Biosensors and Bioelectronics 104 (2018) 102–112

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Ultra-narrow surface lattice resonances in plasmonic metamaterial arrays for biosensing applications

Artem Danilov[a,1], Gleb Tselikov[a,1], Fan Wu[b], Vasyl G. Kravets[b], Igor Ozerov[c], Frederic Bedu[c], Alexander N. Grigorenko[b,*], Andrei V. Kabashin[a,*]

[a] Aix Marseille Univ, CNRS, LP3, Marseille, France
[b] School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK
[c] Aix Marseille Univ, CNRS, CINAM, Marseille, France

ARTICLE INFO

Keywords:
Plasmonic surface lattice resonances
Diffraction coupling
Biosensor
Attenuated total reflection
Phase sensitivity
Plasmonic metamaterials for biosensing

ABSTRACT

When excited over a periodic metamaterial lattice of gold nanoparticles (~ 100 nm), localized plasmon resonances (LPR) can be coupled by a diffraction wave propagating along the array plane, which leads to a drastic narrowing of plasmon resonance lineshapes (down to a few nm full-width-at-half-maximum) and the generation of singularities of phase of reflected light. These phenomena look very promising for the improvement of performance of plasmonic biosensors, but conditions of implementation of such diffractively coupled plasmonic resonances, also referred to as plasmonic surface lattice resonances (PSLR), are not always compatible with biosensing arrangement implying the placement of the nanoparticles between a glass substrate and a sample medium (air, water). Here, we consider conditions of excitation and properties of PSLR over arrays of glass substrate-supported single and double Au nanoparticles (~ 100–200 nm), arranged in a periodic metamaterial lattice, in direct and Attenuated Total Reflection (ATR) geometries, and assess their sensitivities to variations of refractive index (RI) of the adjacent sample dielectric medium. First, we identify medium ($PSLR_{air}$, $PSLR_{wat}$ for air and water, respectively) and substrate ($PSLR_{sub}$) modes corresponding to the coupling of individual plasmon oscillations at medium- and substrate-related diffraction cut-off edges. We show that spectral sensitivity of medium modes to RI variations is determined by the lattice periodicity in both direct and ATR geometries (~ 320 nm per RIU change in our case), while substrate mode demonstrates much lower sensitivity. We also show that phase sensitivity of PSLR can exceed 10^5 degrees of phase shift per RIU change and thus outperform the relevant parameter for all other plasmonic sensor counterparts. We finally demonstrate the applicability of surface lattice resonances in plasmonic metamaterial arrays to biosensing using standard streptavidin-biotin affinity model. Combining advantages of nanoscale architectures, including drastic concentration of electric field, possibility of manipulation at the nanoscale etc, and high phase and spectral sensitivities, PSLRs promise the advancement of current state-of-the-art plasmonic biosensing technology toward single molecule label-free detection.

1. Introduction

Over the last decade plasmonic biosensing has become a technology of choice for label-free characterization of biomolecular binding interactions between a target analyte (antigens, DNA, ligand etc.) and its corresponding receptor (e.g. an antibody, DNA capture, protein etc.) immobilized on the gold surface (Liedberg et al., 1983, 1995; Schasfoort and Tudos, 2008; Homola, 2006; Quidant, 2017). Plasmonic biosensors take advantage of a resonant dependence of conditions of plasmon excitation on refractive index (RI) of the medium contacting the plasmon-supporting metal. Conventional plasmonic biosensors employ the phenomenon of Surface Plasmon Resonance (SPR), which is associated with the excitation of surface plasmon polaritons over a thin (~ 50 nm) gold film using Attenuated Reflection Geometry (Kretschmann-Raether arrangement). SPR effect leads to a dip in the reflected intensity at a defined combination of the angle of incidence and the wavelength, whose values are resonantly dependent on the RI of a thin layer near gold (Liedberg et al., 1983). Any change of the thickness of biological film on gold due to mass accumulation is accompanied by a RI change, which can be monitored by following spectral (Zhang et al.,

* Corresponding authors.
E-mail addresses: Alexander.Grigorenko@manchester.ac.uk (A.N. Grigorenko), kabashin@lp3.univ-mrs.fr (A.V. Kabashin).
[1] Equal contributions.

https://doi.org/10.1016/j.bios.2017.12.001
Received 19 August 2017; Received in revised form 27 November 2017; Accepted 1 December 2017
Available online 09 December 2017

1988), angular (Liedberg et al., 1983) or phase (Kabashin et al., 1998, 1999; Kabashin and Nikitin, 1997) characteristics of reflected light. With the lower detection limit of 1 pg/mm^2 of biomaterial accumulated on the biosensor surface, SPR biosensors are efficient for studies of many biomolecular interactions (Schasfoort and Tudos, 2008), but they are hardly compatible with current trends in biosensing focusing on the development of compact (Patskovsky et al., 2004; Piliarik et al., 2003; Nemova et al., 2008) and nanoscale (Anker et al., 2008; Kabashin et al., 2009a; Sreekanth et al., 2016; Aristov et al., 2016) transducer implementations.

A huge potential for the upgrade of plasmonic biosensing technology is now expected from localized plasmon resonances (LPRs) excited over nanoscale structures (Anker et al., 2008), and metamaterial arrays (Kabashin et al., 2009a). Such biosensors are much better compatible with nanoscale biochemical architectures (beacons, hybrid structures etc.), as well as can offer novel functionalities such as size-based selectivity, possibility for a drastic localization and concentration of electric field to profit from SERS and other field-enhanced effects (Nie and Emory, 1997), resolution beyond the diffraction limit (Kawata et al., 2009), nanotweezing (Grigorenko et al., 2008), etc. Plasmonic Surface Lattice Resonances (PSLR) produced in conditions of diffraction coupling of LPR are of particular interest for biosensing applications due to their exceptional resonance quality (Grigorenko et al., 2008; Auguie and Barnes, 2008; Chu et al., 2008). To excite PSLR, gold nanoparticles (nanodics, nanopillars etc.) having the size of about 100 nm are arranged in a 2D lattice in such a way that one of diffracted beams, appearing due to the periodicity of this structure, propagates over the array plane and can couple in far field localized plasmons over individual nanoparticles (Fig. 1a). Such a coupling leads to a drastic narrowing of resonances in reflected and transmitted light down to 2–3 nm full width at half maximum (FWHM). In addition, the diffraction coupling gives rise to vanishing of light intensity in resonances, leading to the generation of singularities of light phase (Kravets et al., 2010, 2013). When used as a signal parameter to monitor refractive index variations, such phase singularities can be used to lower the detection limit of label-free plasmonic biosensing schemes down to single molecule level (Kravets et al., 2013, Huang et al., 2012).

However, the excitation of diffraction-coupled PSLR is critically dependent on refractive index of the media surrounding a nanoparticle array. When the array is illuminated under normal incidence of light, the excitation of PSLR typically requires uniform surrounding, i.e. the match of refractive index of the substrate and that of the medium contacting the particles (Auguie and Barnes, 2008), although certain narrowing of resonances is possible via a proper choice of size and geometry of nanoparticles (Chu et al., 2008; Thackray et al., 2014). On the other hand, the excitation of PSLR becomes possible under oblique incidence of light on the array structure and the monitoring of optical parameters in reflected light (Kravets et al., 2008, 2010). In all cases, direct geometry of PSLR excitation is not fully compatible with biosensing experimental arrangement, as it implies light direction through a sample liquid leading to a dependence of PSLR parameters on bulk RI fluctuations inside the flow cell. Alternatively, PSLR can be excited in Attenuated Total Reflection (ATR) geometry (Kravets et al., 2010), but conditions of excitation and sensitivity of such resonances have not yet been systematically studied.

In this paper, we compare conditions of PSLR excitation in direct and ATR geometries and examine sensitivities of different PSLR modes under these conditions. Our analysis shows that PSLR can be excited in both geometries and exhibit distinct resonance features with the spectral width of a few nm FWHM and high resonance quality. We also show that the PSLR can provide spectral sensitivity correlating with the periodicity of the structures and exceptionally high phase sensitivity, which makes them very promising candidates for biosensing applications.

2. Methodology

2.1. Sample preparation

High-quality regular and homogenous square arrays of gold nanoparticles were produced by e-beam lithography (LEO-RAITH and PIONEER-RAITH) on a clean microscopic glass substrate covered by a thin *Cr* sublayer. A double layered resist was used to improve lift-off (80 nm of 495 kD *PMMA* cast from a 3 wt% solution in anisole for the bottom resist layer and 50 nm of 95 kD PMMA cast from a 2 wt% solution in anisole for the top layer). For nanofabrication of several samples, we used bare (without Cr seed layer) borosilicate glass substrates (WBO-251 from UQG Optics) successively coated by a single layer of PMMA (from Allresist, Germany) diluted in ethyl-lactate at 2%) and by the second layer of a conductive polymer (SX AR PC 5000/90.2 from Allresist) used in order to prevent the charging of the dielectric substrates during e-beam exposure. After developing in 1:3 MIBK:isopropanol solution, rinsing the samples in deionized water and drying under clean nitrogen flow, we deposited 3–5 nm of *Cr* (to improve adhesion) and 80–90 nm of Au by evaporation using electron beam or Joule effect (Auto 306 tool from Edwards). Then the excessive metal deposited onto the areas protected by the resist was removed from samples by the lift-off procedure in ultrasonic bath of pure ethyl-lactate. The typical array size was 0.2 × 0.2 mm^2. The samples on a clean glass substrate were obtained from the samples fabricated on a 5 nm *Cr* sublayer in which the *Cr* sublayer has been wet-etched after the fabrication procedure. Typical Scanning Electron Microscopy images of single and double nanodot arrays are shown in Fig. 1(b),(c), respectively.

2.2. Optical measurement setup

In our experiments, we used commercially available M-2000 ellipsometer system (Woollam Inc, USA), which makes possible independent sample rotation and displacement, relative to illumination and collection light paths, thus granting the possibility for precise alignment of focal plane with respect to the examined area on a sample. Xenon wide spectrum lamp was used as a light source. The sample was illuminated with weakly focused light (about 0.5 mm spot diameter). Device output data represented in standard for ellipsometry Ψ-Δ values so that $E_p/E_s = tan(\Psi)exp(i\Delta)$, where E_p and E_s are the reflected field amplitudes for the incident light E_i of p and s polarizations and their values are $R_p = |E_p/E_i|$ and $R_s = |E_s/E_i|$ of p and s polarizations, respectively.

A homemade liquid flow cell was designed for sensitivity measurements. The cell contained a rubber O-ring with input and output holes fixed between two cover slides for direct illumination measurements and a cover slide with 45–45–90 deg. glass prism (n = 1.5) on the other side for attenuated total reflection (ATR) configuration. In ATR geometry, the light beam was passed through a prism and reflected from its opposite facet where nanoparticle arrays were deposited. Immersion oil (n = 1.5) was used to fill the gap between the prism and the cover slide, maintaining uniform optical path. General setup scheme could be found in Supporting information.

2.3. Sensitivity assessment

In our experiments, the sensitivity of plasmonic metamaterial transducers was evaluated by using a model, which simulated changes of bulk refractive index of the aqueous medium contacting nanoparticle arrays similarly, to how it was done in previous studies (Law et al., 2007; Kabashin et al., 2009a, 2009b; Kravets et al., 2013). A set of ethanol-water mixtures of different concentrations were prepared for evaluation of sample sensing capabilities. Ethanol has excellent solubility in water and does not affect the quality of glass-supported nanoparticle arrays. Since ethanol has slightly higher refractive index