Surface plasmon-enhanced terahertz emission from a hemicyanine self-assembled monolayer

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Abstract: Emission of terahertz radiation is observed when surface plasmons are excited on a thin film of gold, in the Kretschmann geometry. When a hemicyanine-terminated alkanethiol self-assembled monolayer of thickness 1.2 nm is deposited on the gold film, stronger terahertz emission is observed. Our experimental results confirm that enhanced terahertz emission is possible from planar gold surfaces when surface plasmons are excited.

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References and links
1. Introduction

Optical rectification (OR) of femtosecond laser pulses is widely used for the generation of broadband terahertz (THz) pulses [1]. Similar to second harmonic generation (SHG), OR is a second-order nonlinear optical process in which a femtosecond laser pulse forms an ultrafast, quasi-static electric polarization in a medium, which emits a pulse of THz radiation into the far-field [2, 3]. For such a second-order nonlinear optical process to occur, the medium should lack a centre of inversion symmetry [4]. However, OR is possible from the surfaces and interfaces of inversion symmetric materials because at the surface, the symmetry is broken abruptly. For that reason OR, like SHG, can be effectively used as a probe of changing conditions at the surface.

Recently, the emission of coherent THz pulses, resulting from ultrafast laser illumination of plain and nano-structured gold (Au) surfaces, was reported by several groups [5–13]. Kadlec et al, who used an amplified Ti:sapphire laser to illuminate plain Au films of a few hundred nanometer thickness, observe that the emitted THz fluence depends on the square of the incident pump fluence [5]. In contrast, Welsh et al and Polyushkin et al, also using amplified lasers, observe a third, fourth or higher-order dependence of the emitted THz fluence on the incident laser pump intensity, when they illuminate nano-structured Au surfaces [7, 9]. They attribute this higher-order dependence to multiphoton ionization and ponderomotive acceleration of electrons in the evanescent field of surface plasmons [7–9, 14]. In contrast with the above works, we recently reported a second-order dependence of the emitted THz amplitude on the incident laser power, when a nano-structured Au surface, with an effective thickness of 8 nm, was illuminated with light pulses from a Ti:sapphire laser oscillator, and observed no THz radiation from a plain, flat Au surface [13].

Interestingly, either a second-order or a higher-order pump-power dependence of the emitted THz electric field and, consequently, different physical explanations for the emission are reported in these experiments [5–9, 13]. However, these results do not necessarily contradict each other. The relatively low peak-power of laser pulses emitted by Ti:sapphire laser oscillators...
makes it less likely that very high nonlinearities can be observed with these lasers. Ti:sapphire laser oscillators have a high repetition rate which facilitates high frequency signal modulation and sensitive lock-in detection and are therefore much better in detecting relatively weak signals from second-order nonlinear optical processes, if present. At the same time, the high peak power of amplified Ti:sapphire lasers selectively favors higher-order nonlinear generation of THz pulses, but their low repetition rate makes the detection of weak THz pulse from a second-order nonlinear process, one that might become dominant at low excitation powers, less likely. An interesting question is, whether the excitation of surface plasmons that appears to play an important role in the high-power experiments, also plays a role in low-power experiments in which a second-order nonlinearity seems to be responsible for the THz emission.

In this context, it is very interesting that, recently, Uzawa et al reported OR of nanosecond laser pulses by a self-assembled monolayer (SAM) of hemicyanine-terminated alkanethiol molecules on an Au coated glass prism, using surface plasmon excitation in the attenuated total reflection (ATR) geometry [15]. The authors suggested that the same geometry could, in principle, be used to generate THz radiation from such a layer if femtosecond laser pulses are used.

In this paper, we report on surface plasmon mediated generation of THz radiation at the surface of a thin continuous Au layer deposited on a glass prism. Surface plasmons are excited in the Au film with weakly focused laser pulses from a femtosecond Ti:sapphire oscillator. THz emission from the Au surface is observed only when surface plasmons are excited. No measurable amount of THz radiation is observed when the film is excited directly from the air-side, strongly suggesting that surface plasmon excitation increases the THz yield. When the Au surface is covered with a SAM of hemicyanine terminated alkanethiol molecules, the emitted THz electric field amplitude increases by a factor of about three, confirming the prediction made earlier by Uzawa et al [15, 16]. The results emphasize the role played by surface plasmons in the generation of THz radiation and show that even a single (oriented) monolayer of molecules with a thickness of 1.2 nm can lead to significantly enhanced THz emission in this geometry, compared to a bare Au surface [17].

2. Experimental

The experimental setup is shown in Fig. 1(a). The laser source is a Ti:sapphire oscillator (Scientific XL, Femtolasers) generating pulses of 50 fs duration, centered at a wavelength of 800 nm with a repetition rate of 11 MHz. The average output power from the laser is 800 mW. The beam is split into two arms by a 20/80 beam splitter. The 80% part is used as the pump beam, and the 20% part as the sampling beam. The laser beam is p-polarized. The pump beam is sent to an in-plane retro-reflector mounted on a loudspeaker oscillating at 50 Hz, and is then focused onto the prism, as shown in the figure. Care was taken to avoid a tight focus as it was seen to damage the Au layer. The THz radiation generated from the sample is collected in the direction of pseudo-transmission of the pump beam from the prism, using off-axis parabolic mirrors and focused onto an electro-optic (EO) detection crystal (500 μm thick zinc telluride, ZnTe (110)). We note here that at the prism, the pump beam gets reflected at about 90°and no remaining pump light travels along the THz beam after the prism. This configuration thus serves as an effective method to avoid the pump beam going into the detection crystal along with the THz beam. The synchronized sampling pulse is also focused onto the detection crystal [18]. The THz electric field elliptically polarizes the probe beam to an extent proportional to the instantaneous THz electric field value. The probe beam then propagates towards a differential detection setup consisting of a quarter wave plate, a Wollaston prism and a differential detector. The setup measures the ellipticity of the polarization of the probe beam which is proportional to the instantaneous THz electric field strength. Since the optical delay between the pump pulse (and
Fig. 1. (a) Schematic of the setup. $\theta$ is the angle of incidence outside the prism, side $a = 10$ mm. (b) The optical geometry for the ATR excitation of the SAM on the Au film (not to scale). (c) Chemical structure of hemicyanine disulfide. $\phi$ is the angle between the molecular axis $\xi$ and the z-axis which is normal to the sample surface.

thus the THz pulse) and the sampling pulse oscillates at 50 Hz, a full 25 ps long THz electric field time-trace is obtained every 20 ms [19, 20]. Au films of 44 nm thickness were prepared on the hypotenuse side of the right-angled prisms, using vacuum evaporation. A hemicyanine SAM was prepared on the prisms as described previously [16].

The optical geometry of the excitation of the SAM deposited on the Au layer is shown in Fig. 1(b). The chemical structure of hemicyanine disulfide is shown in Fig. 1(c). Hemicyanine disulfide was dissolved in ethanol and used as a 0.01 mM ethanol solution. The hemicyanine SAM was formed on the Au film by immersion of the substrate in the solution for two hours. The thickness of the SAM is estimated to be 1.2 nm [17]. Hemicyanine has a dominant second-order molecular polarizability along the molecular axis $\xi$. This originates from the strong intramolecular charge transfer from the dibutylamino group to the pyridium ion group. The synthesis, EO, SHG, and OR properties are separately described in detail in papers published earlier [15–17, 21, 22].

3. Results and discussion

3.1. THz emission from a thin continuous Au layer

A scanning electron microscope (SEM) image of the surface of the Au film deposited on the prism is shown in Fig. 2. The surface looks rather featureless. In Fig. 3(a), we plot the measured THz electric field as a function of time, emitted by this Au film. The signal, although somewhat noisy, consists of a quasi-single-cycle oscillation of the electric field, and is only observed when the Au film is illuminated from the glass-side (in the ATR geometry) under the right angle of incidence as discussed below. No measurable THz emission is observed when this film or any other continuous smooth Au surface is illuminated from the air-side. At the surface plasmon
resonance (SPR) condition, the reflected pump power from the prism goes to a minimum and a bright patch of scattered 800 nm light is observed on the Au coated hypotenuse side of the prism. When the incident pump beam is at any other angle, such a patch does not appear. This provides visual confirmation that surface plasmons are excited around this angle of incidence. In Fig. 3(b) we plot the emitted THz amplitude as a function of the incident laser power. The THz amplitude increases linearly with the incident laser power. This suggests that a second-order nonlinear optical process is responsible for the THz emission.

Our present experimental results thus point to the fact that THz emission by second-order OR is possible at thin film Au surfaces when surface plasmons are excited. OR can originate from the lack of inversion symmetry at the Au surface. When direct excitation of the sample is done from the air side, the intensity at the sample surface is presumably not strong enough to result in the generation of any detectable THz light. THz emission is facilitated by the excitation of surface plasmons, since they have stronger fields exactly at the surface, where the nonlinear process of converting pump light into THz light takes place [23]. Propagating surface plasmons can also lead to an increased interaction distance at the Au surface, thus enhancing the yield further.

![Fig. 2. SEM image of the Au layer.](image)

![Fig. 3. (a) The emitted THz electric fields vs. time, emitted by the bare Au layer on the prism (black), and by the SAM on the Au layer (red). (b) THz amplitude emitted by the bare Au surface, normalized, by dividing by the largest THz amplitude measured, as a function of the incident laser power. The red line is a guide to the eye.](image)
3.2. THz emission from self-assembled monolayer of hemicyanine

In Fig. 3(a), we plot the THz electric field emitted from the hemicyanine-SAM coated Au layer when excited in the ATR geometry. The emission is observed only when the angle of incidence of the pump beam fulfills the SPR condition. Remarkably, the emitted THz electric field from the monolayer covered surface is a factor of three larger than from the bare surface even though the layer is only 1.2 nm thick. Since hemicyanine SAM is known to have a large $\chi^{(2)}$, this THz emission can be considered as the sum of the contribution from OR at both the Au surface and the hemicyanine SAM [21]. Due to the presence of this thin monolayer, the resonance angle where plasmons can be excited, is expected to shift a little with respect to that for a bare Au film [16, 17, 21]. The THz signal consists of a quasi-single cycle oscillation followed by rapid oscillations. These oscillations are mainly due to the absorption and re-emission of THz radiation by water vapor in the atmosphere. No detectable THz emission is observed when the SAM was directly illuminated by a focused pump beam from the air-side. Figure 4(a) shows the emitted THz amplitude and the reflected pump power from the prism as a function of the angle of incidence $\theta$. The dip in the reflected pump power observed around $\theta = 42^\circ$ corresponds to the angle where surface plasmons are excited at the Au surface. We note that compared to the results reported in references [15, 16], a broader resonance is seen in Fig. 4(a). In our case, the pump beam is focused onto the sample using a plano-convex lens with $f = 150$ mm. Thus the curve shown in Fig. 4(a), is a summation over a small range of incidence angles. Because we use laser pulses, the pump beam has a bandwidth of about 30 nm. This also contributes to a smearing-out of the resonance. The three times larger THz amplitude emitted from the SAM compared to the bare Au layer, is consistent with the earlier observation of SHG from similar samples by Naraoka et al [21].

Fig. 4. (a) Emitted THz amplitude (red) from the SAM and the reflected pump power (blue) plotted as functions of angle $\theta$. (b) THz amplitude emitted by the SAM (on the Au layer), normalized by dividing by the largest THz amplitude measured, as a function of the incident laser power. The red line is a guide to the eye.

In Fig. 4(b), we plot the emitted THz amplitude as a function of the incident laser power. The dependence is, to a good approximation, linear, suggesting that a second-order nonlinear optical process is responsible for the THz emission. At the SPR condition, the electric field of the pump light is enhanced close to the metal surface [23]. This provides a localized high intensity at the SAM. As a result of this, the THz polarization developed in the SAM can be significantly enhanced. This enhancement is very similar to the surface-plasmon mediated enhancement of other nonlinear processes like SHG and Raman scattering reported from metal surfaces [21,23]. The ATR geometry is very suitable for the excitation of very thin (of a few nanometers) layers.
of nonlinear materials, because of the strong field localization near the metal surface [15]. In the ATR geometry, the pump beam is focused on the hypotenuse side of the prism to a spot size of diameter $\sim 1$ mm. We can thus calculate that the THz light is emitted from a tiny volume of only $\sim 10^{-15}$ m$^3$.

It is interesting to speculate whether the generated THz light can also be coupled into a surface wave propagating along the same interface. In the present geometry, this seems to be unlikely as the condition for phase-matching requires that the group velocity of the 800 nm plasmon and the phase velocity of the THz surface wave are equal [24]. Since it is known that THz surface waves on metals propagate at nearly the speed of light in vacuum whereas the 800 nm light propagates at a much lower velocity, phase-matching in the present geometry is not possible. It may be possible with nano- or micro-structured surfaces, but this is beyond the scope of this paper.

4. Conclusion

In conclusion, we observe the emission of coherent THz pulses when surface plasmons are excited on a planar thin film of Au, using femtosecond laser pulses in the ATR geometry. Our results suggest that this emission is by second-order OR of the laser pulses taking place at the Au surface, where the local laser intensity is enhanced by the excitation of surface plasmons. This is supported by the enhancement of THz emission by OR on a hemicyanine-SAM deposited on the Au film. Surface plasmon-enhanced THz emission may provide an effective way to probe local $\chi^{(2)}$ from such thin films.

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