Tailored second harmonic generation from self-organized metal nano-wires arrays

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Abstract: Here we report the second harmonic emission properties of self-organized gold nanowires arrays supported on dielectric substrates with a sub-wavelength periodic pattern. The peculiar morphology of the nanowires, which are locally tilted with respect to the average plane of the substrate, allows to generate maximum second harmonic signal at normal incidence with a polarization direction driven by the orientation of the wires (perpendicular to the wires). The generation efficiency was increased by tailoring the growth process in order to tune the metal plasmon resonance close to the pump field frequency and also by increasing the local tilt of the nanowires.

OCIS codes: (190.2620) Harmonic generation and mixing; (190.4400) Nonlinear optics, materials; (220.4241) Nanostructure fabrication; (240.4350) Nonlinear optics at surfaces.

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1. Introduction

Metal nanostructures supported on dielectric substrates have attracted great interest as building blocks of nanoscale optical devices. Large interest was devoted in developing molecular sensors, by using metal enhanced fluorescence [1-2], surface enhanced Raman scattering [3-4] or second harmonic (SH) emission from nanostructures synthesised by e-beam lithography [5-9]. The interest in the development of metallo-dielectric substrates providing high SH conversion efficiency is due to the possibility of realising new optical (multiphoton) microscopy schemes where vertical illumination and detection are adopted.

Here we studied the SH emission properties of a self-assembled gold nanowire arrays supported on sub-wavelength (160 nm) patterned glass templates produced recurring to a novel self-organised maskless approach. Different morphologies were here investigated in order to highlight and overcome the typical constraints which frustrate SH generation on flat metal surfaces: the emission is forbidden at normal incidence and it is always polarized along the plane of incidence, when the pumping light is set to be either s- or p- polarized; these peculiarities arise because most metals posses cubic crystal structure and the electric dipole term in the Maxwell equations, responsible for the standard SH signal, vanishes when inversion symmetry is present in the lattice structure. In a metal, the SH source terms consist of a magnetic dipole term, originating from the Lorentz force on the conduction electrons, and of an electric quadrupole contribution, through the Coulomb force. The expression of the nonlinear polarization at frequency 2\omega which acts as a source term for the SH field was calculated by considering a free electron model for the metal [10,12]. Starting from the equation of motion for the free electrons, within a perturbative approach we can write:

\[ \hat{P}_{2\omega} = \left( \frac{i}{\gamma_{2\omega}} - \frac{e}{2\omega^2 m_{\omega}^2} \right) \left( \nabla \cdot \vec{J}_\omega \right) \vec{E}_\omega - \frac{e\mu_0}{m_{\omega}^2} \left( \vec{J}_\omega \times \vec{H}_\omega \right) \],

where \( e \) is the modulus of the electron charge, \( m \) is the electron effective mass, \( \gamma \) is a damping coefficient taking into account ohmic losses. The contribution of the second term on the right hand side of Eq. (1) is limited by the weak penetration of the electric current inside the metal due to the skin effect (\( \approx 15 \) nm at optical frequencies); the first term gives a nonzero contribution only at the surface [12] (\( \approx 1 \) nm, much smaller than the skin depth). We note that both terms in Eq. (1) are always polarized in the incidence plane (p- polarized) when the pump is either s- or p- polarized. Moreover, pumping at normal incidence, the transverse component of the nonlinear polarization (responsible for collinear SH generation) is zero. We experimentally demonstrate that the nonlinear properties of our samples, consisting of a tilted array of self-organized gold nanowires (NW) with sub-wavelength separation, are characterized by maximum SH emission at normal incidence with a polarization direction driven by the orientation of the wires (perpendicular to the wires). On the contrary, measurements of SH generation from reference samples (flat gold layer, corrugated gold layer, untitled wires) are in agreement with the expectations of ordinary centro-symmetric metal films i.e. they exhibit a minimum in the SH generation efficiency at normal incidence.

2. Sample fabrication

Nanowire arrays have been fabricated by combining ion beam sputtering (IBS) [13] to kinetically controlled deposition (KCD) [14-15]. The dielectric substrates (0.2 mm standard microscope glass slides) were patterned via IBS. The substrates were irradiated by a 800 eV Ar\(^+\) defocused ion beam at an incidence angle of 35 deg from the surface normal. Under such conditions we obtained the formation of a nanoscale ripple pattern with a periodicity of 160 +/- 20 nm and an amplitude of 16+/-5 nm (samples A,B,C,D,G). Then the synthesis of the
metal nanowires is performed by means of glancing angle deposition of gold (80 deg with respect the surface normal). In this way, due to the shadowing effect imposed by the glass ripples, agglomeration of a disconnected array of metal nanowires with a tilt of 12 deg takes place onto the illuminated ridges of the glass ripple pattern. The derivative of the AFM image in the inset of Fig. 1(a) highlights the contrast between the unexposed glass and the polycrystalline structure of the gold NWs. In Fig. 1(b) a comparison between the derivative of two line profiles (before and after Au deposition) is shown, in order to retrieve information on the nanowire lateral size and disconnection.

By modifying the Au dose we fabricated NW test samples (samples A,B,C,D) with different NW cross-sections ranging from 11 nm to 70 nm. The absorption spectrum for each sample (see Figs. 2(a)-2(d)) has been measured revealing the direct correlation between the resonance in the transmission spectrum and the absorbance, in correspondence to the excitation of localized plasmons by TM polarized light. An increase in the cross section of the NWs when increasing Au dose results in a red-shift of the plasmon resonance. This fact allows to tune the plasmon resonance closer to the pumping wavelength at $\lambda_{\text{p}} = 800\text{nm}$.
Fig. 2. Test samples. (a)-(e) red and black traces refer to the optical transmission spectra of samples A,B,C,D,E obtained at normal incidence for two perpendicular polarization states of the incoming light (parallel–red and perpendicular-black with respect to the NW axis). The blue stars represent the differential absorption spectra (\(\Delta A = A_\perp - A_\parallel\)). The black arrows indicate the estimated plasmon absorption peak position. The Au coverage was varied from \(h \cong 11\text{ nm}\) (Sample A) to \(h \cong 70\text{ nm}\) (Sample D and E). In panels (f)-(l) the corresponding SH conversion efficiency \(\eta = I_{2\omega}/I_\omega\) is plotted. On the left side the samples morphology is sketched.

3. Second harmonic generation measurements

We then performed SH measurements at \(\lambda_{2\omega} = 400\text{ nm}\) on all the samples as a function of the incidence angle of the pumping beam for two different orientations of the samples, with the wires perpendicular or parallel to the incidence plane, named \(\perp\) and \(\parallel\) configuration respectively. The fundamental beam was provided by the output of a p-polarized mode-locked laser system with pulse duration 150 fs, \(\lambda=800\text{ nm}\), repetition rate \(~1\text{ kHz}\). The generated
beam propagating along the forward direction is spectrally filtered to isolate the SHG contribution, then an additional polarizer is placed in front of the photomultiplier tube allowing to analyze the polarization of the emerging SHG emission. The fundamental intensity $I_\omega$ was set to be lower than 4.5 GW/cm$^2$ in order to avoid noise from multiphoton processes. The SH measurements resulted affected by an overall uncertainty of 20%. In Figs. 2(f)-2(i) we plot the SH conversion efficiency $\eta = I_{2\omega}/I_\omega$ as a function of the incidence angle for the NW test samples A,B,C,D. In all cases the SH polarization state is perpendicular with respect to the wires orientation despite the fact that a standard metal surface generates SH signal only with p-polarization. More important, the SH signal presents a maximum efficiency when pumped at normal incidence. The conversion efficiency increases as the plasmon resonance is shifted closer to the pump wavelength reaching the maximum value of $1.2 \times 10^{-11}$ for the sample D. We then fabricated a different glass template (sample E) were the ripple facets are more tilted (20 deg) with respect the previous four samples. In this case, even if the absorption peak is centred far from the pump wavelength (as the samples A,B), the SH measurements (Fig. 2(l)) show a maximum conversion efficiency of $1.6 \times 10^{-11}$ at normal incidence, further demonstrating the importance of a local tilt of the nanowires. Other three samples, with a 20 nm gold thickness each, were prepared in order to provide a reference for the SH measurements. Sample F (Fig. 3(a)) is a flat gold film on a flat substrate.

Fig. 3. Reference samples: in panels (a)-(c) the optical transmission spectra of the three reference samples F,G,H and their differential absorbance are plotted. (a – Sample F) is a flat Au film (20 nm thick), (b – Sample G) represents an Au film conformal capping a nanostructured glass template and (c – Sample H) is an array of Au nanowires locally parallel with respect to the glass substrate. In panels (d)-(f) the corresponding SH conversion efficiency $\eta = I_{2\omega}/I_\omega$ is plotted. On the left side the samples morphology is sketched.

Sample G (Fig. 3(b)) was obtained by fluxing gold at normal incidence with respect to the sculpted glass template, resulting in the deposition of a connected Au film which conformally...
preserves the ripple shape of the underlying substrate. Finally, sample H (Fig. 3(c)), an array of Au nanowires locally parallel with respect to the glass substrate, was obtained by IBS etching a 150 nm thick gold film deposited on a flat glass substrate [16-17]. In Figs. 3(d)-3(f) we report the curves of the SH conversion efficiency as a function of the incidence angle, obtained by measuring the three reference samples F,G,H. In all cases the SH polarization state is p-polarized regardless the sample orientation and the angular dependence shows a negligible efficiency at normal incidence (less than $10^{-13}$), showing a behaviour similar to the flat metal film (Sample F). The maximum efficiency is obtained for large angles (40-50 deg) and ranges from $0.2 \times 10^{-11}$ to $0.4 \times 10^{-11}$. Sample G (the connected undulated Au film) behaves very similarly to sample F (flat gold) both in the linear (transmission and absorption spectrum) and nonlinear regime, presenting a very small anisotropy. Sample H (Fig. 3(f)), similarly to the previous two examples, gives only a negligible contribution to the SH signal at normal incidence though for this sample, due to the presence of disconnected nanowires, a stronger dependence with respect to the pump polarization state is found both in the linear and nonlinear regime.

4. Numerical simulations

Numerical simulations were performed in order to calculate the linear fields and then to retrieve the origin of the nonlinear response by using a dedicated numerical algorithm based on Eq. (1). In Fig. 4 the calculated radiative nonlinear polarization terms are shown for two configurations of the wires, tilted (Fig. 4(b)) and un-tilted (Fig. 4(a)), respectively corresponding to the tilted nanowire arrays (Figs. 2(a)-2(d)) and to the un-tilted nanowire array (Fig. 3(c)) when the p-polarized pump is set to normal incidence.

![Fig. 4. z-component of the nonlinear polarization vector at 2ω (arbitrary units) calculated for a p-polarized wave propagating along the x axis in the case: (a) untitled wires; (b) tilted wires.](image-url)

We remind the reader that the nonlinear polarization vector acts as a source term for the SH field and we note that, in the un-tilted case (i.e. H sample), the polarization contribution from one wire is balanced by a reverse contribution of the adjacent wire (Fig. 4(a)). Thus it is possible to qualitatively predict a vanishing macroscopic SH signal at normal incidence, in agreement with experimental results (Fig. 3(f)). On the contrary, in the tilted case, the net contribution is different from zero due to the asymmetry of the system on a subwavelength scale, thus producing a radiative SH signal (Figs. 2(f)-2(l)). The linear fields have been retrieved by comparing experimental and numerical transmission spectra. The spectral behaviour is strongly dependent on the wire thickness, periodicity and degree of disconnection. For instance, the absorption spectrum for each sample has been performed revealing the direct correlation between the resonance in the transmission spectrum (E field

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perpendicular to wires) and the absorbance. Numerical results are in agreement with experiments; enhanced absorption (black curves in Fig. (5)) is obtained as long as wires are sufficiently separated from each other (Figs. 5(a)-5(b)). On the contrary, when distance between wires is less than 10 nm, interaction between wires is responsible for increased reflectivity (red curves) and lower absorption (Fig. 5(c)).

5. Conclusions

In conclusion our experiments demonstrate that it is possible to fabricate low cost metal nanowire arrays of subwavelength periodicity and size, which are supported on locally tilted transparent glass substrates. Their SHG has maximum emission efficiency at normal incidence with a polarization direction driven by the orientation of the wires (perpendicular to the wires). The efficiency of the SHG can be optimized by tailoring the growth process in order to tune the metal plasmon resonance close to the pump field frequency. The SHG efficiency increases by two orders of magnitude with respect to planar films or to un-tilted NWs due to the strong field localization at the dielectric-metal interfaces, as demonstrated by the theoretical and numerical calculations. A further increase of the SH generation efficiency at normal incidence was obtained by increasing the local tilt of the nanowires, thus demonstrating that adaptable effective medium supported over large areas can be synthesized by the proposed self-organised method. These results appear of clear interest in view of applications in the field of high sensitivity bio-sensing where multiphoton confocal microscopy detection schemes are employed for the study of biological fluorescent samples supported on glass substrates. The amplification of the SH signal, enhanced in the near field of the gold nanoparticles at normal light incidence, provides in fact an efficient way for boosting fluorescence emission from fluorochromes located at the surface of the nanoparticles.

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