Corrugated thin metal films as couplers between propagating and surface modes for plasmonic enhancement of photocatalytic optofluidic microreactors

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***Abstract*— Surface plasmons polaritons (SPP) ensure extreme concentrations of electromagnetic near fields at interfaces between materials with negative and positive dielectric permittivity (i.e. between metals and dielectrics), usually several orders of magnitude compared to fields in free space. This is useful for a number of practical applications, including chemical and biological sensing, enhancement of photodetectors and improvement of photocatalytical reactions. One of the problems to be solved with plasmonic field localization is that wavevectors of SPPs may vastly exceed those of propagating waves, so that a coupling device is mandatory between them. In photocatalytic microreactors one often uses nanoparticles with localized SPP as both couplers and field enhancers. In this contribution we consider the possibility to utilize surface corrugation of thin gold films to simultaneously ensure coupling between propagating and plasmon modes and enlarge effective catalytic surface. To this purpose we utilize wet chemical etching (chemical micromachining). Different surface corrugations are obtained by varying etching conditions. A combination of gold thin film over corrugated surface and titanium dioxide nanoparticles is used. The setup can be used for different photocatalytic processes.**

***Index Terms*— Plasmonics; Microreactors; Photocatalysis; Optofluidics; micromachining**

I. Introduction

PLASMONICS deals with electromagnetic waves that are bound to an interface between conductor with free electron plasma and dielectric and are evanescent in the perpendicular directions. This ensures extreme localizations of electromagnetic near fields in subwavelength volumes [1,2]. Various applications include chemical, biochemical and biological sensors [3], circuits that merge compactness of electrical circuitry with high frequencies of optical circuits [4], super-resolution lithography [5], to name just a few.

Field localization in plasmonics can be tailored to coincide with the volume of micro or nanochanels in microfludics /nanofluidics. This makes it very convenient for optofluidic microreactors, especially for photocatalytic devices, as well as generally for the setups where an increase of the intensity of near field is required.

A number of systems where plasmonic activation is used for photocatalysis has been reported until now [6-9]. A vast majority of these relies on localized surface plasmon resonance on nanoparticles, which may have either monolithic [10] or core-shell structure [11]. Versions include free nanoparticles in sole metal form, nanoparticles embedded in semiconductor, encapsulated in it or isolated in an intert material. Other forms like nanoclusters (powdered or immobilized on a support may be used). We did not encounter in literature microreactors with continuous plasmonic structures.

One of the problems in plasmonic generally is coupling of propagating waves with surface plasmons polaritons (SPP) propagating on plasmonic surfaces [12]. Plasmonic localization of electromagnetic field in subwavelength volumes means shorter wavelengths (larger wave vectors) compared to propagating waves at the same frequency ω. This means that one needs to impart additional momentum Δk to a propagating wave to couple it with SPP modes.

The usual coupling devices for plasmonics are those utilizing ATR (Attenuated total reflection) [13]. Typical examples are the Kretschmann and Otto prism couplers, which are the methods of choice for chemical and biological sensors. Another method for coupling is the use of diffractive gratings [12]. A vast majority of the utilized coupling methods are applied for a single operating frequency. In photocatalysis one almost innvariably utilizes localized surface plasmon resonance on nanoparticles [9]. They are diffractive scatterers and at the same time they offer a large active surface to volume ratios. Different sizes, shapes and materials of nanoparticles offer different resonant frequencies and

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different operating wavelengths.

A way to perform coupling between propagating waves and SPP is to utilize rough (disordered) surfaces. Utilized at the very beginnings of plasmonics [14, 15] it was largely abandoned since it was not easily controllable. Rough surfaces had poor repeatability and it was near to impossible to tune them for a desired wavelength. However, in a number of photocatalytic setups one actually needs to deal with incoherent white light, sunlight being the prime example. A rough surface can be regarded as a superposition of a number of sinusoidal/ordered diffractive gratings for different wavelengths. Thus in principle they offer coupling for a continuous range of wavelengths.

In this work we propose the use of disordered rough plasmonic surface for the enhancement of photocatalytic microreactors. We consider the convenient methods for their fabrication and tailoring and consider possible optimization routes. Experimentally, we concentrate on chemical micromachining/wet etching procedures utilizing potassium hydroxide (KOH) and tetramethyl amonium hydroxide (TMAH). Different surface corrugations are obtained by varying etching conditions. We use a combination of a gold thin film sputtered onto thus corrugated surface and titanium dioxide nanoparticles.

II. SPP Coupling and Rough Surfaces

The dispersion curve of a SPP is nonlinear and its wave vector is typically much larger than the wave vector of a propagating mode, Fig. 1.

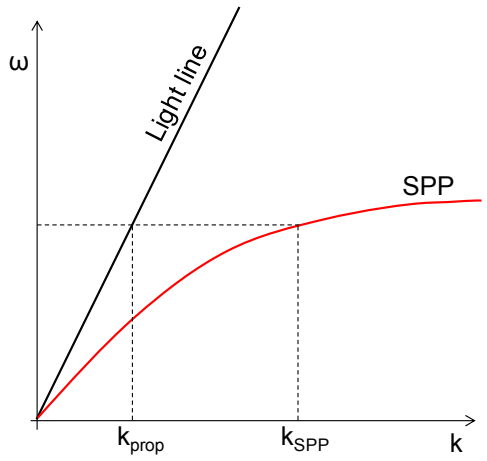

Fig. 1. Dispersion curve of a surface plasmon polariton compared to the straight line of a propagating mode (light line). k_{prop} is a randomly chosen wave vector of a propagating mode, and k_{SPP} that of a SPP mode.

In order to ensure coupling between SPP and a propagating mode, one needs to ensure additional momentum Δk. In case of a diffractive grating, the relation between the lattice constant of the grating a and the wavevector of the diffracted mode is

$$\Delta k = \pm m \frac{2\pi}{a} \tag{1}$$

where m is an integer. Thus matching between the propagating and the evanescent mode is ensured as

$$\vec{k}_{SPP} = \vec{k}_{prop} + \Delta\vec{k} \tag{2}$$

and the propagating mode is defined as

$$k_{prop} = \frac{\omega}{c}\sin\theta \tag{3}$$

where ω is the angular frequency, c is the speed of light in the medium above the plasmonic surface and θ is the incident angle of the propagating mode. Figure 2 illustrates coupling of SPP with the incident beam.

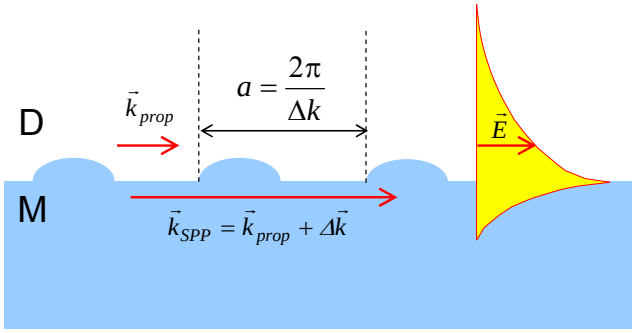

Fig. 2. Coupling between SPP and propagating beam on a diffractive grating. "D" denotes dielectric, "M" is plasmonic material (usually metal). Yellow field illustrates the intensity of the electric field (along the x-axis).

In this work we consider stochastic rough surfaces as a possible means for coupling SPP and propagating waves. An illustration of some possible geometries is shown in Fig. 3.

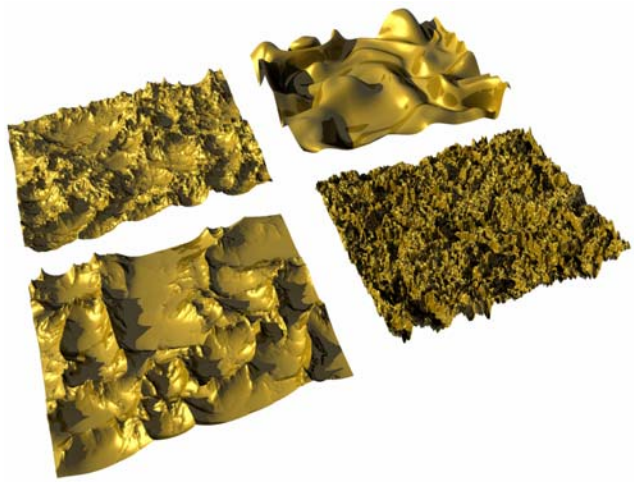

Fig. 3. Illustration of different random profiles of rough surfaces with deposited gold overlayer.

We may observe a stochastic relief on a surface as a superposition of an infinite number od gratings with different spatial periodicities, as shown in Fig. 4. In this manner the

efficiency of SPP-to-propagating coupling would be directly related with the properties of the surface relief.

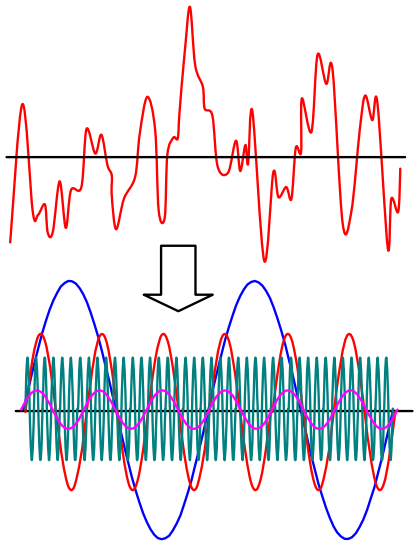

Fig. 4. Stochastically rough surface presented as a superposition of ordered sinusoidal profiles.

We may write the statistical correlation function of a randomly corrugated surface as

$$F(x,y) = \frac{\int_{x_1,y_1} z(x_1,y_1)z(x_1-x,y_1-y)dx_1dy_1}{\int_{x_1,y_1} dx_1dy_1} \quad (4)$$

where x, y are in-plane coordinates, while z is the height of a given point. If we assume Gaussian distribution of the heights of the points at the surface with δ being the root mean square value of z and σ the correlation length

$$F(x,y) = \delta^2 e^{-r^2/\sigma^2} \quad (5)$$

then the Fourier transform of the statistical correlation function is

$$|S(\Delta k)|^2 = \frac{\sigma^2\delta^2}{4\pi}\exp\left[-\frac{\sigma^2(\Delta k)^2}{4}\right] \quad (6)$$

each of the components corresponding to a sinusoidal diffractive grating, i.e. its coupling efficiency being maximal for a single incident angle or a single wavelength. Since a stochastic profile will have a large number of components, it will enable coupling for different angles and for different wavelengths. The price to pay is that the overall efficiency will be smaller, but the structure will be applicable to white light.

As a bottom line, one may expect improved efficiency of coupling between sunlight and surface plasmons polaritons for couplers in the form random rough surfaces owing to the diffraction of the beams at the surface corrugations. In this manner a rough surface coupler will act similarly to antireflective diffractive surfaces [16].

III. Surface Roughening

A number of methods are available for micro/nanoscale surface roughening and the surface profile tailoring [17]. The three main groups are wet chemical etching (micromachining), dry etching, mechanical abrasion (mechanical machining, polishing, grinding) and beaming/irradiation (e.g. laser ablation, UV illumination). Obviously, a surface can be treated directly or a buffer layer/layers can be deposited onto it and further be subject to roughnening (additive technique).

For a chosen surface roughening method different profiles will be obtained in dependence on a particular set of process parameters, e.g. temperature, duration, etc. As an illustration, Fig. 5 shows the time evolution of a random surface profile.

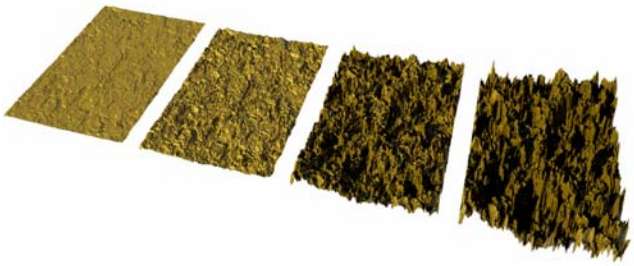

Fig. 5. Illustration of the evolution of a random surface profile with increasing etching time.

One has to keep in mind that surface roughness will affect the performance of the microfluidic channels [17].

In this work we consider wet chemical etching utilizing potassium hydroxide (KOH) and tetramethyl amonium hydroxide (TMAH). It is empirically known that wet-etched surfaces show microscopic facet structures [18]. The following discussion is brought so the best conditions could be found in order to create a surface with the greatest roughness value. KOH and TMAH solution have been taken under consideration because of their widespread use as wet etchants.

Sato et al. [18] used single-crystal Si, mirror-polished with 5-7 nm roughness. Etching in 34 wt.% KOH water solution at 70°C, reaching etching depth 51.09 μm, with etching rate 0.601 μm/min for (100) plane roughed silicon surface 11 nm. The saturated roughness value was 30 nm, though etching depth reached up to 90 μm.

TMAH water solutions as etchants for surface roughening has also been studied e.g. by Shikida et al. [19]. They single-crystal Si, mirror-polished with 5-7 nm roughness. The surface roughness value for (100) plane with etching rate 0.278 μm/min and etching depth 40.65 μm with 25 wt.% TMAH water solution at 70°C was 65 nm. The roughness became saturated after 100 minutes and was 22 nm. Surface roughness increased along with etching depth when the TMAH concentration was 10 wt.%. At 80°C saturated roughness value was 580 nm. The roughness value of the (100) plane was related to micropyramid formation on the etched surface. At 80°C in 20 wt.% TMAH, the roughness

values became saturated at 35 nm. Finally, in the case of 25 wt.% TMAH, at 80°C the roughness value was 6 nm. The effects of etchant circulation were negligible for KOH solutions, but not in the case of some TMAH solutions, especially when the concentration was 10 wt.%. However, the effect was again negligible for TMAH concentrations greater than 20 wt.%. Etching effects increased with temperature. After 70 minutes, roughness value at 70 ˚C was 21 nm but at 80°C after the same amount of time was 35 nm.

V. Jović et al. [20] used single-crystal n-type silicon chips (100) oriented, 50 x 50 mm^2, thickness 525 µm, mirror-polished. Roughness value after etching in 5, 15 and 25 wt.% TMAH water solutions at 80 ˚C were 330 nm, 400 nmand 4.6 nm, respectively. Etching rates were 0.65, 0.56 and 0.45 µm/min for (100) plane. In 30 wt.% KOH water solution at 80°C the initial roughness was 9.9 nm, and after the etching increased to 29 nm.

IV. Microreactor Setup

The basic idea was to fabricate a microreactor structure with the microchannel bottom surface roughened by wet chemical etching and subsequently covered by a thin gold layer (plasmonic material). An illustration of the approach is shown in Fig. 6.

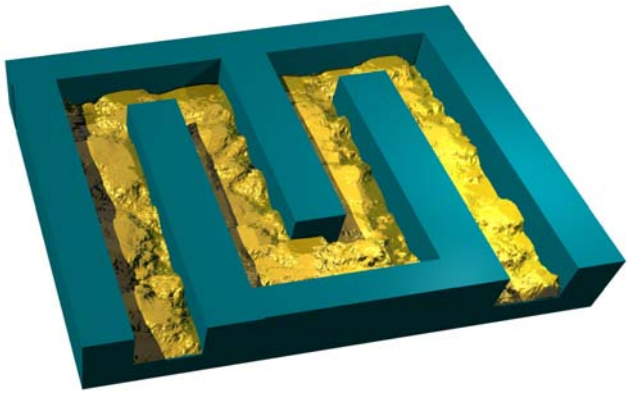

Fig. 6. Simplified illustration of a meandering microreactor with its botton surface roughened by micromachining and covered by a gold layer.

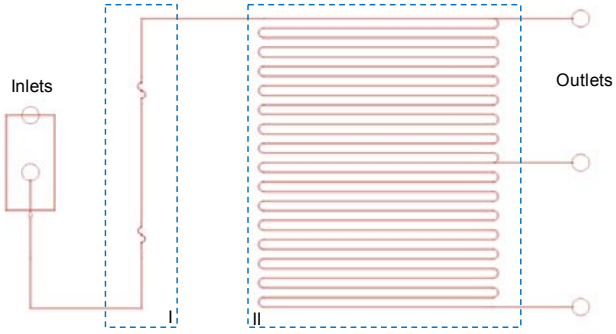

Fig. 7. Photolithographic mask of our microreactor with two inlets shown on the left and three outlets on the right. Part I is dedicated to nucleation and meandering channels of Part II are used for nanoparticles growth. Width and depth of channels are 100 µm and 50 µm, respectively

Figure 7 shows a photolithographic mask for a meander-type microreactor with multiple inlets and outlets. The width and the depth of its microchannels are 100 µm and 50 µm, respectively.

V. Experimental

Experiments in wet chemical etching was performed on two single crystal, n-type silicon wafers, double side polished, 3" in diameter. Thermal oxide was used as a masking layer on Si wafers and it was obtained in a humid atmosphere of oxygen at 1150 °C. The growth of the oxide was at atmospheric pressure and the partial pressure of the water vapor in the atmosphere O_2 was proportional to the water vapor at 90 °C. A protective oxide had a thickness value about 0,6 µm for chemical etching in KOH (potassiumhydroxide) and 1 µm for chemical etching in TMAH (tetramethylammonium hydroxide).

Thermal oxide was etched in BHF (buffered hydrofluoric acid) from the top side of wafers, after that wafers were cut on 6 pieces, samples. Before etching in KOH and TMAH, samples was washed in piranha solution. One set of samples was etched in 30 wt.% KOH water solution for 2 min, 4 min, 6 min, 8 min, 10 min at 80 °C, with etching rate of 1,1 µm/min, while the last sample was used as referent piece. And the other set of samples was etched in 25 wt.% TMAH water solution for 2 min, 3 min, 4min, 5 min, 6 min at 60 °C, with etching rate of 0,16 µm/min, the last sample was used as referent piece.

All samples were cut in half, and one half of each sample was gold sputtered. As a coupler between propagating and surface modes for plasmonic enhancement of photocatalytic optofluidic microreactors thin layer of gold, Au, was used with sublayer of chrome, Cr. Sublayer must be present for purpose of good adhesion of gold on silicon surface. The minimum of thickness value for gold and chrome as sublayer have to be around 20nm, 10 nm respectively. Thickness value of layer and sublayer, combined, must be smaller then value of roughness of silicon surface. In our laboratory we used Perkin – Elmer sputtering system, model 2400, for applying thin metal films on silicon wafers. For gaining thickness of 10 nm of chrome as sublayer we used next conditions in sputtering system: power was 750 W, pressure of Ar was 15 mTorr, duration of process was 10 min, and for thickness of 20 nm of gold conditions were 500W for power, pressure of Ar was 15 mTorr while duration of process was 1min and 30 sec.

The roughness of the surface of the three-dimensional images was determined with atomic force microscope TM Microscopes – Veeco in contactless mode.

Figure 8 shows the measured surface profile of single crystalline (100) mirror-polished wafer after etching in 25 wt.% TMAH water solution for 6 min at 60 °C, while Fig. 9 shows the surface profile for ething of the same wafer in 30 wt.% KOH water solution for 6 min. at 80 °C

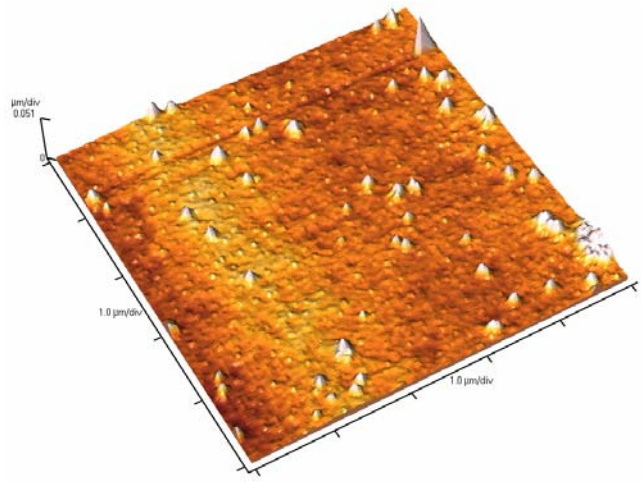

Fig. 8. Measured surface profile of single crystalline (100) wafer etched in TMAH.

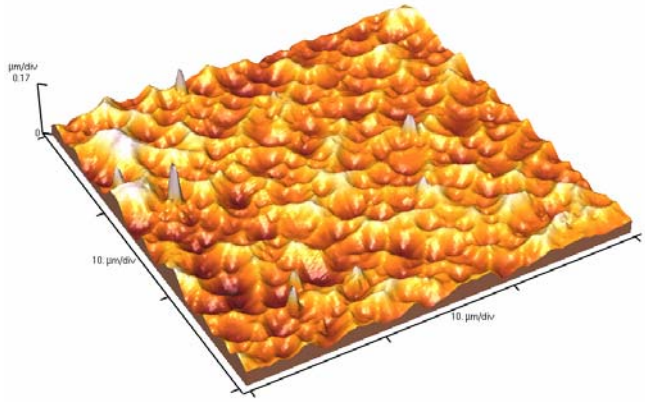

Fig. 9. Measured surface profile of single crystalline (100) wafer etched in KOH.

VI. Conclusion

In this work we considered a possibility to enhance the performance of photocatalytic microreactor by plasmonic localization of electromagnetic field. To this purpose we considered the use of random surface roughness as a coupling device between white light (sunlight) and surface plasmons polaritons without the need of any intermediary structures like ATR. SPP ensure localization of electromagnetic radiation in evanescent near field modes in microscopically small volumes. These volumes are tailored to overlap with the volume of microchannels photocatalytic microreactors. Different surface profiles are obtained by different profiling mechanisms, and even with a single mechanism with varying process parameters. This opens a path toward surface profile tailoring and optimization in the sense of maximizing the coupling efficiency and tuning it to a desired spectral range. The approach can be used in general optofluidics and for lab on chip devices.

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