Nonresonant Local Fields Enhance Second-Harmonic Generation from Metal Nanoislands with Dielectric Cover

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1. **Sample preparation**

Annealing of a 5-nm thick gold film in air at the temperature of 500°C for 120 min resulted in the formation of gold nanoislands shaped as truncated gold spheres with an average diameter of 20 nm but a relatively large size distribution. A scanning electron microscope (Leo 1550 Gemini, Oberkochen, Germany) image of a typical film and the size distribution of the nanoislands are shown in Fig. S1. The islands are seen to be well separated and the film is not percolated. Several similar films were prepared in order to allow them to be coated with TiO₂ films of varying thickness.
Figure S1. SEM image of a gold nanoisland film formed on silica substrate after annealing of evaporated 5 nm gold film at 500 °C for 2 hours with the histogram of the nanoisland size.

The TiO$_2$ coating of the nanoisland films was performed by atomic layer deposition (Beneq TFS-200 reactor, Beneq Oy, Espoo, Finland), using titanium tetrachloride and water precursors. The deposition was performed at the temperature of 120°C and with a nitrogen purge after each deposition cycle. It is known, that under these conditions TiO$_2$ grows in amorphous phase, detailed studies of such films have been reported elsewhere [31].

The thickness and optical constants of bare TiO$_2$ films were first verified with a variable angle spectroscopic ellipsometer (VASE® with a high-speed monochromator system HS-190TM, J.A. Woollam Co., Lincoln, NE, USA). Ellipsometric functions $\Psi$ and $\Delta$ were measured for a set of 5 angles and fitted using Tauc-Lorentz model [21,22]. The coupled fitting of optical constants for all samples shows that the thicknesses of the deposited TiO$_2$ layers are 3.2, 3.8, 6.8, 9.7, 18.8, 28.8, 51.9 and 97.9 nm, which is in a good agreement with the estimations from the ALD process parameters. Individual fitting of samples with given thicknesses demonstrated that the refractive indices at the wavelength of 532 nm and 1000 nm vary from 2.2 to 2.5 and from 2.1 to 2.3, respectively (Fig. S2). This variation is most likely related to the densification of thicker films because of longer ALD process at the elevated temperature of 120 °C. These differences have no influence on the main results of our work. The absorption spectra of the bare and ALD TiO$_2$-covered nanoisland samples were measured by a spectrophotometer (Specord 50, Analytik Jena, Germany).
2. Maker-fringe measurements

The experimental setup is a standard setup for Maker fringe measurements, where polarization and angle of incidence can be varied (see Fig. S3). A Nd:YAG laser (Ekspla PL 2200, Vilnius, Lithuania) with a wavelength of 1064 nm, pulse duration of 70 ps and repetition rate of 1 kHz was used as the source of fundamental light [30]. The beam was weakly focused on the sample and its angle of incidence was varied by rotating the sample with a motorized stage. The SHG signal was detected in transmission by a photomultiplier (Hamamatsu H6779-01) and registered with a computer. Absorptive filters were used to eliminate SHG generated prior to the sample and the fundamental beam after the sample. Polarizations of the fundamental beam and the detected SHG beam were controlled with Glan polarizers.

Figure S2. The real (n) and imaginary (k) parts of the refractive index for ALD-coated TiO$_2$ layers of different thickness.

Figure S3. Schematic of the experimental setup used for the nonlinear experiments.
Both the fundamental and SHG beams were $p$-polarized, which typically gives rise to the strongest SHG signals from surface and thin-film samples. This technique leads to interference fringes between second harmonic signals generated by two sources: the sample surface (source 1) and the back surface of the substrate (source 2) as the angle of incidence is varied. The strength of the SHG signal from the sample can be determined from the relative depth of modulation of the fringes with respect to the signal from the substrate glass.

To estimate effective strength of the SHG signal from this two-source system, we write the total SHG irradiance $I^T$ as

$$I^T = \left( \sqrt{I_1} + \sqrt{I_2} e^{i\phi} \right)^2,$$

where $\sqrt{I_1}$ ($\sqrt{I_2}$) is related to the effective field amplitude from source 1 (2), and $\phi$ is the phase shift between the fields from the two sources. Eq. S1 can be rewritten as

$$I^T = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \phi,$$

with

$$I_{\text{max}} = I_1 + I_2 + 2\sqrt{I_1 I_2},$$

$$I_{\text{min}} = I_1 + I_2 - 2\sqrt{I_1 I_2}.$$  

Using the above, we can write the relative irradiance $I_R = I_1 / I_2$ between the two sources as

$$I_R = \frac{I_{\text{mean}}}{I_2} - 1,$$

where $I_{\text{mean}} = (I_{\text{min}} + I_{\text{max}}) / 2$. Assuming $I_1 \gg I_2$, Eq. (S4) can be further simplified

$$I_R = \frac{I_{\text{mean}}}{I_2},$$

where $I_{\text{mean}}$ can be acquired easily from the Maker fringe data and $I_2$ can be acquired from a blank substrate measurement.

In other words, when the SHG response of the analyzed film sufficiently exceeds that of the backside of the substrate – a situation that corresponds to a low modulation depth in Maker fringe data – the
relative strength of the SHG signal from the film can be evaluated from the average of the neighboring extrema of the fringes. This is the approach taken in the present study.

To obtain the dependence of SH signal on the TiO$_2$ layer thickness we normalized the relative irradiance $I_R$ by the irradiance from uncoated gold nanoisland sample $I_{R,0}$:

$$I_{R,\text{norm}} = \frac{I_{R,i}}{I_{R,0}} = \frac{I_{\text{mean},i}}{I_{\text{mean},0}},$$

(S6)

where $i$ denotes samples with particular thicknesses of the TiO$_2$ layer.

3. Maker-fringe measurements of TiO$_2$ layers on the glass without gold nanoislands

To prove that the gold nanoislands is the only source of strong SH signal observed, we measured Maker fringes from TiO$_2$ layers deposited on glass without gold nanoislands. These are presented in Fig. S4. Here one can see that the SH signal from the layers only is almost independent on the thickness of titanium oxide cover and close to SH signal from bare glass.

![Figure S4.](image)

Figure S4. Maker fringe pattern from a bare glass and differently thick TiO$_2$ layers deposited onto the bare glass substrate.

References from the main text

