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Abstract

Inkjet-Printed Split Ring Resonators for the Detection of Analyte Binding to a Gold Surface †

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Abstract: This work focuses on demonstrating the working principle of inkjet-printed Au nanoparticle (NP) split-ring resonators (SRRs) as a novel platform for the detection of analytes on flexible substrates. Potential applications of this technology include rapid and reusable near-patient diagnostics. In the method, a microwave electromagnetic wave is coupled into the Au SRR via a printed Cu-NP stripline sintered photonically on a solid FR1 substrate. This coupling mechanism facilitates the detection of analytes by inducing resonance shifts in the SRR. To demonstrate the sensing principle of the platform, biomolecules are attached to the SRR and the resulting resonance shift is measured. All experiments show resonance frequency shifts in the range of approximately 20–30 MHz.

Keywords: inkjet-printed sensor; split-ring-resonator; biofunctionalization; photonic sintering; biosensor

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1. Introduction

As a non-contact printing method, inkjet printing offers several advantages over traditional manufacturing, such as eliminating the need for physical masks, reducing material waste, and allowing precise control of material deposition, making it suitable for producing complex structures with high resolution and accuracy. In addition, inkjet printing can be applied to a wide range of materials including metals, polymers, ceramics and biomaterials, making it a versatile platform for diverse applications. For example, inkjet printing has been used to produce electronic circuits, sensors and solar cells [1]. The successful detection of analytes, using this method, holds great promise for the development of reliable and cost-effective biosensors for medical and environmental applications [2]. In conclusion, this work represents a promising step towards the development of practical, real-world applications for inkjet-printed Au-NP SRRs in analytical chemistry and biosensing.

2. Materials and Methods

The SRR is printed with 3–5 nm particles in a solvent from UTDOT (UTDAu25IJ), which is optimized for inkjet printing in terms of flow and contact angle. A 50 µm thick flexible Kapton material (200 HN from DuPont) is used as substrate. The geometry is designed for a resonant frequency of approximately 2.6 GHz and depends strongly on the material thickness and the frequency-dependent susceptibility of the ink. For the coupling stripline, a solution of 110–130 nm copper particles from Novacentrix (Metalon ICI-002HV)

is printed on the solid FR1 platform. The geometry and thickness of the stripline is designed to achieve 50 Ω lossless coupling. In order to achieve optimum conductivity in the printed structures, sintering processes have to be applied. The Cu-stripline was sintered by photonic flashing the material with a high power pulse from a xenon flash lamp. The discharge (2 × 4700 µF at 480 V) takes place in a few milliseconds and results in a homogeneous line with an average thickness of 2.19 ± 1.03 µm (after 13 measurements with the 2D profilometer AMTEK-Surtronic S128) and a conductivity of 2.54 ± 0.82 Ω/□. The Au SRR, on the other hand is thermally sintered at 250 °C for 20 min, resulting in a conductivity of 0.98 ± 0.3 Ω/□. To couple the microwave signals from the R&S ZNB20 network analyzer, SMA connectors are applied to the Cu-stripline using Ag adhesive paste. A 3D-printed platform holds the assembly in place and provides a ground-potential plane for the SRR.

After detection of a sharp resonance, the Au surface is treated in several steps to achieve optimal binding of the analyte. In particular, a 6 mm radius area around the slit is defined for biofunctionalization, where the electric field and thus the influence on the frequency shift is greatest. The functionalization-steps include: cleaning of the Au surface (30 min ultrasound bath in 99.9% Ethanol), Au-thiol coupling and pegylation (60 min with SH-PEG in EtOH, Cytiva Amine Coupling Kit), activation via amine coupling (15 min NHS-EDC), attachment of capture antibody (30 min, anti- human-IgG), deactivation of additional reactive groups (7 min, Ethanolamine-HCl), blocking of additional groups with bovine serum albumin (60 min, 2%BSA in PBST) and finally attachment of the analyte (60 min, Adalimumab human-IgG). The analyte attachment on the sensor surface then is confirmed through ELISA (Enzyme-linked Immunosorbent Assay) by measuring the absorbance of a colorimetric reaction product at 405 nm, which is caused by an enzyme substrate (PNPP) reaction via alkaline phosphatase-conjugated secondary antibody, which binds with high affinity to the analyte with a signal proportional to the analyte binding [3].

3. Discussion

The result of the measurement is the shift of the transmission coefficient S21(f) resonance between the complete setup with SRR and the complete setup with SRR and a biofunctionalized area. There are different ways to determine the frequency shift. If the shift of the minimum value of each resonance is used, the shift is 22.17 ± 11.77 MHz over all measurements. If the FWHM shift of each resonance is used, where half of the minimum value is fitted to an upper and lower frequency limit whose average value represents the comparable resonance frequency, the shift over all measurements is 30.06 ± 14.63 MHz.

The resonant frequency is also strongly dependent on the positioning of the SRR near the stripline. Positioning on the 3D printed platform reduces the standard deviation of the resonance to 1–6 MHz (minimum) and 3–10 MHz (FWHM).

The binding of antibody to the gold surface works well but, the absorbance values from ELISA showed that unspecific binding of the antibody or analyte on the gold surface through reactive cysteine residues (-SH groups) is possible and can be reduced by the blocking agent BSA. Further experiments with larger analytes like exosomes (40–130 nm in diameter) will be performed.

Taking all measurement results and their possible influences into account, a clear frequency shift can be observed subsequent to the attachment of biomolecules.

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