Demonstration of nonlinear absorption in Au semi-continuous film by electrical measurement

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Abstract: We have demonstrated the nonlinear absorption at 532 nm wavelength in an Au semi-continuous film (SF) resulting from smearing of the Fermi distribution and diffusion of conduction electrons into the substrate. The Au SF was irradiated by a pulsed laser with 8 ns pulse width at 532 nm in near resonance with the interband transition of the Au. We determined the temperature increase in the SF for different intensities by electrical measurement. We calculated the temperature increase by using a 1D heat transport equation; comparing the results of the calculation with measured values for the temperature increase, revealed the nonlinear absorption in the Au SF. We employed this deviation from linear behaviour to determine the nonlinear absorption coefficient.

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1. Introduction

Understanding the physics of light-matter interaction at the interfaces of thin metallic films and dielectrics is very important for the development of various applications such as thermoelectronics, nanoelectronics, optics, and photonics. Due to the excitation of coherent oscillations of the conduction electrons, surface plasmon polaritons (SPP) can be sustained at the metal-insulator interface [1] and the propagation of the SPP is strongly affected by its resonant coupling to bulk plasmons [2]. The understanding of light absorption under SPP excitation is especially important for designing photonic devices [3] switches [4] and metal-insulator-metal waveguides [5]. Furthermore, SPP can cause local field enhancements in thin discontinuous metallic films, where the size of nanoislands is much smaller than the light wavelength [6]; this phenomena has a significant impact on surface enhanced Raman scattering (SERS) [7]. Controlling the size and separation of the metallic nanoparticles enables the design of plasmonic structures for a variety of applications [8].

Experimental measurement of the nonlinear absorption coefficient in Au thin film or Au nanoparticles is usually performed by Z-scan measurement [9,10]. In such measurements, the scattering of light from the surface due to its roughness can introduce inaccuracy in measuring absorption nonlinearity [11]. It is especially important for thin semi-islanded self-organized films [12] and metallic nanoislands that can be used in nano-resistors exploiting the electron tunnelling process [13]; such films feature very irregular surfaces and thus it is difficult to estimate the amount of the light scattering.

In this paper, we have developed a technique to minimize such inaccuracies by directly measuring the temperature increase in an Au semi-continuous film (SF). The temperature increase is due to light absorption, where scattering of the light from the surface does not play a major role in the temperature increase of the Au SF. We refer to SF as a thin film of Au where Au does not cover some areas of the substrate. This surface morphology does not have any significant effect on the nonlinear absorption mechanism that we study here. We determined the temperature increase in the Au SF by electrical measurement while the sample was irradiated by a Nd:YAG pulsed laser at 532 nm. We have demonstrated a linear relationship between the laser intensity and the temperature increase at low intensities, and a nonlinear absorption at higher intensities. The results were used to estimate the nonlinear absorption coefficient of the Au SF at 532 nm. At high intensities (>600 kW/cm²), some of the conduction electrons in the Au may diffuse into the substrate, causing the density of unoccupied states below Fermi level to increase (smearing the Fermi distribution). Therefore, optical excitations from the d-band to unoccupied states below the Fermi level are enhanced and consequently a nonlinear absorption is observed.

2. Experimental

The sample with 15 nm Au (1 mm × 0.68 mm × 15 nm) was prepared using DC magnetron sputtering of the Au onto a 500 µm thick polished Si wafer with a 500 nm SiO₂ layer thermally grown on both sides. For electrical measurements, two 500 nm thick Au contacts were deposited on the sample with a 0.55 mm gap in between. In order to perform the electrical measurements, we connected the sample to a DC power supply (ranging from 0.2 V to 0.8 V) in series with a 50 Ω load resistor. The thermal behaviour of the sample was studied by illuminating it with a pulsed Nd:YAG laser (8 ns FWHM) while a DC voltage was applied to the sample. The wavelength of the laser was set to 532 nm by frequency doubling of the laser’s fundamental mode (1064 nm) using a frequency-doubler crystal, which is incorporated...
in the system. The laser pulse illuminating the sample caused an increase of the temperature of the sample at a nanosecond time scale, which resulted in a voltage drop (pulse) on the load resistor (Fig. 1a). This electric pulse was captured using an Agilent digital oscilloscope DSO7104B. To investigate the intensity dependency of the absorbance, the pulse intensity was changed by misalignment of the frequency-doubler crystal. The pulse width (~8 ns) and rise time (~5 ns) of the laser has been characterized by a photodiode sensor (Fig. 1b).

Fig. 1. (a) Sample design and schematic of the measurement circuit. Au sample thickness is 15 nm; laser beam cross-section is much larger than the sample area. (b) Typical pulse shape of the Nd:YAG laser.

The thickness and the surface morphology of the Au sample were characterized by a Dektak 150 Stylus Profiler and Zeiss Ultraplus field emission scanning electron microscope (FESEM); 3D reconstructions of the SEM images of the sample are shown in Fig. 2a and 2b. To calculate the temperature coefficient of the resistance (TCR), we measured the resistance of the sample in the temperature range from 30 K to 300 K using a Physical Property Measurement System (PPMS) Quantum Design Model 6000 (Fig. 3a). Contribution of the inductance and capacitance of the circuit, including the sample and the metal film 50 Ω load resistor was investigated by employing an Agilent 33250A function generator.

Fig. 2. 3D images of the 15 nm Au on SiO$_2$/Si/SiO$_2$ substrate at low (a) and high (b) magnification.

3. Contribution of the impedance of the sample in calculating the temperature variations

In our experiment, we considered the metal film resistor and the sample as DC components and we ignored their frequency-dependent impedances. This can potentially cause errors in calculating the temperature variations, as the impedance of any circuit consisting of inductive and capacitive elements is a function of frequency [14]. In order to investigate whether this approximation is valid in our case, we prepared the following experiment. We replaced the DC voltage source (Fig. 1a) with a function generator. The load resistor and the sample were connected to the digital oscilloscope and the function generator using 50 Ω coaxial cables; the resistance of the cables were negligible. Then we applied electric pulses with different amplitudes to the circuit in the absence of the laser pulse. We adjusted the shape of the electric pulse to the same as the laser pulse (5 ns rise time and 8 ns FWHM). During the experiment with the laser where the sample was irradiated with laser pulse, we triggered the laser manually every few seconds in order to avoid overheating of the sample. To simulate this situation during the investigation with the function generator in the absence of the laser...
illuminated, we applied the electric pulse with a 1 Hz repetition rate. The voltage drop on the load resistor was recorded for the different pulse amplitudes using the digital oscilloscope (Fig. 3b). Assuming that the inductance and capacitance of the sample and the load resistor were negligible in this frequency bandwidth and considering the resistance of each of these components, we calculated the voltage drop on these elements at different pulse amplitudes using the resistor network equation $V_{\text{Load}} = V_{\text{Applied}} \frac{R_{\text{Load}}}{R_{\text{Load}} + R_{\text{Sample}} + R_{\text{Cables}}}$. The calculated values were in a good agreement with the experimental values recorded from the digital oscilloscope (Fig. 3b). Therefore, the contribution of the inductance and the capacitance of the circuit in this frequency bandwidth are negligible, and thus, the amplitude of the electrical pulse generated during the experiment with the pulsed laser can be used directly to evaluate temperature variation of the Au SF.

4. Demonstration of nonlinear absorption in Au SF and calculation of the nonlinear absorption coefficient

When the sample was irradiated by the pulsed laser, its temperature would rise due to absorption of the light at 532 nm. On one hand, considering that the absorption of the light (at 532 nm wavelength) is much smaller in SiO$_2$ than in the Au SF, the Au SF can be considered the heat source for the temperature increase in the sample. On the other hand, the heat transport mechanism (from Au SF to the substrate) can be treated as a 1D heat transport since the area illuminated by the laser (beam diameter, 5 mm) is much larger than the area of the sample. These two conditions facilitate the way to employ the following equation derived in [15] to analyse our results:

$$\Delta T = \frac{2IA\sqrt{t}}{\sqrt{\pi}\gamma\zeta\kappa}$$

(1)

where $\Delta T$ is the maximum temperature change, $I$ the laser intensity, $A$ the absorbance of the Au SF at 532 nm, $t$ the laser pulse width at FWHM, $\gamma$ the substrate mass density, $\zeta$ the substrate specific heat, and $\kappa$ the thermal conductivity of the substrate. In order to determine the values of $\Delta T$ at different laser intensities, we proceed as follows. Firstly, a DC voltage (0.8V) is applied to the sample and then the pulsed laser at different intensities irradiates it. The resistance of the sample increases as its temperature rises; this effect is observed as a voltage drop across the 50 $\Omega$ load resistor, where it is connected to the digital oscilloscope (Fig. 4a). The amplitude of this electric pulse and the TCR of the Au SF are used to calculate $\Delta T$. Then by using the SiO$_2$ values for $\gamma$, $\zeta$, and $\kappa$ [16] in Eq. (1), we extract the value of the absorbance ($A=0.176$) at low intensities for the 15 nm Au SF. By comparing the calculated values from Eq. (1) and measured values for $\Delta T$ at different intensities, a clear deviation from linearity in the $\Delta T$-I diagram is observed (Fig. 4b). Equation (1) assumes a square pulse shape for the laser beam and therefore the estimated value of the absorbance could be inaccurate as...
the real laser pulse shape has a form shown in Fig. 1b. We calculated the value of the absorbance by using two different simulation software packages (OpenFilters, and TFCalc). The results were $A=0.18$, and 0.178, close to the fitted value.

![Graph showing temporal response and nonlinear intensity-dependent absorption](image)

Fig. 4. (a) Temporal response of the sample to pulsed laser at 532 nm (b) Nonlinear intensity-dependent absorption of the Au SF at 532 nm.

The deviation of the measured $\Delta T$ from linearity can be explained by using the relation between absorption coefficient and absorbance in Au SF, $A = (1-R) (1-e^{-\alpha d})$ [15] where $R$ is the reflectance of the Au SF, $d$ is its thickness, and $\alpha = \alpha_1 + \alpha_2 I$ is the absorption coefficient of the Au SF [17]. Here, $\alpha_1$ is the absorption coefficient at low intensities, and $\alpha_2$ is the nonlinear absorption coefficient. At low intensities where linear behaviour is observed, by using $A=0.176$ and $R=0.29$ we determine the value of $\alpha_1=1.9 \times 10^7$ m$^{-1}$, which is less than the bulk value ($5.7 \times 10^7$ m$^{-1}$) of the Au at 532 nm (the value of $R$ was obtained from the simulation). At intensities above 450 kW/cm$^2$ we observed the nonlinearity (Fig. 4b). The nonlinear absorption coefficient is calculated as $\alpha_2=\ln[1-((\Delta T_2-\Delta T_1) (\pi \gamma \zeta \kappa)^{1/2}) / (1.068 I t^{1/2})] / (I d)$, where $\Delta T_2$ is the temperature change obtained from the experiment, and $\Delta T_1$ is the maximum temperature change calculated from the Eq. (1) by considering a constant absorption coefficient ($\alpha_1$). The extracted values of the $\alpha_2$ for the two highest intensities at ~600 kW/cm$^2$ and ~700 kW/cm$^2$ in our experiment are $\alpha_2=3.8 \times 10^{-2}$ cm/W and $6.8 \times 10^{-2}$ cm/W.

5. Discussion

The photon absorption process in noble metals such as Au, and Cu is due to an interband transition mechanism, where electrons from the top of the d-band are excited to energy levels above the Fermi level [18]. In noble metals, the nonlinear absorption occurs because of smearing of the Fermi distribution. The Fermi distribution smearing can occur in two different ways, by either changing the lattice temperature or creating thermal nonequilibrium between the lattice and the conduction electrons.

The lattice temperature can be increased due to electron-phonon (e-ph) interaction, where the excited d-band electrons relax to their initial states resulting in a lattice temperature increase within a few hundreds of picoseconds [19]. At sufficiently high light intensities, where the lattice temperature increases by tens of Kelvin, the p-band electrons below the Fermi level are thermally excited into unoccupied states above the Fermi level (Fermi distribution smearing [18]). In Au the absorption then increases for wavelengths $>510$ nm since the thermally excited p-band electrons create empty states below the Fermi level. This increases the transition probability from the d-band to the p-band below the Fermi level. At wavelengths $<510$ nm, the absorption decreases as the thermally excited p-band electrons now occupy previously empty states above the Fermi level. This decreases the transition probability from the d-band to the p-band above the Fermi level [18]. The above-described mechanism leads to a photon intensity dependent absorption.

In addition, smearing of the Fermi distribution can also occur via illumination of the metal with the laser, where the temperature of the p-band electrons increases above the lattice temperature. This causes a thermal nonequilibrium, where electrons equilibrate to the Fermi distribution in femtoseconds via electron-electron (e-e) interaction. After equilibrating to the Fermi distribution, the lattice temperature increases because of the e-ph interaction,
occurs on a time scale of ~1 ps. Before the relaxation, the electrons can be transported ballistically within the metal. The mean free path (MFP) of the electrons in Au is ~120 nm [19] and the e-ph relaxation time is related to the e-ph coupling constant [20]. To observe the nonlinearity due to the thermal nonequilibrium, the laser pulse width must be smaller than ~1 ps. Otherwise, the smearing of the Fermi distribution caused by increasing the lattice temperature overshadows the Fermi distribution smearing caused by the p-band electrons.

Considering the FWHM of the laser pulse in our experiment (8 ns>>1 ps), we believe that the observed nonlinear absorption can be partly attributed to the smearing of the Fermi distribution caused by increasing the lattice temperature. We assume that before arriving at the maximum lattice temperature the heat diffusion from the Au SF to the substrate is negligible. If we consider that the temporal shape of the laser pulse is Gaussian, the rise time of the electrical pulse would be 16 ns. This rise time is smaller than the rise time of the electrical pulse, which we observed as ~30 ns in the experiment (Fig. 4a). This delay cannot be related to the e-ph relaxation time, which is much smaller than ~16 ns; also, the spatial Gaussian profile of the laser cannot cause such delay since the area of the sample is much smaller than the laser beam cross-section. The possible explanation for this extra delay is to consider the role of the p-band electrons in smearing of the Fermi distribution. It was shown that the electron temperature is strongly affected by the thickness of the sample for thicknesses smaller than the MFP of the electrons. The electrons are reflected from the interfaces where they lose some of their energy to the substrate upon multiple reflections from the boundaries [19]. The positive values of $\alpha_2$ (3.8x10^{-2} cm/W, and 6.8x10^{-2} cm/W) indicate that the nonlinear absorption is the result of the enhanced excitation of the d-band electrons to unoccupied states of the p-band below the Fermi level because, some of the p-band electrons may have diffused into the substrate [21]. The delay of the electrical pulse might indicate that the diffused electrons have taken energy away from the Au SF/SiO$_2$ interface, where they have lost their energy via e-ph interaction with the SiO$_2$ lattice. The subsequently generated heat will arrive at the Au SF with a delay, which is related to the thermal diffusivity of the SiO$_2$.

6. Conclusion

In summary, we have demonstrated that the nonlinear absorption of an Au SF at 532 nm can be observed using the thermal properties of the Au SF by means of electrical measurements. This technique facilitates the way to investigate the nonlinear absorption process in semi-continuous metallic films. Scattering of the light from the rough surfaces can potentially cause error in estimating the reflectivity of the sample; we have overcome this problem by directly measuring the temperature increase of the sample. We have employed the 1D heat transport equation to demonstrate the linear absorption process at low laser intensities. At intensities higher than 450 kW/cm$^2$, deviation from the linear behaviour was observed (Fig. 4b). We have compared the value of the temperature variations obtained from the measurements with the values estimated from the theory. We have evaluated $\alpha_2$ as being 3.8x10^{-2} cm/W and 6.8x10^{-2} cm/W at ~600 kW/cm$^2$ and ~700 kW/cm$^2$, respectively.

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