Percolation-enhanced generation of terahertz pulses by optical rectification on ultrathin gold films

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Emission of pulses of electromagnetic radiation in the terahertz range is observed when ultrathin gold films on glass are illuminated with femtosecond near-IR laser pulses. A distinct maximum is observed in the emitted terahertz amplitude from films of average thickness just above the percolation threshold. Our measurements suggest that the emission is through a second-order nonlinear optical rectification process, enhanced by the excitation of localized surface plasmon hot spots on the percolated metal film. © 2011 Optical Society of America

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Ultrafast optical excitation of nonlinear optical materials and semiconductors is widely used as a source for electromagnetic radiation in the terahertz (THz) range [1]. In 2004, the generation of THz pulses by optical rectification on “thick” metal films was reported by Hilton *et al.* [2] on iron (Fe) films and by Kadlec *et al.* [3] on Au and silver (Ag) films. Second-order nonlinear processes (except for Ag) were suggested as the mechanism for the generation of THz light. In the following year, Kadlec *et al.* reported further studies of the optical rectification on metal films using terahertz time-domain spectroscopy, and showed that the THz emission had a nonlocal characteristic and that no emission was found from Au films of less than 100 nm thickness [4].

In 2007, Welsh *et al.* were able to generate THz radiation by illuminating metal-coated glass gratings with femtosecond laser pulses. A 30 nm thick layer of Au was used in their experiments [5]. They argued that multiphoton excitation can take place at the structured metal surface under the strong evanescent field of surface plasmons. Ponderomotive acceleration of electrons in this strong field close to the metal surface was considered as the major mechanism for the generation of THz pulses [5,6]. It has to be noted that they observed a third- to fourth-order power dependence in their work and ruled out the possibility of second-order nonlinear optical rectification [5]. A very recent report by Garwe *et al.* briefly discussed a new mechanism based purely on the propagation of surface plasmons on the metal-coated glass gratings [7]. To our knowledge, however, no results were reported for metal films of <30 nm thickness. This is unfortunate because the optical properties of ultrathin gold films are very different from those of bulk gold. The reason for this is that when ultrathin films of gold (Au) are prepared on a substrate-like glass, using physical vapor deposition techniques like thermal evaporation or sputtering, randomly placed isolated Au nanoislands are initially formed. As more and more Au is deposited on the substrate, these islands start to coalesce, forming irregularly shaped fractal structures [8–10]. As the average thickness increases further, an extended Au cluster is formed which spans the whole surface. The thickness where this occurs is

known as the percolation threshold. For Au deposited on glass substrates, the percolation threshold is expected at an average thickness of ~7 nm [9]. This was also experimentally confirmed by THz transmission experiments by Walther *et al.* [10] who found that the average thickness of Au on silicon (Si), where percolation occurs, is 6.5 nm.

Various nonlinear optical phenomena have been shown to become enhanced on metal films near the percolation threshold, due to disorder-induced localization of plasmons leading to hot spots of local field enhancement. Enhanced second-harmonic generation (SHG), higher-harmonic generation, surface-enhanced Raman scattering, and spectral continuum generation have been reported from such semicontinuous metal films [8,11,12].

In this Letter, we report the first observation of the emission of THz pulses from ultrathin Au films illuminated with femtosecond laser pulses. Our results show a distinct enhancement in the emission of THz light from semicontinuous Au layers of average thickness just above the percolation threshold. In contrast with previous reports, [3–6] here we show that THz emission is possible from ultrathin Au films of thickness as low as 8 nm, and is based on a second-order nonlinear optical process.

The experiments were performed using a standard THz generation setup as shown in Fig. 1(a) [13]. The laser source used is a Ti:Sapphire oscillator (Scientific XL, Femtolasers) that generates pulses of 50 fs duration and centered at a wavelength of 800 nm with a repetition rate of 11 MHz. The average power output from the laser is 800 mW. The 80% part of this is used as the pump beam, and the 20% part as the sampling beam. The pump beam is weakly focused onto the sample surface to a spot size of about 2 mm, at a 45° angle of incidence, as shown in Fig. 1(a). Care is taken to avoid a tighter focus, as this was seen to lead to damage and/or restructuring of the metal film. The THz radiation generated from the sample is collected in the specular reflection direction of the pump beam using off-axis paraboloidal mirrors and focused onto a 500 μm thick zinc telluride (ZnTe (110)) detection crystal. The synchronized, copropagating

Fig. 1. (Color online) (a) Schematic of the setup used in the experiment. (b) SEM image of 8 nm Au deposited on a glass substrate. The gray parts are randomly shaped clusters of Au, and the darker regions are the substrate surface. (c) A typical example of the emitted THz electric field from 8 nm Au on glass.

sampling pulse is also focused onto the detection crystal. The THz electric field elliptically polarizes the probe beam to an extent proportional to the instantaneous THz electric field value. This ellipticity of the beam is measured by a differential detection setup consisting of a quarter wave plate, a Wollaston prism, and a differential detector.

The samples were prepared by electron-beam evaporation of Au under high vacuum conditions (below a pressure of 10^{-6} mBar). The glass slides were first treated with 100% fuming nitric acid (HNO_3) in an ultrasonic bath for five minutes, followed by cleaning with deionized water. After drying with dry nitrogen flux, they were cleaned with acetone and isopropanol and dried again. All Au films were prepared under similar conditions and with a deposition rate of $1 \text{ \AA/s}$. A quartz crystal thickness monitor was used to estimate the thickness. Only an average thickness can be defined for Au thin films below the percolation threshold [9]. Figure 1(b) shows a scanning electron microscope (SEM) image of an Au film of 8 nm average thickness, deposited on the surface of a glass slide. The random morphology of the percolated film is fractal-like. One of the interesting properties of fractal structures is their scale invariance. For that reason, percolated Au films are reported to show a broad surface plasmon resonance near the percolation threshold, as a wide range of interaction lengths is available because of all available sizes of resonating clusters [14].

A typical example of an emitted THz electric field from 8 nm Au on glass, is shown in Fig. 1(c). It consists of a nearly single-cycle pulse followed by an oscillating tail. These weak oscillations are caused by the absorption and the re-emission of the THz light by the water vapor molecules in the atmosphere. The THz electric field emitted from the samples was found to be mainly p -polarized and did not show any dependence on the azimuthal orientation of the sample. No THz emission was detected when the angle of incidence of the pump beam was 0° . This suggests that the generated THz dipole is oriented normal to the sample surface. We note that the emitted THz amplitude from 8 nm Au on glass is relatively weak and is only 0.2% of that emitted from an unbiased

semi-insulating gallium arsenide (SI-GaAs (100)) surface emitter.

The amplitude of the emitted THz electric field and the 800 nm pump light absorption, as a function of the average Au film thickness, are shown in Fig. 2(a). The figure shows that the THz emission is detected only in the range of thicknesses where the metal layers show enhanced absorption of the pump light. No THz emission from bare glass surfaces could be detected in our experimental setup. Figure 2(b) shows the transmission, reflection, and absorption of the pump light as a function of average Au layer thickness. We see a distinct and broad peak in the absorption near the percolation threshold, which is attributed to the excitation of hot spots of strong localized surface plasmons [14,15]. This indicates that the excitation of these hot spots plays a role in the THz emission. For average thicknesses above 14 nm, no THz emission could be detected. We note that the 800 nm reflection and transmission measurements are nearly identical to those done using 632.8 nm of light of a He-Ne laser by P. Gadenne in 1977 [16].

In Fig. 3, we plot the measured THz amplitude as a function of incident laser power. For an average power

Fig. 2. (Color online) (a) Emitted THz electric field amplitude from different thickness Au layers on glass. The red curve shows the emitted THz amplitude. Below 6 nm and above 14 nm average Au layer thickness, no significant THz emission could be detected in our setup. The blue curve shows the absorption of the 800 nm light by the sample. (b) The reflection (green curve), transmission (red curve), and absorption (blue curve) of the 800 nm light by different thickness Au films on glass.

Fig. 3. (Color online) Emitted THz electric field amplitude is shown as a function of the incident laser power. The red line is a guide to the eye.

density of up to 3.5 W/cm^2 , the THz amplitude clearly increases linearly, suggesting that a second-order nonlinear process is responsible for the THz emission. This contradicts the earlier observations by Welsh *et al.*, where a higher-order nonlinear process resulted in the THz emission from an Au surface [5,6]. On the other hand, Kadlec *et al.* reported a second-order process from Au films but only above a thickness of 100 nm [4]. We add that in our experimental setup, we were unable to reproduce the results by Kadlec *et al.* from evaporated thick (200 nm) Au films, perhaps because of the much lower laser power density in our case. A direct comparison of their work with our work is difficult, however, as percolated metal films are known to behave differently from bulk metals [10]. For their work, Kadlec *et al.* used an amplified laser source, whereas we use a Ti:Sapphire oscillator generating pulses with a much lower energy. We note that a tighter focus of the pump beam led to the appearance of a white glow from the percolated sample, accompanied by photodamage and even removal of the Au layer.

Enhancement of second-order nonlinear processes like SHG has been reported from percolated Au films on glass [12,17]. Lack of inversion symmetry is essential for such a process. For an ultrathin Au film, the inversion symmetry is broken in the direction perpendicular to the sample surface. Femtosecond laser excitation can thus lead to the formation of a THz dipole oriented normal to the sample surface, through a second-order optical rectification process [18]. Excitation of hot spots of localized field, near the percolation threshold, leads to the enhancement of this process, resulting in increased emission of THz light. The maximum of THz amplitude is

observed from an Au film of 10 nm average thickness. This average thickness is slightly higher than that for the maximum of the pump light absorption. This suggests that the degree of percolation plays a role in the THz emission process.

In conclusion, we have experimentally demonstrated that the generation of THz pulses by optical rectification is enhanced for ultrathin Au films just above the percolation threshold.

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