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Spectral analysis of enhanced third harmonic generation from plasmonic excitations

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We experimentally achieved enhanced third harmonic generation (THG) from hole-array in gold film. The surface plasmon polarition excitations, considered as the major contribution to this THG enhancement, are elaborately studied by a spectrum-resolved femto-second laser system. The momentum matching conditions between the fundamental and harmonic waves are well established, giving results of a series of clear THG beam spots with respect to different excitation wavelengths. This efficient THG beaming from the pure metallic structure would considerably broaden the research in the field of nonlinear plasmonics. © *2011 American Institute of Physics*. [doi:10.1063/1.3604794]

Nonlinear optical process mediated by plasmonic structures has made great progress in surface enhanced Raman scattering[1] and tip enhanced Raman scattering. In comparison, other nonlinear optical phenomena such as second harmonic generation (SHG) and third harmonic generation (THG) do not benefit so much from plasmonic effects of noble metals.[2–4] Since the report of extraordinary optical transmission phenomenon, linear optical properties of such metallic structures and metamaterials have been extensively studied in the past decade.[5–8] Recently, nonlinear plasmon enhanced SHG (Refs. 9–15) and THG (Refs. 16–19) in artificial nanostructures have been extensively studied. Surface induced plasmonic excitations, including localized and nonlocalized ones, have demonstrated fascinating enhanced effects in contributing to the nonlinear optical process.[20–22]

Since the plasmonic mode[23] plays so important roles in the enhancement of THG, it is necessary to make detailed investigations on their properties with respect to the nonlinear process. By using angled resolved plasmonic excitations, some THG studies have been carried out on metal film,[3] 1-D gratings,[16,17] and two dimensional patterns.[18] In this letter, we emphasized the spectral resolved THG on a 2-D gold hole-array nanostructures. With a tunable femto-second laser excitation (from 1.6 to 2.0 μm), a spectral resolved THG process was obtained, which possibly allows for a convenient identification on the different kinds of the plasmonic contributions. Enhanced THG (with visible wavelength) was definitely exhibited with clear THG beaming spots recorded by the CCD camera. These strong THG signals are observed closely related to the excitation of the surface plasmon polariton (SPP) excitations of pumping laser.

Using E-beam lithography and metal lift-off process, a two dimensional gold hole-array nanostructures (area: 500 μm by 500 μm) was fabricated on a 50 nm thick chrome (Cr) coated quartz substrate (Figs. 1(a) and 1(b)), and the thickness of gold film is 100 nm. The 50 nm thick Cr layer has dual functions, first, the adhesion property of gold is improved, and second, the opaque Cr film was used to attenuate the laser propagation and avoid the THG emission from quartz substrate. The period of two dimensional square hole-array is 960 nm with aperture size of 320 nm.

The plasmonic excitation at gold nanostructure/air surface is defined by the following equation:[24]

$$k_{sp}(\omega) = k_0(\omega)\sin(\theta) + m\frac{2\pi}{p_x} + n\frac{2\pi}{p_y}, \qquad (1)$$

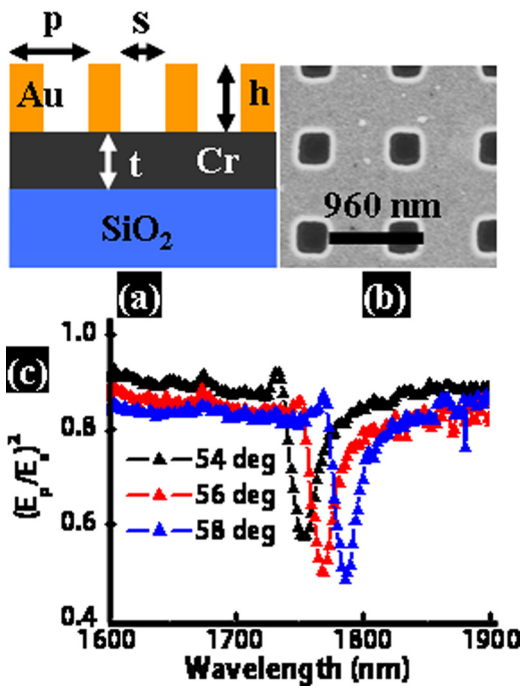

FIG. 1. (Color online) (a) Cross-section of the gold nanostructures, period of the plasmonic device is p = 960 nm, square hole size: s = 320 nm; thickness of gold h = 100 nm; thickness of chrome t = 50 nm; (b) scanning electron microscope image; (c) ellipsometric spectra on 2D gold nanostructures.

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where k_{sp} is the SPP propagation constant on gold/air interface, k_0 is the vacuum wavevector, p_x and p_y are the periodicity of the gold hole-array in x and y directions, and m and n are integers. To characterize the plasmonic band of the gold hole-array device, reflection spectrum of the hole-array nanostructures was measured by UV-visible-NIR spectroscopic ellipsometer.[25] In Fig. 1(c), the intensity ratio of reflected p and s polarized light is plotted as a function of incident angles and wavelength. The resonant dips in NIR region (1.6-1.9 μm) correspond to the plasmonic excitations. The full width at half maximum (FWHM) of the plasmonic resonance is about 14 nm.

In nonlinear optical experiment, NIR femto-second (fs) laser from optical parametric amplifier (OPA) system was used to excite THG on gold hole-array nanostructures. The output wavelength of OPA could be tuned from 1.6 μm to 2.0 μm with repetition frequency of 1000 Hz and pulse duration of ~100 fs. The horizontally polarized light was focused on the sample area by a lens with focal length of 150 mm. Momentum conservation condition in THG determines the radiation direction of THG which satisfies the following equation:[16–18]

$$k_0(3\omega)\sin(\phi) = 3k_0(\omega)\sin(\theta) + m\frac{2\pi}{p_x} + n\frac{2\pi}{p_y}, \qquad (2)$$

where ϕ is the radiation angle of THG to the surface normal of the nanostructures and m and n represent the diffraction orders. The THG efficiency of gold nanostructures is expected to be enhanced when the fundamental wave is coupled to SPP at Au/air interface. In that case, surface THG is evanescent in nature and strong localized around Au/air surface, the localized surface THG is then coupled to free space with the help of the same reciprocal vectors. It should be noted that bulk contribution of THG is also not negligible since THG is electric dipole allowed in bulk gold. The tunable NIR laser is incident at an angle of ~55° in this experiment. The THG radiation could be experimentally found at directions with high order modes ($m = \pm 1$, $n = 0, \pm 1$), however, we only record the in-plane first order ($m = -1$, $n = 0$ in Eq. (2)) emission of THG. The THG radiation was collected by fiber coupled spectrometer after filtering the fundamental wave. The radiation angle of in-plane first order THG could be calculated from Eq. (2), its value (ϕ) ranges from 13.3° to 9.98° with excitation wavelength range of 1700 nm to 1860 nm. The directional radiation of THG radiation is useful for controlling optical parametric process in nonlinear optical system and may have important application in ultrafast optical switching, high resolution bio-imaging, and so on.

Relative efficiency of spectra dependent THG is shown in Fig. 2(a), in which the normalized THG efficiency is plotted as a function of wavelength of pumping laser. It is found that the THG efficiency has a resonant peak at about 1760 nm with FWHM of about 20 nm. From the linear optical property of our gold plasmonic nanostructures in Fig. 1(c), the peak position of THG spectrum fits well with the wavelength of grating coupled surface plasmon resonance at its first order. However, FWHM of THG resonant peak is broader than that of the linear optical resonant dip; this is because the linewidth of the pumping laser at excitation wavelength is up to

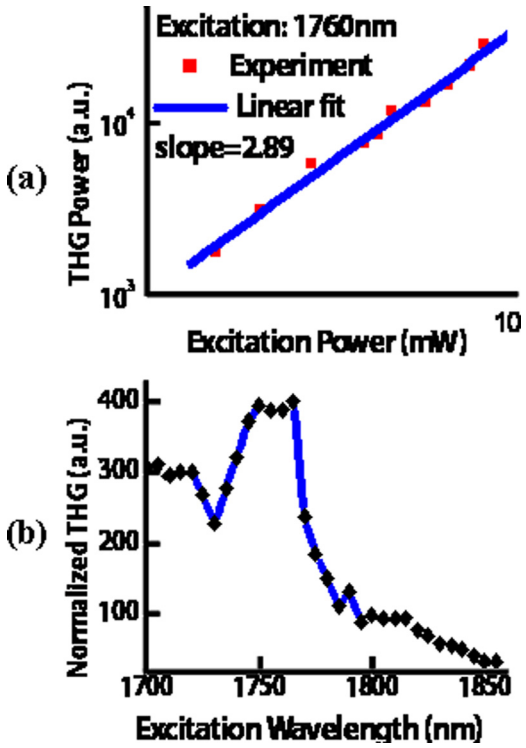

FIG. 2. (Color online) (a) Relative efficiency of THG spectral response on 2-D gold nanostructures; (b) power dependence of THG at plasmonic resonance wavelength (1760 nm).

25 nm. The THG at resonant excitation wavelength has an enhancement factor of about 2 compared to non-resonant background signals (Fig. 2(a)). In the meantime, the THG radiation at non-resonant wavelength is also very efficient (due to the strong $\chi^{(3)}$of gold). This is interpreted as that pumping laser is strongly diffracted into the nano-holes and thus improves the interaction cross-section between pumping laser and Au nanostructures. In comparison, the THG on a planar gold film cannot be detected at the same radiation direction. That is why we declare that the highly efficient THG was realized on gold hole-array nanostructures in near-IR regime.

As the efficiency of THG is sensitive to the peak power of pumping laser, there should be a balance to get the efficient radiation of THG while not destroying the plasmonic device with excessive laser radiation. Power dependent measurement of THG (Fig. 2(b)) shows that it has a near cubic dependence (~2.89) on the excitation power, confirming that it is a third order nonlinear optical process. At the resonant excitation wavelength of 1760 nm, efficiency of THG along the in-plane first order direction is up to 5.8×10^{-8} under excitation power of 6.7 mW.

Direct far-field imaging of THG was captured with CCD camera. In Fig. 3, intense radiation of THG with visible wavelength was captured at the direction of in-plane first order diffraction. The dark field image of THG clearly shows the efficient nonlinear optical process on gold nanostructures.

In conclusion, we reported an enhanced emission of THG on two dimensional gold hole-array nanostructures. At the surface plasmon excitation wavelength of fundamental wave (1760 nm), THG is greatly enhanced due to the strong light localization effect. Another interesting thing is that the

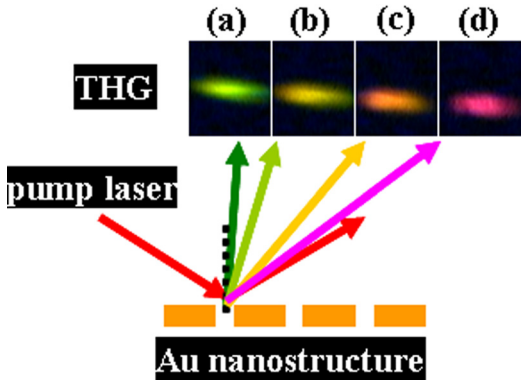

FIG. 3. (Color online) THG image from in-plane first order diffraction. Excitation wavelength is at (a) 1660 nm, (b) 1700 nm, (c) 1740 nm, (d) 1800 nm.

non-SPP background of THG signal is very intense. This may provide us with an alternate avenue to efficiently produce THG by combining both SPP and hole-array nanostructures together. The dark field imaging of efficient THG (with visible wavelength) was realized, and the high image contrast of THG provides potential applications as bio-imaging, visible ultrafast optical probe, and so on.

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