigated for optical and MEMs biosensor systems, resulting in new detection limits [15-17]. For instance, to address environmental and nonspecific effects, a label free Micro RNA cantilever has been employed as an internal reference for detection of cancer in cell lysates [18]. In this paper, we report on an IR laser-based process of selective area desorption of SAM from the surface of GaAs/AlGaAs biochips investigated for the formation of an internal reference in the operation of a DIP biosensor.

## 2. Experimental section

### 2.1. Fabrication of self-assembled monolayers

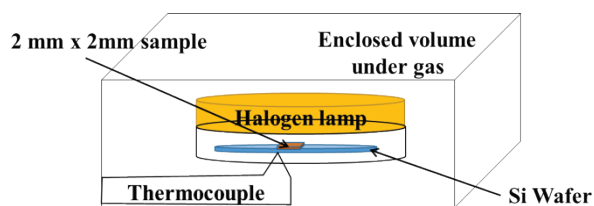
Prior to deposition of 16-mercaptohexadecanoic acid (MHDA) SAM, 2 mm x 2 mm double sided polished samples of the GaAs/AlGaAs nanoheterostructures (Wafer D3422, CMC microsystems) were cleaned following the procedure described elsewhere [9]. After ultrasonication with OptiClear, acetone and isopropanol during 5 min in each solution, the samples were dried with ultra high-purity 5.0 grade nitrogen (99.999%) and etched in ammonium hydroxide (28 % aqueous solution of  $\text{NH}_4\text{OH}$ ) for 2 min to remove native oxides from the GaAs surface. Then, the samples were rinsed with degassed ethanol, and immediately incubated in MHDA solution (1 mM, deoxygenated ethanol) for 20 h at room temperature and in darkness. A freshly cleaned sample was incubated in degassed ethanol for 20 h and used as background for FTIR measurements and PL analysis. After SAM formation, the samples were rinsed with degassed ethanol and ultrasonicated to remove any physisorbed thiol molecules from the surface. Finally, the samples were dried with nitrogen and stored in darkness under gas nitrogen atmosphere.

### 2.2. Conventional RTA setup

Initially, the desorption of SAMs from the GaAs surface was investigated in pristine conditions provided by the commercial Rapid Thermal Annealing setup (RTA, JIPELEC, JetFirst) as schematically illustrated in Figure 1. This setup comprises a bank of halogen lamps as a heat source operating up to 1200 °C, and a supply of 4.3 grade oxygen (99.993%) and 5.0 nitrogen (99.999%) to create a desired controlled atmosphere (30%  $\text{O}_2$  and 70%  $\text{N}_2$  was used in these experiments) maintained at a pressure of around 1040 mbar. The temperature was controlled with a thermocouple (K type) in contact with the backside of a silicon wafer used to support the investigated samples.

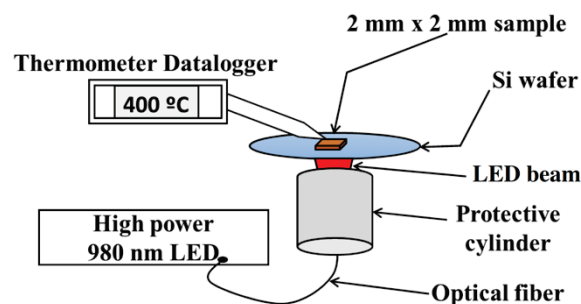
### 2.3. Light Emitting Diode RTA setup

The light emitting diode (LED) RTA setup, as schematically shown in Figure 2, was used for the annealing experiments carried out in a normal atmospheric environment. The setup consists of a CW LED emitting up to 150 W of the 980 nm radiation. The LED emission is coupled with the fiber whose output faces a 2-inch diameter silicon wafer used to support processed samples. The fiber numerical aperture of 0.22 allows to heat the Si wafer in excess of 500 °C [19]. The temperature of processed GaAs/AlGaAs samples was measured with a thermocouple (K type) remaining in contact with the top surface of a sample. The temperature measurements and control were carried out with a dedicated Datalogger. A PM30 sensor connected to Molectron EPM2000



**Fig. 1** Schematic illustration of the conventional RTA setup (JIPELEC).

power meter was used to measure the LED output power. To induce a temperature of around 400 °C, the LED was driven with a current of ~16 A allowing to generate output power of up to ~22 W. For the 30 mm distance between the output fiber and the silicon wafer, these conditions allowed to irradiate the silicon wafer area of ~13 mm in diameter with estimated power density of 0.15 W/mm<sup>2</sup>.



**Fig. 2** Schematic illustration of the 980 nm LED RTA setup.

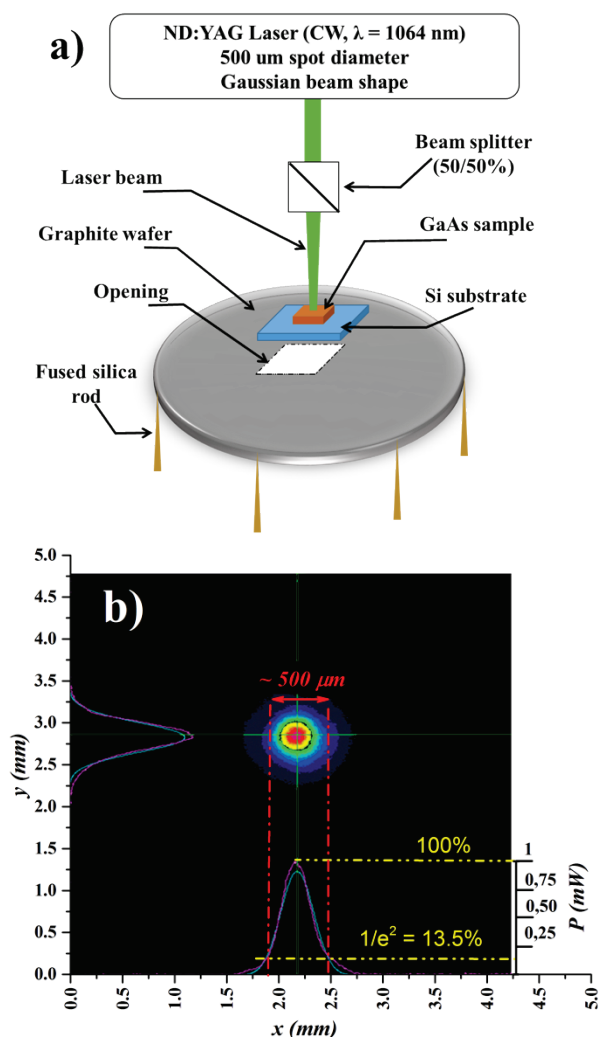
### 2.4. Nd:YAG Laser RTA setup

An Nd:YAG laser setup was used for selective area irradiation of MHDA SAM coated samples. A schematic illustration of the setup is shown in Figure 3 a). It consists of a CW Nd:YAG TEM<sub>00</sub> laser emitting at 1064 nm and delivering power of up to 30 W. To deliver 1 to 12 W power to the sample surface, a 50/50 beam splitter was used, which allowed to avoid running a noisy laser operating in the vicinity of its operational threshold.

In order to minimize the potential contamination of processed samples with graphite released impurities, the samples were installed on a 6 mm x 5 mm Si substrate mounted above a 4 mm x 4 mm opening in the graphite wafer that was suspended by the needle-tip fused silica rods. A Gaussian beam of the laser was focused to a 500 μm diameter spot on the surface of GaAs/AlGaAs biochips. The profile of a laser beam as obtained with the Coherent beam profiler (LaserCam-HR II) employing a 1064 nm filter (MYQ-51-1064/HPTF6279, Optics for Research) is shown in Figure 3b). The laser spot diameter was calculated with the associated "BeamView-USB" software for the beam intensity reduced to 1/e<sup>2</sup> of the peak value. The focal plane was at 250 mm from the employed lens.

### 2.5. Photoluminescence measurements

The photoluminescence (PL) intensity monitored DIP of GaAs/AlGaAs nanoheterostructures was performed in a custom designed Quantum Semiconductor Photonic Biosensor (QSPB) Reader-2 [1, 4, 5]. The QSPB-2 Reader consists of an LED emitting at 625 nm for exciting GaAs/AlGaAs samples, an 812 nm long pass filter to collect PL data, and a CCD camera. The samples were mounted in a flow cell filled with 0.1X phosphate buffered saline (PBS) solution, or with PBS suspension of bacteria, both flown at 0.04 mL/min. The DIP process was induced with a 14 mW/cm<sup>2</sup> radiation (1.8 s irradiation in each 15 s period, and PL was simultaneously monitored by collecting images of processed samples using a CCD camera.



**Fig. 3** Schematic illustration of the Nd:YAG laser RTA setup (a), and 2D profile of the laser beam employed for desorption of SAM (b).

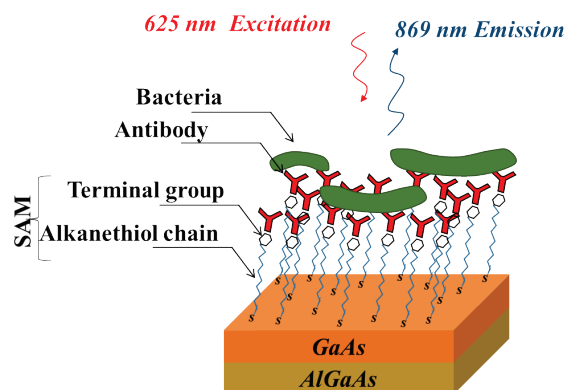
## 2.6. FTIR measurements

Spectra of SAM formed on the GaAs surface were analyzed by Fourier transform IR (FTIR) transmission spectroscopy of asymmetric and symmetric  $\text{CH}_2$  stretch vibrations of alkane chains. The measurements were carried out with Bruker Vertex 70v vacuum spectrometer equipped with a RockSolid interferometer and a Global IR source covering spectral range between 6000 and  $10\text{ cm}^{-1}$ . The signal was collected with a liquid-nitrogen cooled mercury cadmium telluride (MCT) IR detector. The spectral resolution and the numerical aperture were set to  $4\text{ cm}^{-1}$  and 1.5 mm, respectively. All measurements were carried out 5 min after evacuation of the FTIR chamber. The spectra were averaged over 1000 scans and subtracted from the spectrum of a freshly etched GaAs/AlGaAs sample considered as a background. MHDA SAM coated GaAs samples were characterized before and after thermal treatment designed to evaluate the effect of thermally induced desorption.

## 2.7. Biofunctionalization protocol

The specific capture of bacteria by GaAs/AlGaAs biosensors is achieved with an architecture comprising SAM and antibodies (Abs) as schematically illustrated in Figure 4.

To capture Abs, the samples were incubated for 30 min in an EDC-NHS solution (0.4 M-0.1 M). This allowed for activation of the COOH terminal group of MHDA, as illustrated in Figure 5. Following washing with deionized (DI) water, the sample were exposed to *E. coli* Abs that bind through their amine group to the activated COOH. To saturate the unreacted COOH groups, the chips were exposed for 1 hour at pH 8 in a 1M ethanolamine solution. Finally, the chips were washed with a 1% Tween 20 solution in PBS, to remove the non-covalently bound Abs [9]. Before optical microscopy measurements, the chips were washed again with DI water and dried under nitrogen to remove the remaining Tween solution.



**Fig. 4** Schematic illustration of the GaAs/AlGaAs biochip architecture with the excitation and emission wavelengths.

## 3. Experimental results and discussion

### 3.1. RTA under controlled gas atmosphere

The FTIR spectra shown in Figure 6 illustrate the quality of MHDA SAM coated GaAs samples before and after RTA annealing at  $440\text{ }^\circ\text{C}$ . The formation of MHDA SAM on GaAs surface is confirmed by absorbance spectra of the asymmetric and symmetric  $\text{CH}_2$  stretch vibration modes at  $2920\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ , respectively [20, 21]. It can be seen that the maximum absorbance intensity of the asymmetric stretching mode is about  $1.3 \times 10^{-3}$  with a full width-at-half-maximum (FWHM) of  $22\text{ cm}^{-1}$ , which suggests the formation of a well-ordered SAM with the quality comparable to the best MHDA SAM reported in the literature [22]. In contrast, the spectra of the samples annealed for 10 and 15 s at  $440\text{ }^\circ\text{C}$  show the absence of  $\text{CH}_2$  features, consistent with a desorption of the MHDA SAM under these conditions. Figure 7 shows PL runs of DIP fresh (uncoated and non-annealed) and RTA samples. A weak PL intensity maximum is observed at 15 min for the uncoated and non-annealed sample, while the MHDA SAM coated and non-annealed sample revealed a broad PL maximum formed at 35 min. This behaviour is consistent with the photocorrosion of similar nanoheterostructures reported elsewhere [6, 2, 24]. The PL intensities of the annealed samples evolve much slower and do not reveal formation of maxima within the 60 min DIP process. These results are consistent with desorption of MHDA SAM and accumulation of the DIP delaying residual products (oxides) on the surface of samples processed at  $440\text{ }^\circ\text{C}$  [6].

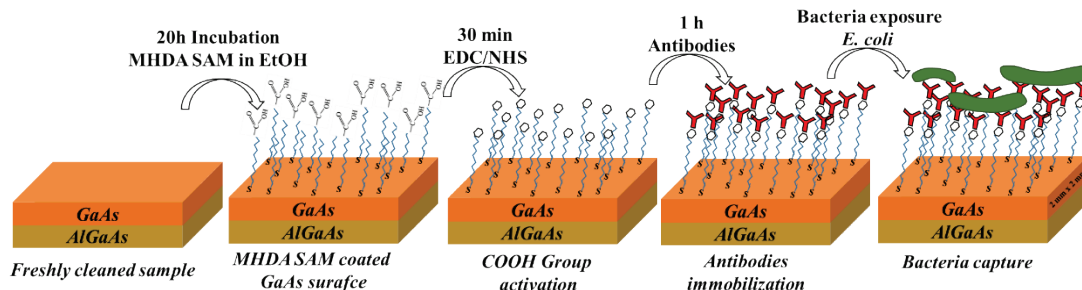


Fig. 5 Biofunctionalization scheme of a GaAs/AlGaAs biochip designed for the capture of bacteria.

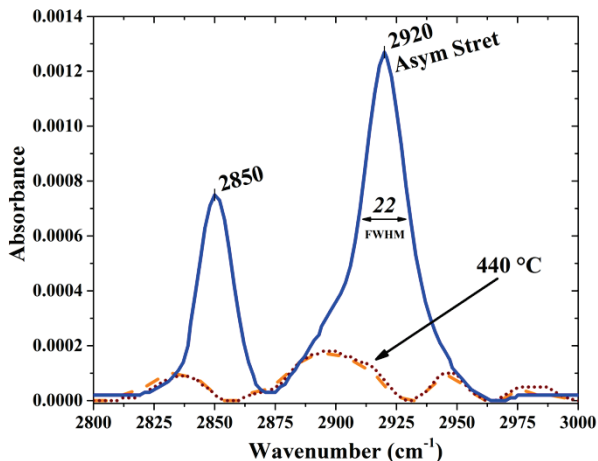


Fig. 6 FTIR absorbance spectra of an intact MHDA SAM coated GaAs/AlGaAs sample (blue), and of similar samples annealed at 440 °C for 10 s (dash) and 15 s (dotted).

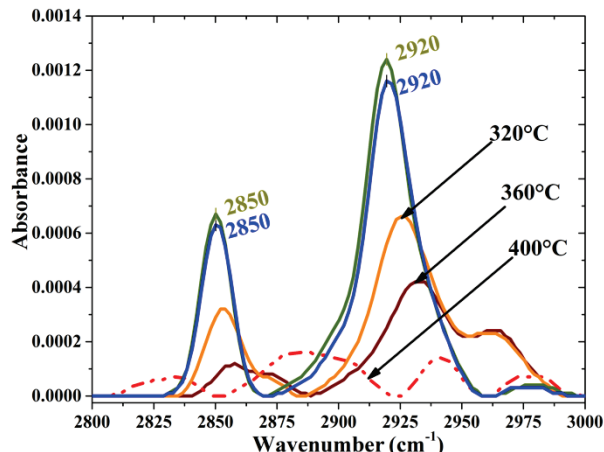


Fig. 8 FTIR absorbance spectra of as-fabricated GaAs/AlGaAs samples coated with MHDA SAM (solid blue) and annealed at 320 °C (solid yellow), 360 °C (solid brown) and 400 °C (dot-dash red). Notice that ammonia processing of as-fabricated sample (solid green) does not affect the quality of SAM.

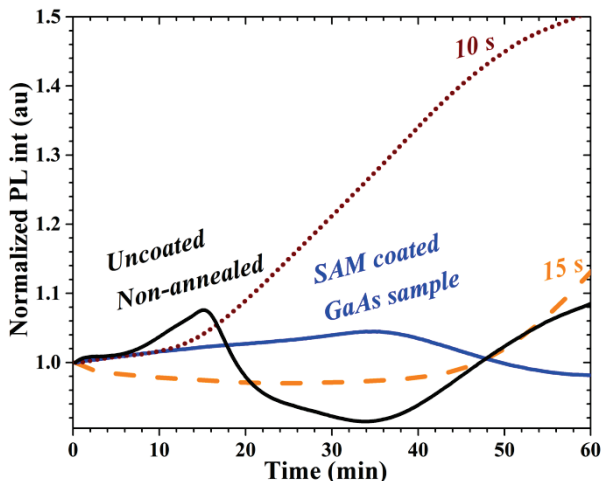
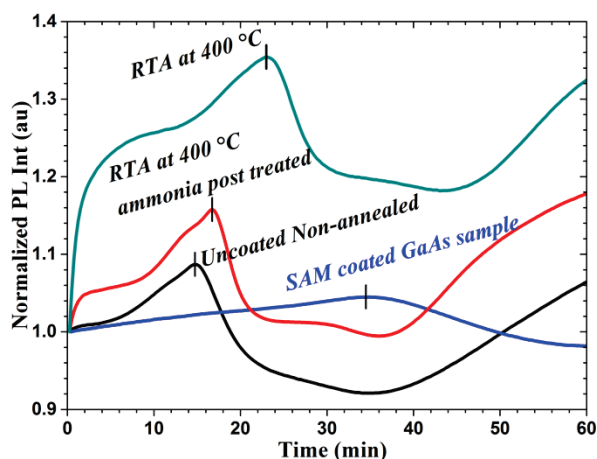


Fig. 7 PL monitored DIP of a fresh GaAs/AlGaAs sample (black), as-fabricated MHDA SAM coated sample (blue), and MHDA SAM coated samples annealed at 440 °C for 10 s (brown-dotted) and 15 s (yellow-dash).

The FTIR absorbance spectra of the samples annealed at lower temperatures are shown in Figure 8. It can be seen that while the annealing at 400 °C for 15 s leads to a similar result as that observed for the processing temperature of 440 °C, the annealing at 360 and 320 °C only partially removes SAM as illustrated by the weak absorbance spectra of CH<sub>2</sub> stretch vibration features. The 3 to 5 cm<sup>-1</sup> shifts of these features to higher energies suggest the presence of less organized SAM. These results are consistent with the observations made by

Huang et al., [25] who reported a partial dissociation of short alkanethiol SAM from the GaAs surface in vacuum at ~ 247 °C, and their complete decomposition at 392 °C.

Figure 9 compares PL plots collected during DIP of a freshly cleaned GaAs/AlGaAs sample, an MHDA SAM coated sample and an MHDA SAM coated sample annealed at 400 °C. A delayed position of the PL intensity maximum from 15 to 35 min is consistent with the presence of MHDA SAM that slows down the photocorrosion process [6, 2, 24]. The annealing of an MHDA SAM coated sample at 400 °C removes SAM from its surface, and the position of a related PL intensity maximum is observed at 23 min, i.e., delayed by 8 min in comparison to that maximum observed for the as-fabricated (uncoated) sample. It has been known that high-temperature processing of GaAs leads to surface accumulation of As- and Ga-oxides [26]. While As-oxides are relatively easily dissolvable in water [27], Ga-oxides are etchable, e.g., in ammonium hydroxide [28]. To verify if such oxides have contributed to the deceleration of the DIP process, the 400 °C annealed sample was subjected to a 2-min exposure of an aqueous solution of ammonium hydroxide (28 %). The associated PL plot in Figure 9 exhibits a maximum at ~ 16 min that coincides well with the 15-min maximum revealed for the uncoated and non-annealed sample. This result suggests that the ammonia post treatment of annealed samples allows to remove excessive oxides,



**Fig. 9** PL intensity plots of DIP uncoated (black) and MHDA SAM coated (blue) samples compared to the 400 °C annealed MHDA SAM coated sample (turquoise). The photocorrosion of ammonia processed MHDA SAM coated sample annealed at 400 °C (red) proceeds similarly to that of the as-fabricated sample.

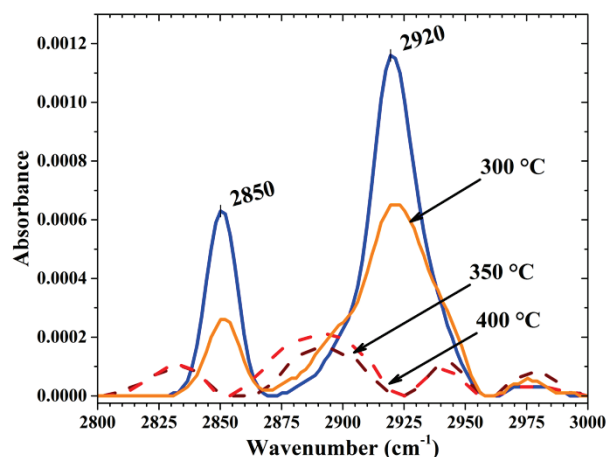
formed during annealing, and fabricate attractive samples with a built-in reference. We have also verified if ammonia processing of MHDA SAM coated sample is not detrimental to the quality of the formed SAM and allows preserving its integrity. Indeed, as shown in Figure 8, the FTIR spectrum of an ammonia processed sample for 2 min (green) is practically undistinguishable from that of the original, non-processed sample (blue).

### 3.2. LED RTA in atmospheric environment

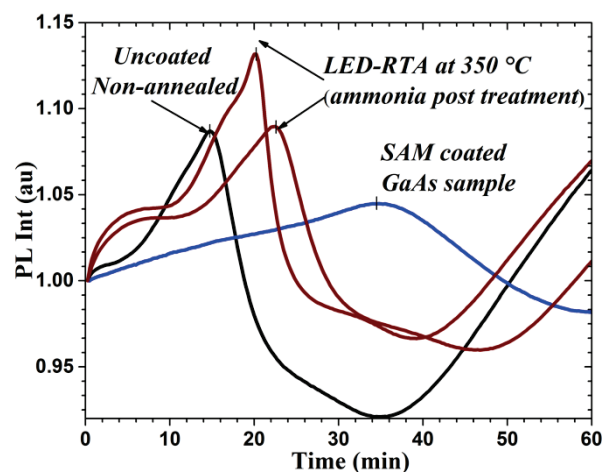
The FTIR absorbance spectra of samples processed by LED-RTA for 15 s at 300, 350 and 400 °C are shown in Figure 10. The results suggest that the desorption of SAM takes place for the samples annealed at 400 and 350 °C, consistent with the disappearance of the absorbance spectra corresponding to the CH<sub>2</sub> vibrations. A sample annealed at 300 °C shows the presence of a partially removed SAM. Figure 11 shows the results of the PL monitored DIP process of as-fabricated and annealed at 350 °C samples treated in ammonia. The formation of PL maxima for the uncoated and SAM coated samples can be seen, respectively, at 15 and 35 min, while the 350 °C annealed and ammonia post-processed samples show PL maxima at 20 and 23 min. Slightly delayed PL maxima positions for the LED-RTA samples, in comparison to the PL maximum of the uncoated and non-annealed sample may be related to the surface presence of some oxides that were not etched with ammonia in this case.

### 3.3. Bacteria immobilization on LED-RTA processed biochip

Figure 12 compares scattering light optical images of an MHDA SAM coated sample functionalized with Abs and exposed for 1 hour to *E. coli* PBS suspension at 10<sup>9</sup> CFU/mL, followed by washing with DI water and drying under a flow of nitrogen (Fig. 12a), with that of a similar sample that was 15 s annealed at 350 °C before the exposure to the same *E. coli* suspension (Fig. 12b). The significant capture of bacteria, estimated at 2542 bacteria/mm<sup>2</sup>, has been observed for the as-fabricated sample (Fig. 12 a). In contrast, the entire surface of the 2 mm x 2 mm sample annealed at 350 °C did



**Fig. 10** FTIR absorbance spectra of as-fabricated GaAs/AlGaAs samples coated with MHDA SAM (blue) and annealed at 300 °C (yellow), 350 °C (dashed red) and 400 °C (dashed brown).



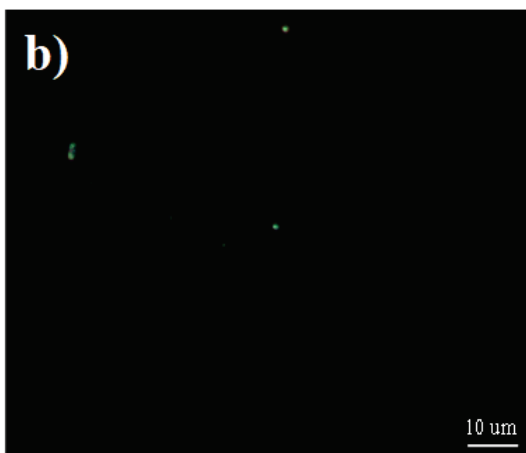
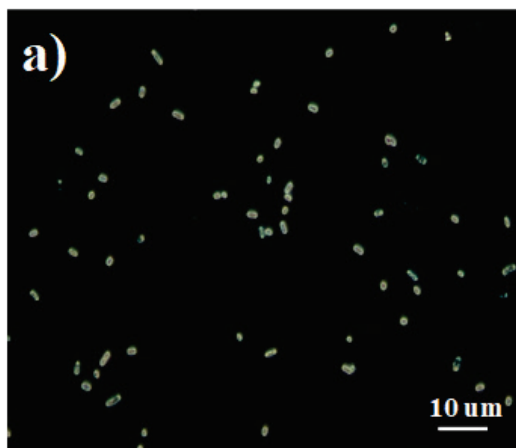
**Fig. 11** PL intensity plots of DIP uncoated (black) and MHDA SAM coated (blue) samples compared to the plots of the MHDA SAM coated samples annealed for 15 s at 350 °C (brown).

not show a measurable presence of the captured bacteria. This result is consistent with the absence of Abs, but also with the absence of MHDA SAM that is expected to desorb under these conditions. It is relevant to mention that a chemically etched and non-functionalized surface of GaAs does not provide conditions favouring the capture of bacteria [29]. Furthermore, the washing with the 1 % Tween 20-PBS solution employed in this experiment, allowed to remove the non-specifically attached *E. coli* [30].

### 3.4. Selective area functionalization by Nd:YAG Laser RTA

#### 3.4.1 Irradiation at 43 W/mm<sup>2</sup> for 30 s

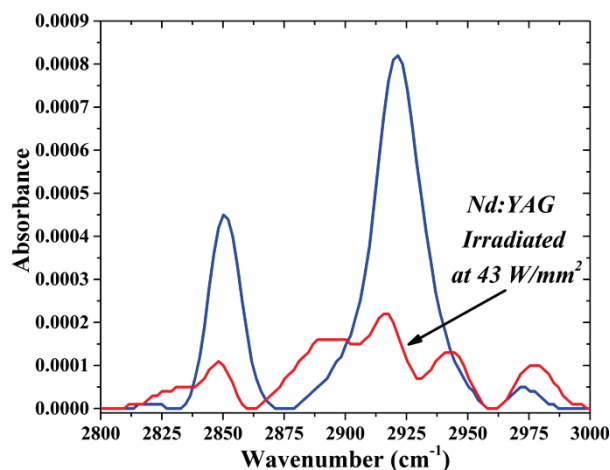
To desorb MHDA SAM from a selected area of the GaAs/AlGaAs biochip, the irradiation was carried out with an Nd:YAG laser beam focused 1 to a 0.5 mm diameter spot. Figure 13 shows FTIR absorbance spectra of MHDA SAM coated GaAs surface before and after irradiation at 43 W/mm<sup>2</sup> for 30 s. We have estimated that the maximum temperature induced under these conditions was ~ 500 °C in the



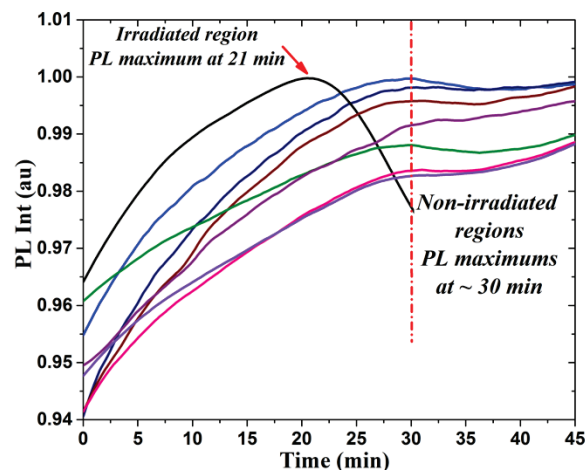
**Fig. 12** Scattering light optical microscopy images of a) antibody biofunctionalized GaAs sample, and b) antibody biofunctionalized sample following LED-RTA at 350 °C for 15 s. In both cases, the samples were exposed to *E. coli* PBS suspension at  $10^9$  CFU/mL for 1 hour.

center of a laser spot. Notice that the irradiation of a thermally isolated 10 mm x 10 mm GaAs sample with the same laser delivering power of 1 W/mm<sup>2</sup> allowed to induce the temperature of ~ 820 °C in the center of a 3 mm diameter spot [14]. However, the sample in that case was double sided coated with a 270 nm thick layer of SiO<sub>2</sub> that was acting as an anti-reflection and allowed decreasing the reflected power from 34 to 10 % of the IR radiation [31-33].

The spectra shown in Figure 13 were collected from a 1-mm diameter surface area defined by the applied contact mask. A weak intensity spectrum, with poorly defined positions of the asymmetric and symmetric stretch vibrations peaks characterizes the Laser-RTA sample. Given that some contribution to this spectrum originated from the non-irradiated surface of the sample, this result suggests the complete desorption of MHDA SAM in the center of the laser irradiated spot. Following the irradiation, the sample was exposed for 2 min in ammonia and its PL-monitored DIP revealed a PL intensity maximum at 21 min, as illustrated in Fig. 14. In contrast, several PL scans of the non-irradiated areas exhibit a slower photocorrosion rate with PL maxima revealed at ~ 30 min, which is in a reasonable agreement with the position of such maxima revealed for other,



**Fig. 13** FTIR absorbance spectra of as-fabricated GaAs/AlGaAs sample coated with MHDA SAM (blue), and a sample irradiated with an Nd:YAG laser at 43 W/mm<sup>2</sup> (red).



**Fig. 14** PL intensity plots of a DIP sample with an irradiated region (black) showing faster photocorrosion rate than those from MHDA SAM coated regions (colored).

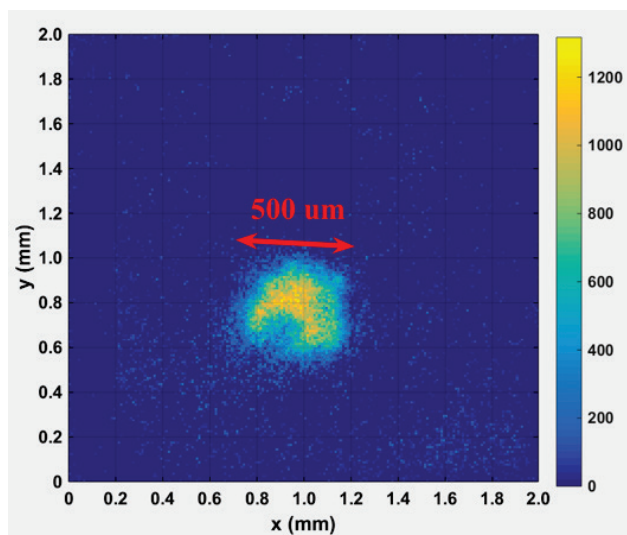
non-annealed MHDA SAM coated samples (see also Figure 11).

Figure 15 shows a PL intensity map of an Nd:YAG RTA sample that was DIP for 21 min. The background PL signal was removed from this map to illustrate more clearly the laser irradiated area of ~ 500 μm in diameter. Notice that the DIP process is sensitive to the presence of surface imperfections that could also act as non-radiative recombination centers generated during the Laser RTA step. This seems to be the reason of a slight deviation in the uniformity of the PL intensity of the laser annealed area compared to the TM<sub>00</sub> mode of the laser beam (see Fig. 3) used for the annealing. The inspection of PL intensity plots collected for different DIP non-annealed regions of this SAM coated sample revealed distinctive maxima located at ~30 min, as illustrated in Figure 14.

### 3.4.2 Bacteria capture on Nd:YAG-RTA biochip

An Nd:YAG laser irradiated MHDA SAM coated



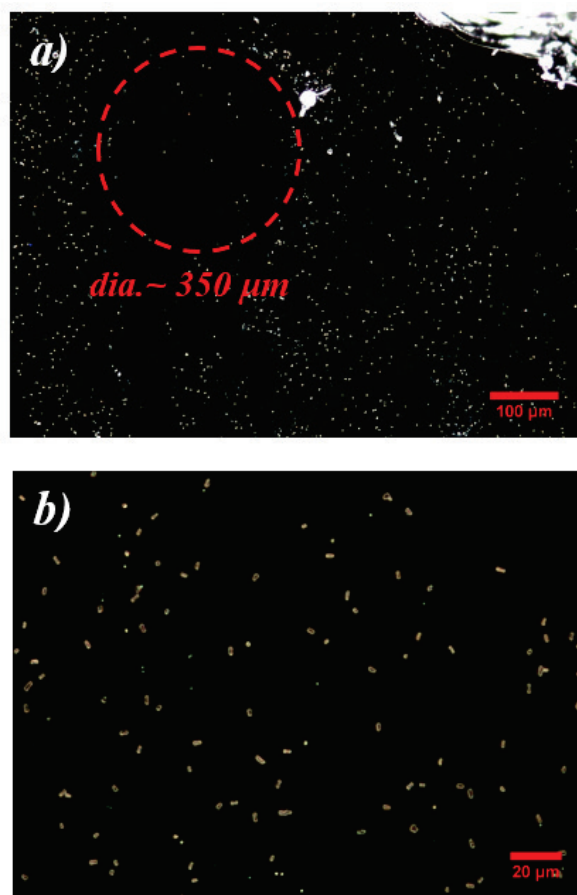


**Fig. 15** Photoluminescence intensity map of an MHDA SAM coated sample that was Nd:YAG RTA at  $\sim 500$  °C for 30 s and, subsequently, photocorroded for 21 min.

GaAs sample was post-treated in ammonia, biofunctionalized with Abs (achieved in the non-annealed portion of the sample) and immediately exposed to *E. coli* suspension at  $10^9$  CFU/mL. Following this step, the sample was rinsed with DI water to remove weakly bound biomolecules and bacteria from the surface of the biochip. Figure 16 a) shows an optical image of the sample covered with bacteria, except in the laser irradiated area identified with a circle of  $\sim 350$   $\mu\text{m}$  in diameter. Although some bacteria could be identified in the laser annealed region, their surface density is negligible compared to that in the non-annealed region. Clearly, some non-specific attachment of bacteria is expected on many surfaces exposed to highly concentrated bacterial suspensions, such as  $10^9$  CFU/mL employed in this experiment. Nevertheless, we argue that this result is consistent with the absence of Abs in the laser processed spot. While the bare surface of GaAs does not immobilize bacteria, the presence of EDC-NHS processed MHDA SAM would be required to immobilize Abs. Figure 16 b) shows a high-resolution image of the non-annealed fragment of the sample. The presence of uniformly distributed bacteria can be easily identified in that image. We estimated that the concentration of bacteria captured in this case is at 2585 bacteria/ $\text{mm}^2$ , which is comparable to the concentration of *E. coli* captured on the surface of a non-annealed bio-functionalized GaAs sample (see Fig. 12 a). Thus, this result confirms the feasibility of a concept of selective area desorption of MHDA SAM from GaAs for the realization of a DIP GaAs/AlGaAs biochip with an internal reference.

#### 4. Conclusion

We have investigated selective area functionalization of GaAs/AlGaAs biochips by employing the effect of thermal desorption of MHDA SAM. The conventional RTA experiments and LED-based RTA of MHDA SAM coated GaAs samples allowed to determine conditions for annealing with a CW Nd:YAG laser operating at 1064 nm, designed for selective area desorption of SAM. Following the exposure to a bacterial suspension at  $10^9$  CFU/mL, the EDC-NHS activated MHDA SAM functionalized with Abs allowed



**Fig. 16** Low-magnification (a) and enhanced magnification (b) scattering light optical microscopy images of a bio-functionalized GaAs sample following selected area Nd:YAG laser irradiation and exposure to *E. coli* at  $10^9$  CFU/mL. The laser irradiated area is identified with a circle.

capturing bacteria at  $\sim 2500$  bacteria/ $\text{mm}^2$ . The irradiation of an Abs functionalized biochip with a TEM<sub>00</sub> beam of the Nd:YAG laser delivering  $\sim 43$  W/ $\text{mm}^2$  radiation for 30 s to a 2 mm x 2 mm sample, allowed to fabricate a  $\sim 350$   $\mu\text{m}$  diameter SAM-free and, thus, Abs-free zone. The SAM-free zone photocorroded at a rate comparable to that of a freshly cleaned, uncoated chip. The similar photocorrosion rate was also observed for the SAM-free sample fabricated by LED-RTA at 350 °C for 15 s. Our results demonstrate the feasibility of employing the concept of selective area desorption of MHDA SAM from GaAs for the realization of a DIP GaAs/AlGaAs biochip with an internal reference. The currently available low-cost IR LED sources delivering power densities sufficient to induce spot annealing of GaAs at 350-400 °C offer the potential for the realization of advanced DIP biosensors with internal references.

#### Acknowledgements

This project was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant (RGPIN-2015-04448) and the NSERC Strategic Partnership Grant (SPG-2016-494057).

#### References

- [1] E. Nazemi, W. M. Hassen, E. H. Frost, and J. J. Dubowski: Biosens. Bioelectron., 93, (2016) 234.

- [2] E. Nazemi, S. Aithal, W. M. Hassen, E. H. Frost, and J. J. Dubowski: *Sens. Actuators B: Chem.*, 207, (2015) 556-562.
- [3] M. R. Aziziyan *et al.*: *Sens. Actuators B: Chem.*, 304, (2020) 127007.
- [4] M. R. Aziziyan, W. M. Hassen, D. Morris, E. H. Frost, and J. J. Dubowski: *Biointerphases*, 11, (2016) 019301.
- [5] S. Aithal and J. J. Dubowski: *Appl. Phys. Lett.*, 112, (2018) 153102.
- [6] H. Sharma, K. Moumanis, and J. J. Dubowski: *J. Phys. Chem. C*, 120, (2016) 26129.
- [7] S. Aithal, N. Liu, and J. J. Dubowski: *J. Phys. D: Appl. Phys.*, 50, (2017) 035106.
- [8] X. Ding and J.J. Dubowski: *Proc. of SPIE on Photon Processing in Microelectronics and Photonics VI*, 6458, (2007) 64581C.
- [9] V. Lacour, C. Elie-Caille, T. Leblois, and J. J. Dubowski: *Biointerphases*, 11, (2016) 019302.
- [10] L. Wu *et al.*: *Chemical Physics Letters*, 717, (2019) 152.
- [11] X. Jiang and S. F. Bent: *J. Phys. Chem. C*, 113, (2009) 17613.
- [12] K.-H. Lee *et al.*: *Organic Electronics*, 11, (2010) 748.
- [13] D. Cuypers *et al.*: *Chem. Mater.*, 28, (2016) 5689.
- [14] R. Stanowski, O. Voznyy, and J. J. Dubowski: *J. Laser Micro/Nanoeng.*, 1, (2006) 17.
- [15] Y. Lin *et al.*: *Anal. Chem.*, 91, (2019) 3717.
- [16] S. Wang *et al.*: *ACS Appl. Mater. Interfaces*, 11, (2019) 1917.
- [17] X. Wang *et al.*: *Anal. Chem.*, 91, (2019) 12006.
- [18] J. Duffy, F. Padovani, G. Brunetti, P. Noy, U. Certa, and M. Hegner: *The Royal Society of Chemistry - Nanoscale*, 10, (2018) 12797.
- [19] R. Stanowski and J. J. Dubowski: *Appl. Phys. A*, 94, (2008) 667.
- [20] X. Huang, N. Liu, K. Moumanis, and J. J. Dubowski: *J. Phys. Chem. C*, 117, (2013) 15090.
- [21] P. Mancheno-Posso and A. J. Muscat: *Appl. Surf. Sci.*, 397, (2017) 1.
- [22] X. H. Huang, N. Liu, K. Moumanis, and J. J. Dubowski: *J. Phys. Chem. C*, 117, (2013) 15090.
- [24] M. R. Aziziyan, H. Sharma, and J. J. Dubowski: *ACS Appl. Mater. Inter.*, 11, (2019) 17968.
- [25] T. P. Huang, T. H. Lin, T. F. Teng, Y. H. Lai, and W. H. Hung: *Surf. Sci.*, 603, (2009) 1244.
- [26] C. D. Thurmond, G. P. Schwartz, G. W. Kammlott, and B. Schwartz: *J. Electrochem. Soc.*, 127, (1980) 1366.
- [27] G. P. Schwartz, G. J. Gualtieri, J. E. Griffiths, C. D. Thurmond, and B. Schwartz: *J. Electrochem. Soc.*, 127, (1980) 2488.
- [28] G. C. DeSalvo *et al.*: *J. Electrochem. Soc.*, 143, (1996) 3652.
- [29] M. A. Islam, W. M. Hassen, A. F. Tayabali, and J. J. Dubowski: *Biochem. Eng. Journal*, 154, (2020) 107435.
- [30] C. Wu, J. Y. Lim, G. G. Fuller, and L. Cegelski: *Langmuir*, 29, (2013) 920.
- [31] J. Grames *et al.*: *Phys. Rev. Special Topics - Accelerators and Beams*, 14, (2011) 043501.
- [32] R. E. Morrison: *Phys. Rev.*, 124, (1961) 1314.
- [33] X. Peng *et al.*: *Phys. Rev. Appl.*, 12, (2019) 064002.

(Received: February 17, 2020, Accepted: July 26, 2020)