

Surface plasmon enhanced photoconductance of gold nanoparticle arrays with incorporated alkane linkers

M. A. Mangold,^{1,a)} C. Weiss,¹ M. Calame,² and A. W. Holleitner^{1,b)}

¹Physik Department and Walter Schottky Institut, Technische Universität München, Am Coulombwall 3, D-85748 Garching, Germany

²Departement für Physik, Universität Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

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We report on a photoconductive gain effect in two-dimensional arrays of gold nanoparticles (NPs) in which alkane molecules are inserted. The NP arrays are formed by a self-assembly process from alkanethiol-coated gold NPs, and subsequently they are patterned on a Si/SiO₂ chip by a microcontact printing technique. We find that the photoconductance of the arrays is strongly enhanced at the frequency of the surface plasmon of the NPs. We interpret the observation as a bolometric enhancement in the conductance of the NP arrays upon excitation of the surface plasmon resonance. © 2009 American Institute of Physics. [DOI: 10.1063/1.3116148]

The excitation of surface plasmons in two-dimensional arrays of metal nanoparticles (NPs) can lead to a strong enhancement in the electromagnetic field at the surface of the particles at visible and near-infrared wavelengths.¹ Recent experimental and theoretical work on the plasmonic enhancement effect focused on surface enhanced Raman spectroscopy^{2–4} and biosensing applications^{5,6} as well as the photonic band gap⁷ and the photoelectrochemical properties of such NP arrays.⁸ In the context of molecular electronics, densely packed two-dimensional NP arrays have been exploited to electrically contact molecules.^{9,10} Optical studies revealed a strong plasmonic absorption in such NP arrays, where alkanes or conjugated molecules have been inserted.¹¹ Experiments with photochromic molecules, which were immobilized in the NP arrays, showed that the optical excitation of organic photoswitches in NP arrays is possible and that changes in the conductance of the NP arrays due to optical switching of the molecules can be observed.^{12,13} However, an open question remains whether surface plasmon resonances can be exploited to induce charge transport across nanoscale metal junctions with molecules embedded.¹⁴

Here, we experimentally investigate the photoconductance properties of well ordered two-dimensional gold NP arrays consisting of millions of metal junctions in which alkane molecules are incorporated. We measure the photoconductance of the arrays as a function of laser intensity, modulation frequency, bias voltage, spatial coordinates, and wavelength.^{15,16} We find a clear enhancement in the photoconductance at the surface plasmon resonance of the NP arrays. We interpret the findings such that the conductance of the arrays is bolometrically increased when the surface plasmons in the NP arrays are optically excited. We find good agreement between the data and a simple model, which estimates the conductance change of the NP arrays due to an optically induced temperature increase.

Starting point is a two-dimensional array of alkane coated gold NPs. After self-assembly at an air-water interface the arrays are patterned in 25 μm wide stripes on a

SiO₂ chip by a microcontact printing technique.^{17–19} In a shadow mask evaporation step, these stripes are contacted by macroscopic gold electrodes with a separation of ~8 μm, leaving a contacted area with dimensions of 25 × 8 μm². The electrodes are electrically connected to a chip carrier with gold wires using a wedge bonder. The scanning electron microscope (SEM) image in Fig. 1(a) shows a high resolution image of such a NP array. Predominantly, the NPs are arranged in a hexagonal array with a lattice constant of approximately 12 nm and a particle-particle distance of about 2–3 nm.⁹ Figure 1(b) shows a typical room temperature current-voltage characteristic of the NP arrays, which is measured in a two-terminal configuration. The corresponding array exhibits an almost Ohmic behavior in the voltage range from –10 to +10 V with a conductance of 5.1 nS.

All photoconductance measurements are carried out at room temperature in a vacuum chamber at a pressure of about 10^{–5} mbar. Optical excitation occurs by focusing the light of a mode-locked titanium:sapphire laser with a repetition rate of 76 MHz through the objective of a microscope

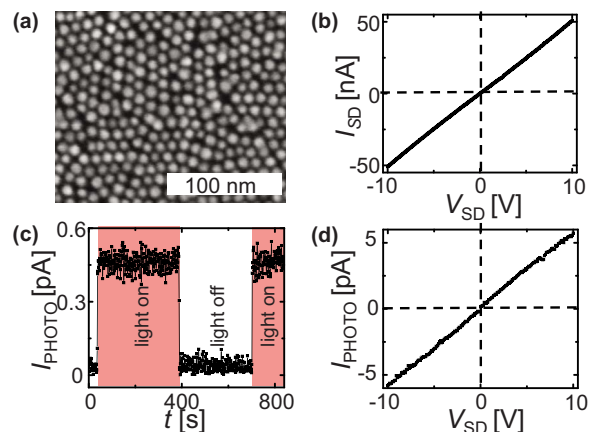


FIG. 1. (Color online) (a) SEM image of an array from gold NPs coated with octane thiols. (b) Current-voltage characteristic of a NP array at room temperature. (c) Optically induced current as a function of laboratory time ($V_{SD}=10$ V, $f_{CHOP}=814$ Hz, $I_{opt}=0.4$ kW/cm², $\lambda_{PHOTON}=620$ nm). The highlighted areas indicate times where the laser light is on. (d) Light induced current as a function of source-drain voltage ($f_{CHOP}=1716$ Hz, $I_{opt}=4.1$ kW/cm², $\lambda_{PHOTON}=620$ nm).

^{a)}Electronic mail: mangold@wsi.tum.de.

^{b)}Author to whom correspondence should be addressed. Electronic mail: holleitner@wsi.tum.de.

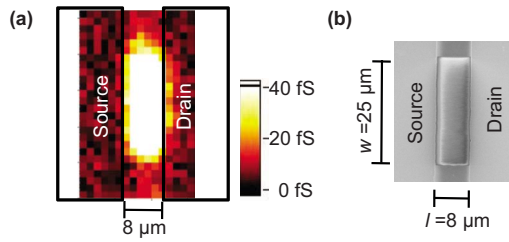


FIG. 2. (Color online) (a) Photoconductance as a function of the laser spot position ($V_{SD}=10$ V, $f_{CHOP}=812$ Hz, $I_{opt}=2$ kW/cm², $\lambda_{PHOTON}=562$ nm). Source and drain electrodes are drawn schematically as a guide to the eye. (b) SEM-graph of a 25 μ m wide stripe of NP array contacted by gold electrodes with a distance of 8 μ m.

onto the NP array. Laser light is available in the spectral ranges from $400 \text{ nm} < \lambda_{PHOTON} < 500 \text{ nm}$ and $550 \text{ nm} < \lambda_{PHOTON} < 1000 \text{ nm}$. With a spot diameter of $\sim 2 \mu\text{m}$ the light intensity I_{opt} is on the order of 1 kW/cm^2 for all wavelengths. For the photoconductance measurements, we chop the laser at a frequency f_{CHOP} . The resulting current is amplified by a current-voltage converter and detected with a lock-in amplifier utilizing the reference signal provided by the chopper. Figure 1(c) depicts the optically induced current I_{PHOTO} measured on a NP array as a function of time, while the laser light is switched on and off. We infer from this measurement that the photoconductance does not change over time even for an illumination period of several minutes. Figure 1(d) shows I_{PHOTO} as a function of V_{SD} . We find that I_{PHOTO} depends linearly on V_{SD} , and we detect no finite value of I_{PHOTO} at zero bias. Thus, the measured signal is due to an optically induced change in conductance, and we use the term ‘‘photoconductance,’’ i.e., $G_{PHOTO}=I_{PHOTO}/V_{SD}$, to describe the observed phenomenon.

In Fig. 2(a), the spatially resolved photoconductance of the area shown in Fig. 2(b) is depicted. To this end, G_{PHOTO} is measured, while the position of the sample is moved in the x - y -plane in steps of $2 \mu\text{m}$. We observe a photoconductance signal clearly above the noise level for an area of exactly the size of the electrically contacted stripes of the NP array. In Fig. 3(a) we show the photoconductance for different excitation wavelengths. We observe a clear maximum of the pho-

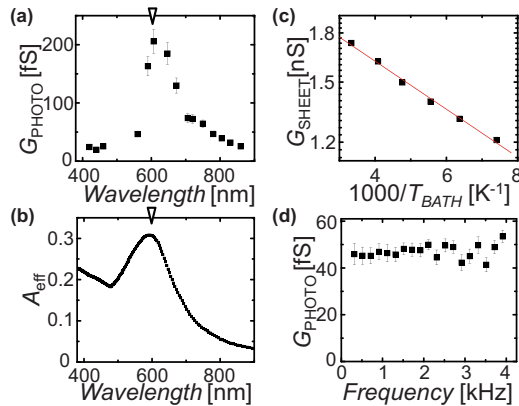


FIG. 3. (Color online) (a) Photoconductance for different excitation wavelengths ($V_{SD}=10$ V, $f_{CHOP}=812$ Hz, $I_{opt}=1.3$ kW/cm²). (b) Calculated absorption spectrum of the NP array according to Eqs. (1) and (2). (c) Logarithmic plot of the sheet conductance of the NP array without laser excitation vs the inverse bath temperature at $V_{SD}=10$ V. (d) Photoconductance as a function of the chopper frequency ($V_{SD}=10$ V, $I_{opt}=0.4$ kW/cm², $\lambda_{PHOTON}=620$ nm).

toconductance at approximately 600 nm [triangle in Fig. 3(a)], which coincides with the surface plasmon resonance of two-dimensional arrays made out of octane coated NPs.¹¹ Therefore, the strong maximum of the photoconductance at that wavelength suggests that surface plasmons play an important role in the creation of the photoconductance.

In order to describe our observations, we start with the Drude–Lorentz–Sommerfeld model where the dielectric function of an isolated Au NP is given by $\epsilon_{NP}=\epsilon_{1,NP}+i\epsilon_{2,NP}$, with $\epsilon_{1,NP}=1-\omega_p^2/(\omega^2+\Gamma^2)+\epsilon_{1,core}$ and $\epsilon_{2,NP}=1-\omega_p^2\Gamma/[\omega(\omega^2+\Gamma^2)]+\epsilon_{2,core}$ as the real and imaginary parts. Here, ω_p denotes the bulk plasmon frequency of gold, and $\epsilon_{1,core}$ ($\epsilon_{2,core}$) is the real (imaginary) part of the core electron contribution to the dielectric response of the NPs. $\Gamma(R_{NP})$ is a size-dependent damping constant, which is given by $\Gamma(R_{NP})=v_F/l_\infty+Pv_F/R_{NP}$, with v_F the Fermi velocity in gold, l_∞ the mean free path of conduction electrons in gold, R_{NP} the NP diameter, and P a proportionality factor.²⁰ The absorption of a two-dimensional layer of NPs in a dielectric medium can be calculated as the absorption A_{eff} of an effective medium and it reads as $A_{eff}=1-e^{-\kappa d_{NP}}$, with $d_{NP}=12$ nm the thickness of a layer of alkane coated NPs and the absorption coefficient²¹

$$\kappa = \omega \text{Im}[\epsilon_{eff}]/(cn_{eff}), \quad (1)$$

where $\hbar\omega$ is the energy of the absorbed photons and c is the velocity of light in vacuum. ϵ_{eff} and $n_{eff}=\text{Re}[\sqrt{\epsilon_{eff}}]$ are the dielectric function and the refractive index of the effective medium. The Maxwell–Garnett effective medium theory predicts^{21–23}

$$\epsilon_{eff} = \epsilon_m \frac{\epsilon_{NP}(\omega)(1+2f) + 2\epsilon_m(1-f)}{\epsilon_{NP}(\omega)(1-f) + \epsilon_m(2+f)}, \quad (2)$$

with ϵ_m the dielectric constant of the medium surrounding the NPs and f the volume fraction of the gold. Following Ref. 11, we use $f=0.34$ for arrays of C8 coated NPs, $\epsilon_m=2.5$ for the alkanes bound to the NPs, and $P=2.0$. In addition, we use $\omega_p=1.37 \times 10^{16}$ Hz,²⁴ $v_F=1.4 \times 10^6$ m/s,²⁵ and $l_\infty=29.4$ nm (Ref. 25) and take the values of $\epsilon_{1/2,core}$ according to Ref. 26. As a result, we obtain an absorption spectrum with a maximum absorption at a wavelength of 595 nm [triangle in Fig. 3(b)], which is consistent with recent measurements.¹¹ Hereby, the calculation corroborates the interpretation that the photoconductance maximum at 600 nm results from a surface plasmon resonance in the two-dimensional gold NP arrays.

In the following, we demonstrate that the photoconductance maximum at the plasmon resonance is consistent with a bolometrically induced conductance. To this end, we show in Fig. 3(c) that an increase in the bath temperature T_{BATH} gives rise to an enhanced (dark) sheet conductance $G_{SHEET}=(dI_{SD}/dV)(l/w)$, with l the length and w the width of the array. We find an exponential dependence of G_{SHEET} on the inverse temperature, as it is expected for a NP array at temperatures above the Coulomb blockade regime.²⁷ From a linear approximation of the measurement at 300 K, we deduce the gradient of the sheet conductance to be $dG_{SHEET}/dT_{BATH}=+2.4$ pS/K. Inspired by a study by Gonorov *et al.*,²⁸ which demonstrates that the heat generation in NPs is strongly enhanced by excitation of the surface plasmon resonance, we calculate the temperature increase in the NP array due to the absorbed light. To that end, we assume

that thermal equilibrium is reached on time scales much shorter than the typical illumination times in our experiment, which will be justified below. We equate the absorbed light intensity $I_{\text{abs}} = A_{\text{eff}} I_{\text{opt}}$ with the heat conducted away from the array through the underlying SiO_2 layer. Since the heat conductivity of SiO_2 is lower by more than a factor 100 compared to the heat conductivity of Si, we do not consider the heat conductance in the bulk of the silicon chip.²⁶ Also, we neglect the heat conductance inside the array due to its small cross section. The heat conductance per unit area of SiO_2 is given by $Q = \lambda \Delta T / d_{\text{SiO}_2}$, with λ the thermal conductivity of SiO_2 , d_{SiO_2} the thickness of the SiO_2 layer, and ΔT the temperature increase in the NP array.²⁹ We evaluate the temperature increase in the NP array at the surface plasmon resonance to be $\Delta T = 0.55$ K (for $I_{\text{opt}} = 1.3$ kW/cm², $A_{\text{eff}} = 0.31$ at 600 nm, $\lambda = 1.1$ W/(m K) for SiO_2 ,³⁰ and $d_{\text{SiO}_2} = 150$ nm). Since the laser spot has a diameter of only ~ 2 μm , we then describe the NP array by four times 12.5 resistors, each of which has an area of 2×2 μm^2 . The resistors are connected in a rectangular lattice geometry. In the experiment, only one resistor at a time is excited by the laser beam, and in turn, its conductance is increased by $\Delta G = (dG_{\text{SHEET}}/dT_{\text{BATH}})\Delta T = (+2.4 \text{ pS/K})0.55 \text{ K} = 1.32 \text{ pS}$. Then we calculate the photoconductance as the difference between the conductance for one resistor being illuminated and the dark conductance, i.e., $G_{\text{PHOTO}} = [3/(12.5G_{\text{SHEET}}) + 1/(12.5G_{\text{SHEET}} + \Delta G)]^{-1} - 12.5G_{\text{SHEET}}/4$. Hereby, we determine the photoconductance value at 600 nm to be $G_{\text{PHOTO}} = 81$ fS. The latter value is of the same order of magnitude as the experimentally determined photoconductance signal of 200 fS at 600 nm [Fig. 3(a)]. The discrepancy between both values can be explained by the fact that the simple model does not consider the rather bad thermal coupling between the NPs and the SiO_2 substrate. Hereby, a further heat accumulation is very plausible.

In Fig. 3(d), we show the photoconductance as a function of the chopper frequency f_{CHOP} . We do not find a dependence of the photoconductance on f_{CHOP} for frequencies between 300 and 4000 Hz. This reveals that the effect causing the photoconductance occurs on a time scale shorter than $\sim (4000 \text{ Hz})^{-1} = 250$ μs . In Ref. 28 it is reported that the heat accumulation in metal NP layers builds up faster than 1 μs . From the complete lack of chopper frequency dependence of the photoconductance, we conclude that the system reaches thermal equilibrium faster than the experimentally accessible time of 250 μs . Finally, we note that the observed photoconductance signal depends linearly on I_{opt} over two orders of magnitudes (data not shown). This observation is consistent with the above interpretation that the photoconductance is caused by a bolometrically enhanced conductance of the NP arrays.

In summary, we report on the photoconductance properties of two-dimensional arrays of gold NPs, which are formed by a combination of a self-assembly process and a microcontact printing technique. The photoconductance of the NP arrays is strongly enhanced through the excitation of

surface plasmons. We interpret the observation by a bolometric enhancement of the conductance of the NP array.

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