# Laser patterning of biotinylated nanobeads immobilized on (001) GaAs surface\*

X. Ding and J. J. Dubowski

Department of Electrical and Computer Engineering, Université de Sherbrooke Sherbrooke, Québec J1K 2R1, Canada

E-Mail: jan.j.dubowski@usherbrooke.ca

*Abstract* – We demonstrate the process of laser patterning of the surface of (001) GaAs that has been functionalized with biotinylated nano-beads (*b*-NBs) via the avidin – biotin – alkanethiol interface. The results indicate that this approach makes possible patterning with high lateral resolution.

# I. INTRODUCTION

Recently, owing to the attractive optical properties of GaAs, there has been observed a steady growing interest in studying this material for the construction of SAM-enabled biosensors [1-5]. Amino group terminated alkanethiols, in addition to their potential to protect the surface of cleaned GaAs exposed to an atmospheric environment, are especially attractive as they provide a suitable platform for the attachment of various biomolecules. A study of attachment of DNA molecules directly or via 6-Mercapto-1-hexanol to (001) GaAs [6] and of various peptides to (001) GaAs [7] has been reported. Our investigation of the deposition of alkanethiols with various terminal groups and lengths of methylene chains to the surface of (001) GaAs has indicated that the alkanethiol organization depends on the hydrophobic vs hydrophilic nature of their terminal groups.[8] We have demonstrated immobilization of avidin on thiolated surface of (001) GaAs [9] and, consequently, binding of biotinylated nano-beads on top of the avidin-biotin-thiol architecture built on (001) GaAs. [10] The ability to fabricate arrays of bio-moieties on GaAs is one of the critical issues in demonstrating the potential of this material for innovative bio-diagnostic applications. While numerous studies have reported patterning of SAMs on Au [11], silicon oxide [12], glass [13] and mica [14], only limited data have been available on patterning of thiolated surfaces of GaAs [15]. Here, we report on patterning of (001) GaAs surface that has been functionalized with the thiol-biotinavidin and biotinylated nanobead architecture.

### II. RESULTS AND DISCUSSIONS

The biotinylated and fluorescein stained nanobeads (*b*-NB) of 200 nm in diameter have been immobilized on (001) GaAs using a bio-architecture as shown in Fig. 1. Although many other approaches are available to immobilize biomolecules on solid substrates, this architecture is expected to provide maximum probe biomolecules uptake and it will consequently capture more target moieties for detection. –NH<sub>2</sub> terminated alkanethiols attached to the (001) GaAs surface through S-As and/or S-Ga bonding were left to bind NHS (N-



Fig. 1. The architecture of *b*-NB immobilization on (001) GaAs surface *via* avidin, biotin and alkanethiol.

hydroxysuccinimid) activated biotin. Considering the relatively larger cross-sectional area of the biotin headgroup compared with that of the alkanethiol chain, the surface density of biotin is expected to be lower than that of the -NH<sub>2</sub> groups. XPS measurements of biotin exposed samples showed an increase of the N1s signal by approximately 20% in comparison to that observed after alkanethiol deposition [16]. This indicates that only 10% of the -NH2 groups on the surface reacted and connected with biotin. Avidin is immobilized on the biotinylated surface via the biotin-avidin specific interaction. However, it could also be physically (weakly) adsorbed at the uncovered surface of GaAs. Therefore, in addition to the *b*-NB material attached to the GaAs surface through the empty pockets of the immobilized avidin, some b-NBs could be attached to the avidin molecules which were physically adsorbed on the bare surface of GaAs.

To test the strength of *b*-NB immobilization on GaAs surface via avidin, biotin and thiol, the *b*-NB exposed samples were, firstly, exposed to a detergent washing procedure, which is a routine step applied in clinical studies of various specimens. Secondly, the samples were exposed to a 1-minute ultrasonic cleaning in deionized water. A control sample with *b*-NB directly deposited on GaAs was used to investigate the effect of physical adsorption.

Atomic force microscope (AFM) image shown in Fig. 2 demonstrates a coverage density of  $1.4 \times 10^6$  beads/mm<sup>2</sup> achieved for the bio-functionalized surface. Similar surface coverage was also observed for bare GaAs samples. Following detergent washing, both types of samples showed practically the same density of *b*-NB as confirmed by both fluorescence microscopy and AFM measurements. However, no fluorescence could be observed from the sample covered with physically adsorbed *b*-NBs following the 1-min ultrasonic treatment. In contrast, the *b*-NBs immobilized on the bio-functionalized surface of GaAs survived the ultrasonic bath treatment.

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Fig. 2 AFM image of the surface of (001) GaAs bio-functionalized with biotinylated nan-beads using a thiol-biotin-avidin architecture

Fig. 3 shows a fluorescence microscopy grid pattern of *b*-NB functionalized GaAs sample exposed to 20 pulses of an ArF excimer laser delivering 50 mJ/cm<sup>2</sup> per pulse. The relatively sharp edges of the 10  $\mu$ m wide lines make it possible to estimate the patterning resolution of the process as not worse than 3  $\mu$ m. Of particular interest for development of a multi-analyte detector is the ability to deposit different biological moieties in the windows fabricated by laser ablation. The excimer patterning process was tested for the 193 nm



Fig.3 Fluorescence microscope image of a grid pattern achieved following the irradiation with an excimer laser of a *b*-NS functionalized (001) GaAs sample.

excimer irradiation up to 1000 pulses at 20 mJ/cm<sup>2</sup> per pulse. The measurements revealed a significant reduction of the GaAs photoluminescence (PL) signal, which indicates formation of surface defects responsible for non-radiative recombination of excited carriers. In contrast, irradiation with a 248 nm excimer laser under similar conditions (N = 1000 pulses, F = 20 mJ/cm<sup>2</sup>) lead to efficient patterning and produced an electronically unchanged surface of GaAs, as indicated by the practically unchanged PL signal.

# **III.** CONCLUSIONS

We have investigated the process of laser patterning of the surface of (001) GaAs that has been functionalized with biotinylated nano-beads (b-NBs) via the avidin – biotin – alkanethiol interface. The robustness of the fabricated interface was confirmed by tests involving sonication in

deionized water. Both 193 and 248 nm excimer laser ablation allows patterning of bio-functionalized (001) GaAs. However, it appears that for the same laser fluence and number of pulses, patterning at 248 nm leads to a less damaged surface of GaAs. Thus, this approach holds the promise of successful fabrication of a device capable of addressing the simultaneous bio-detection of different biomolecules.

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