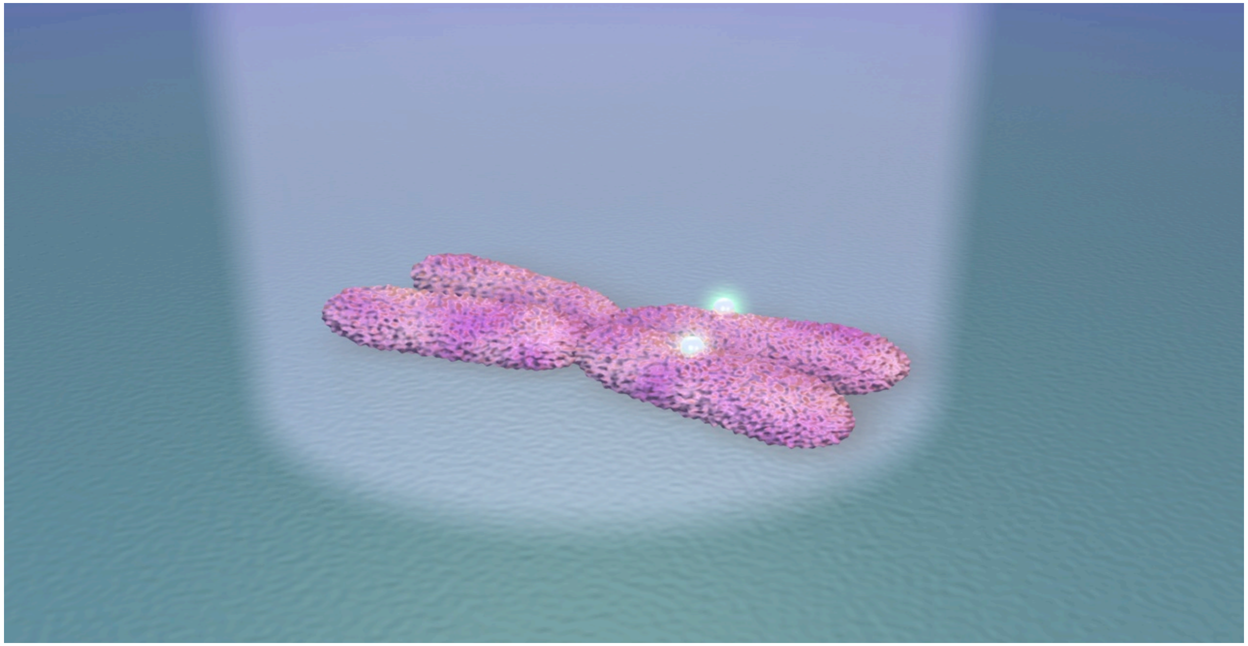
06.07.11

Wechselwirkung von Licht mit metallischen Nanopartikeln in dielektrischer Umgebung



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GLIEDERUNG

1. TEIL: Die Grundlagen - Plasmonen-Polaritonen Resonanz in Metall NP

Intro: Hochlokale und schnelle Temperaturerhöhung - Ablation der NP

2. TEIL: Wirkungen hoher Feldstärken in dielektrischer Umgebung von NP

3. TEIL: Plasmon Polariton Resonanz unterstützte **S**econd **H**armonic **G**eneration (SHG)

4. TEIL: Terahertz Abstrahlung von metallischen Nanostrukturen

Abspann: Coulomb Explosion - Ablation der NP

Summary: ZUSAMMENFASSUNG UND AUSBLICK

1. TEIL: Plasmonen-Polaritonen Resonanz in Metall NP

(Wechsel von Transmission/Reflexion, aber auch Absorption)

Plasmon

In Metallen stattfindende Dichteoszillationen freier Ladungsträger ρ in Ihrem eigenen Feld

$$\frac{\partial^2}{\partial t^2}\rho + g\frac{\partial}{\partial t}\rho + f_p\rho = 0 \qquad f_p = \omega_p^2$$

$$\varepsilon^*(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + ig\omega}$$

gedämpfter Oszillator liefert x(t)

P.B. Johnson, PRB 6, 4370 (1972)

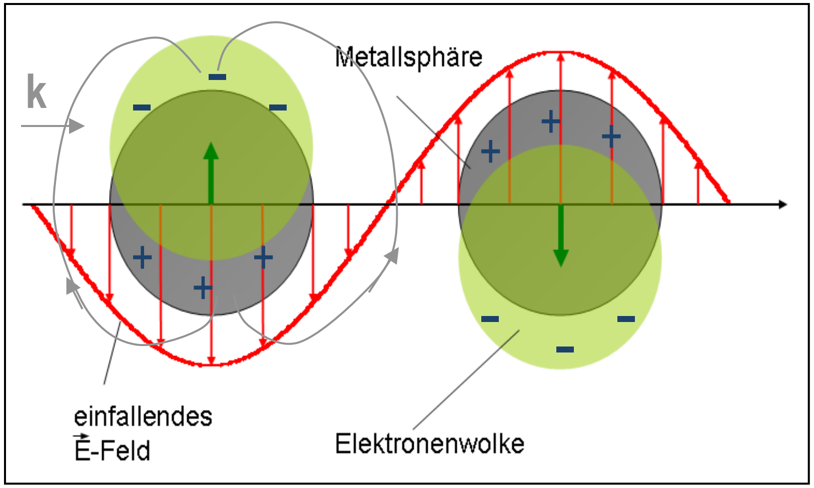
$\omega_p = 6{,}8 \cdot 10^{15}$ s-1 g=2,5*10^{14} s-1

ε' = 0.31 ε'' = 4.84 λ = 530 nm

Partikel Plasmon Polariton

koppelt den Zustand von Photonen mit einer elektronischen Materialanregung

resonantes Verhalten: durch die Beschränkung der Elektronen auf das Partikel

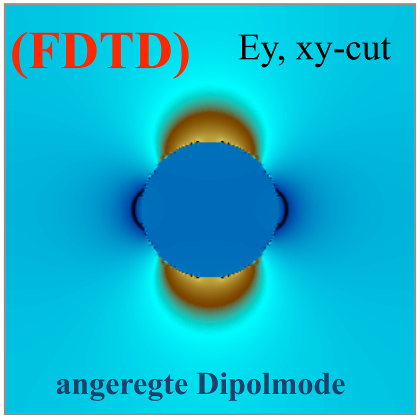


Polarisierbarkeit α einer Kugel in dielektrischer Umgebung ε_a

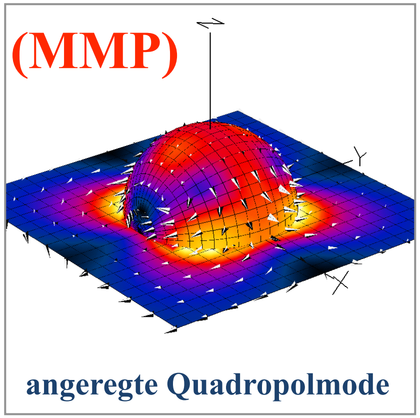
$$\alpha = 3\frac{\varepsilon_p/\varepsilon_a - 1}{\varepsilon_p/\varepsilon_a + 2} = 3\frac{\varepsilon_p - \varepsilon_a}{\varepsilon_p + 2\varepsilon_a}$$

in Resonanz = 0

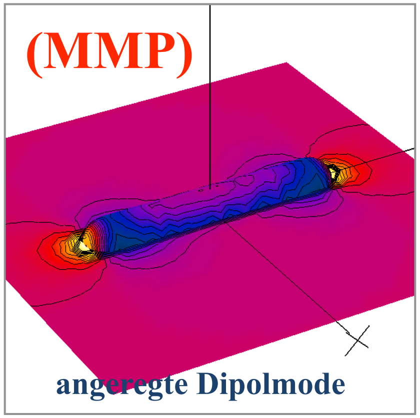
$$2\varepsilon_a + \varepsilon_p(\omega) = 0 \rightarrow \varepsilon_p = 1 - \frac{\omega_p^2}{\omega^2} \rightarrow \omega_R = \frac{\omega_p}{\sqrt{1 - 2\varepsilon_a}}$$



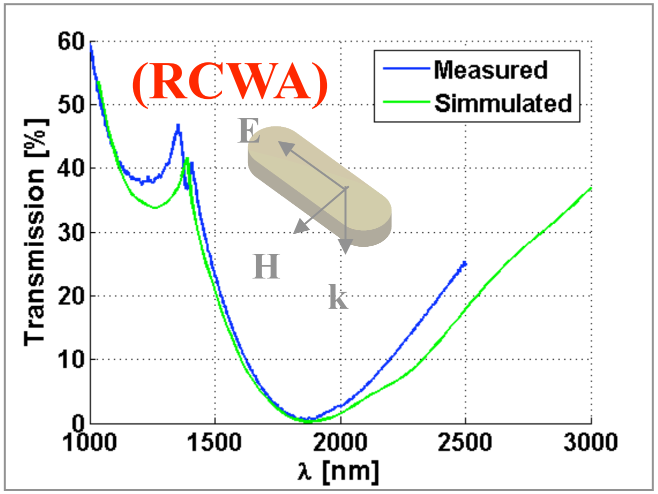
Au-Kugel d=30nm, λ = 530 nm

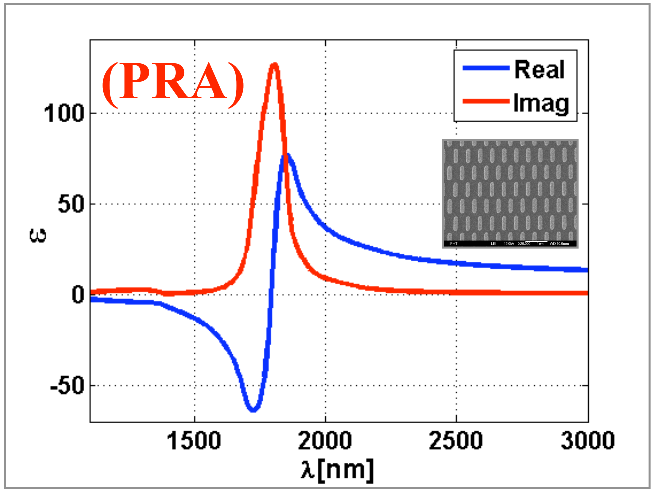


Au-Kugel d=60nm, λ = 550 nm



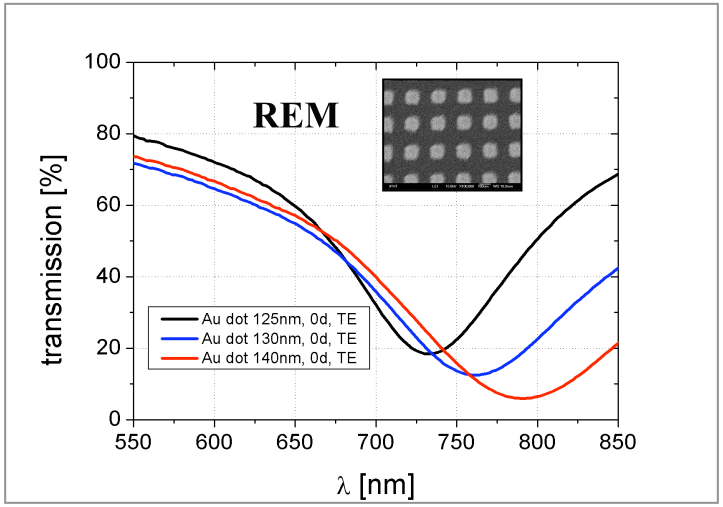
Au-Draht, λ = 1700 nm, E parallel



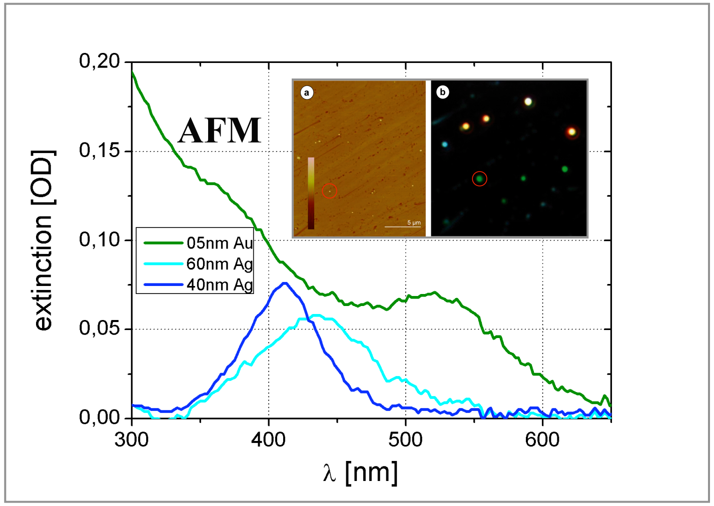


F. Garwe, Appl. Phys. B, 84, p139 (2006)

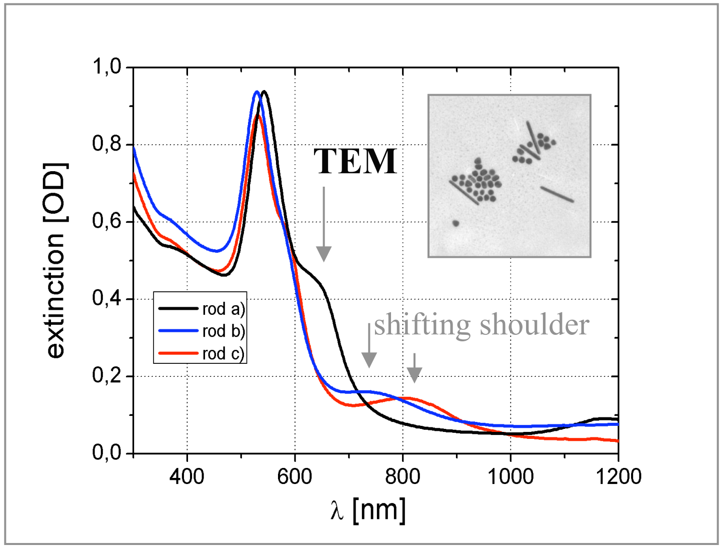
size



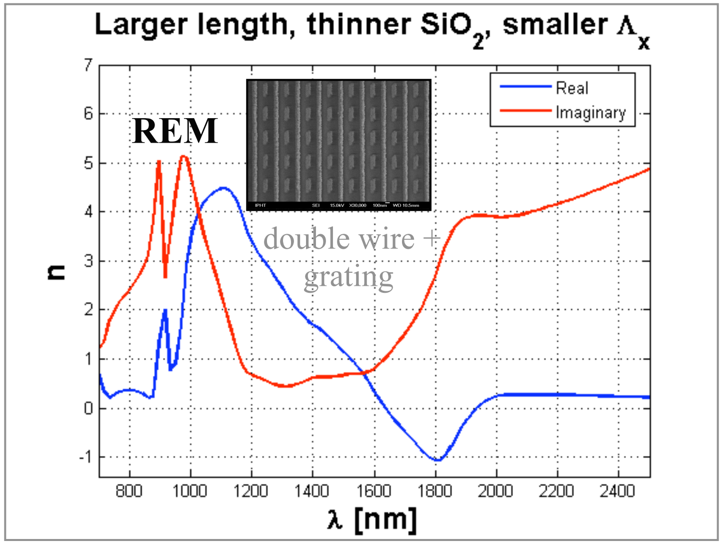
kind of metal



shape

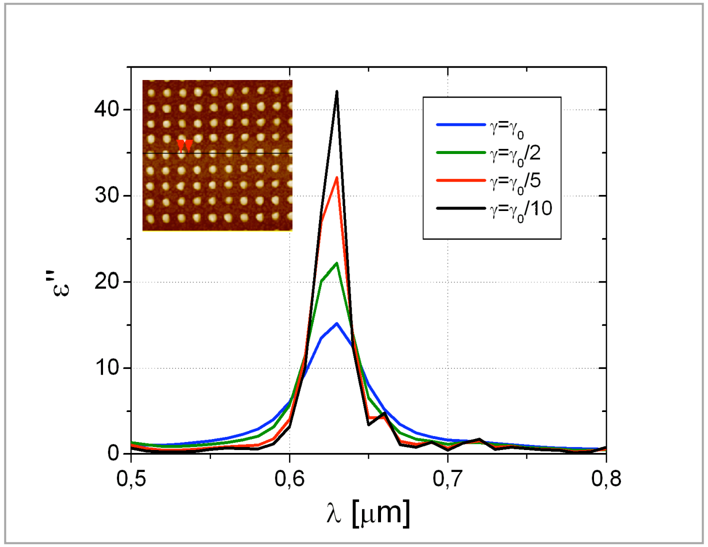


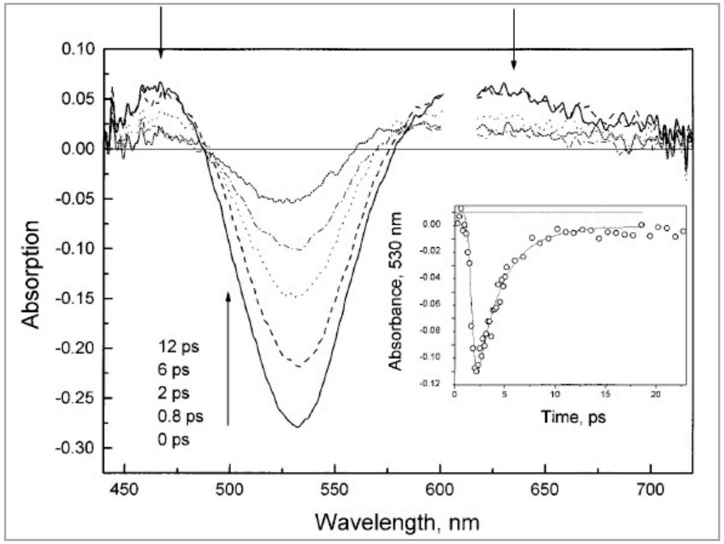
composition



A. Csáki et. al. In *Gold Nanoparticles: Properties, Characterization and Fabrication*, Chow, P. E., Ed. Nova Science Publishers: 2010.

F. Garwe, Appl. Phys. B, 84, p139 (2006)





Mie: interaction of nanoparticle with light: resonance -> **problem:**
Kramers-Kronig: in resonance – high imaginary part of material parameters too
Drude: damping mechanism is loss of phase coherence of collective electron oscillation caused by e^- - e^-, e^- -phonon-,e^- -defect- and e^- -surface scattering **->** rise of electron temperature, e^--phonon collision form new thermal equilibrium
-> **phase destruction** of amplified evanescent wave **->** unvafourable for image below the Abbe limit
-> **no** significant **improvement** by **deep temperatures** (4K) and metalic **single crystal** structures

How we can use a high damping mechanism for another applications?

increase damping by nonlinear interaction
-> fs-laser pump-probe experiments on 30 nm gold nanoparticles show **27% transient absorption** [1]

[1] S.L.Logunov, El-Sayed et al., J. Phys. Chem. B **101** p3713 (1997)

Intro: hochlokale und schnelle Temperaturerhöhung – Ablation der NP

(eine Folge der hohen Absorption in Resonanz)

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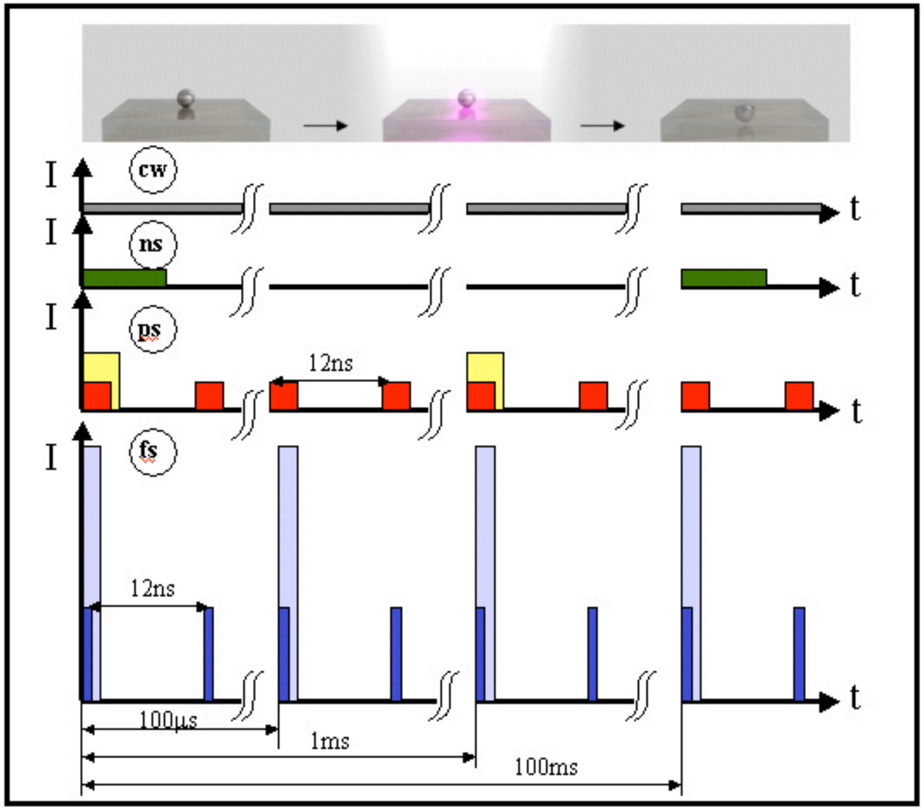


ns - Laserparameter für Ablationsschwelle

$P = 0.8$ W
$E_p = 80$ mJ
$F = 200$ mJ/cm^2
$P_p = 25$ MW/cm^2

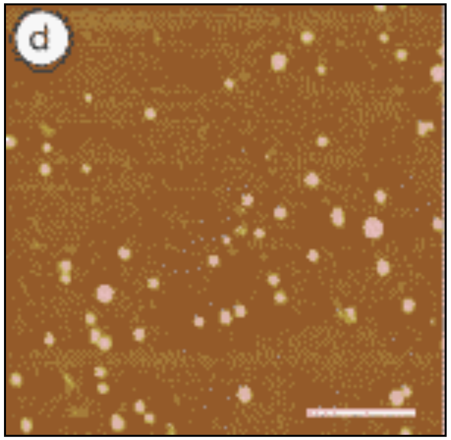
ps – Laserparameter für Ablationsschwelle

$P = 70$ mW
$E_p = 0.7$ µJ
$F = 100$ mJ/cm^2
$P_p = 300$ MW/cm^2

fs - Laserparameter für Ablationsschwelle Nanopartikel

P = mittlere Leistung [W]	1W	(cw Laser)
E_p= Pulsenergie = P/f [J]	5 nJ	(Pulswiederholrate)
F = Fluenz = Energiedichte/Puls = P/A*f [J/cm^2]	3 mJ/cm^2	(Fokusierung)
P_p= Leistungsdichte/Puls = F/tp [W/cm^2]	30 GW/cm^2	(Pulslänge)

AFM picture bevor laser radiation:

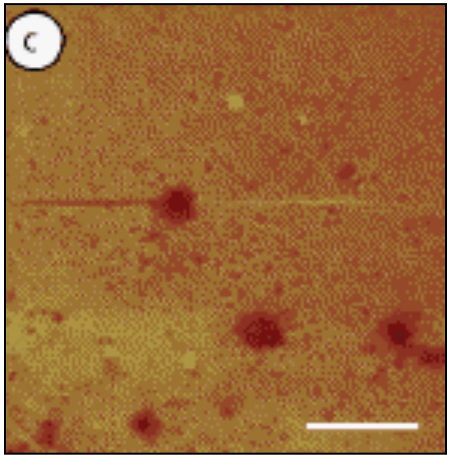


d) 30nm Au NP on top of a 50 nm e^- and T sensitive PMMA layer

c) hot fragments of NP sink into PMMA

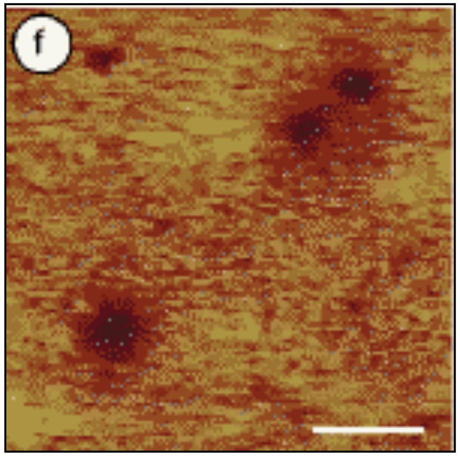
f) hot fragments of NP sink into PMMA,
fragments smaller and nearby former NP

8 ns, 350mJ/cm^2



Thermische Ablationsschwelle:
200mJ/cm^2

35 ps, 240mJ/cm^2



Thermische Ablationsschwelle:
100mJ/cm^2

heat equation

$$\rho\, C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = q$$

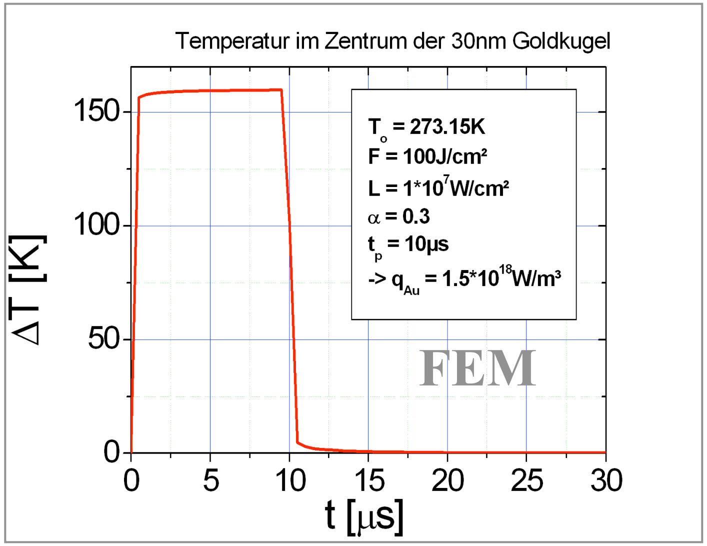
domains: Au NP (sphere with r=15nm), H_2O arround the Au NP

boundary between the two subdomains

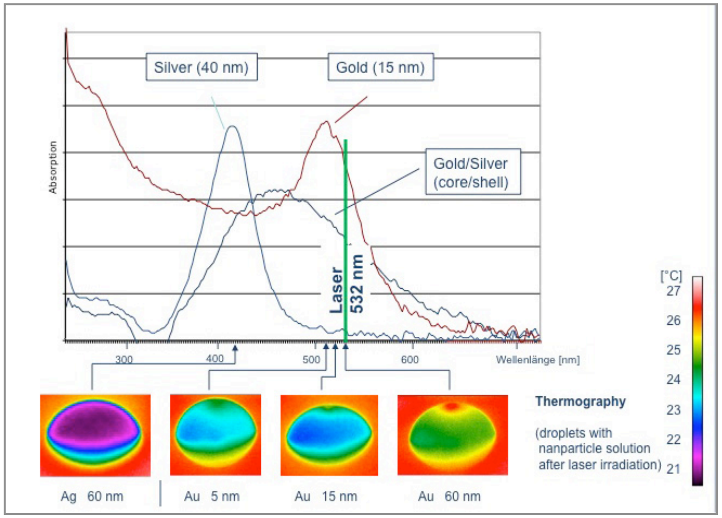
$$-\mathbf{n}_{Au} \cdot (-k_{Au} \nabla T_{Au}) - \mathbf{n}_{H2O} \cdot (-k_{H2O} \nabla T_{H2O}) = 0$$

- conductive heat transfer from Au NP -> H_2O starts during the laser pulse

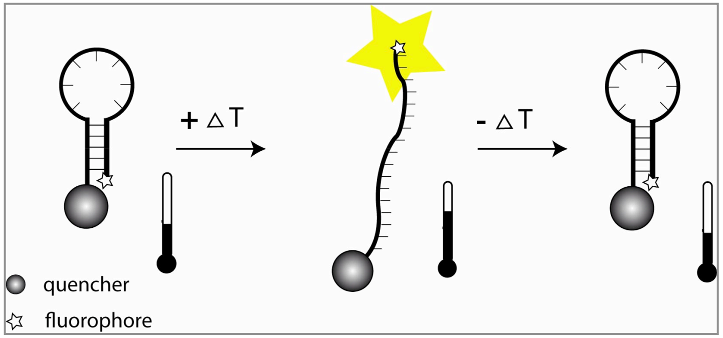
ρ - density, c_p – heat capacity, k – thermal conductivity,
q – heat source



t_p=10µs, λ=532 nm , F=100J/cm² , $T_e = T_l$
-> $T=T_0$+**160K**, 200 nm surrounding

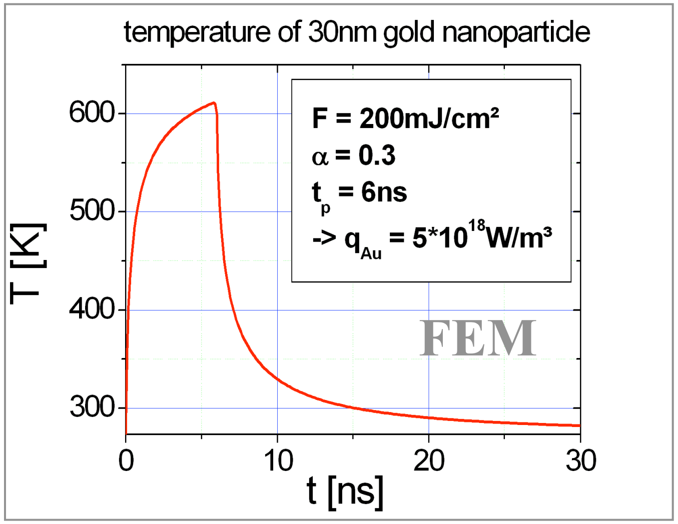


cw, λ=532 nm, 25mW, d=0.2mm, F=830 000 J/cm²
-> $T=T_0$+**4K**, the complete medium in the laser focus



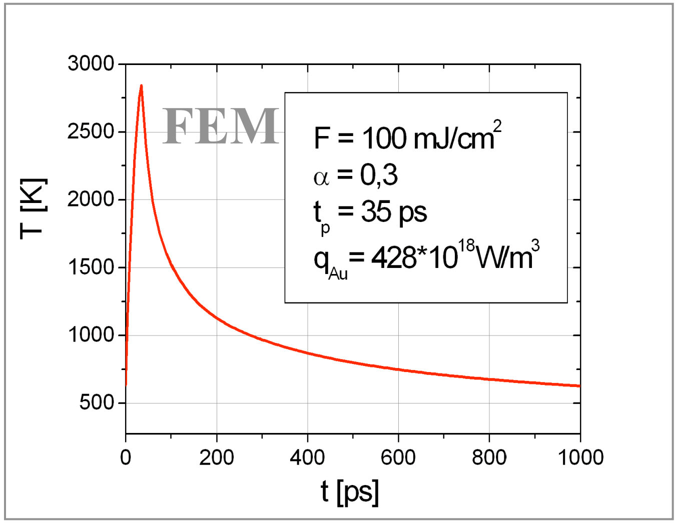
Prinzip der optisch schaltbaren Fluoreszenzsonden

-> NP 10µs erwärmt -> Dissoziation DNA Doppelstrang
-> gequenchtes Fluorophor kann fluoreszieren



t_p=6ns, λ=532 nm, F=200mJ/cm²

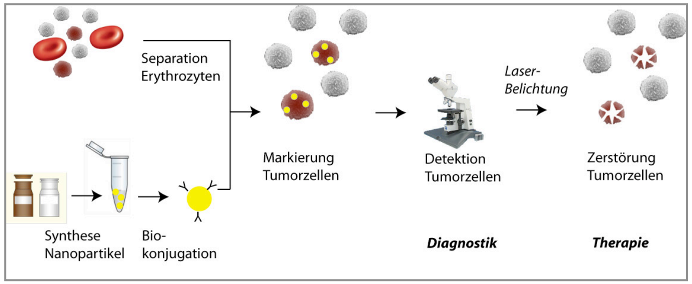
-> $T=T_0$ + **330K**, 70nm surrounding, after 100 ps heat cond.



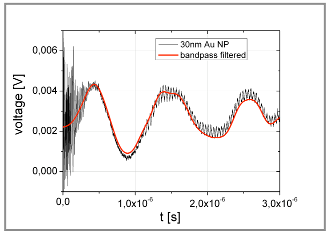
t_p=35ps, λ=532 nm, dec. F=100mJ/cm²

-> $T=T_0$+**2700K**, **(to high ->c_e(T)!!)** 70 nm surrounding,

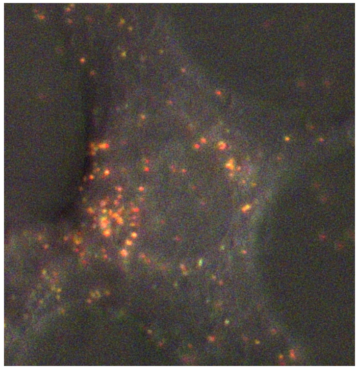
-> during pulse no heat conductance (10nm)



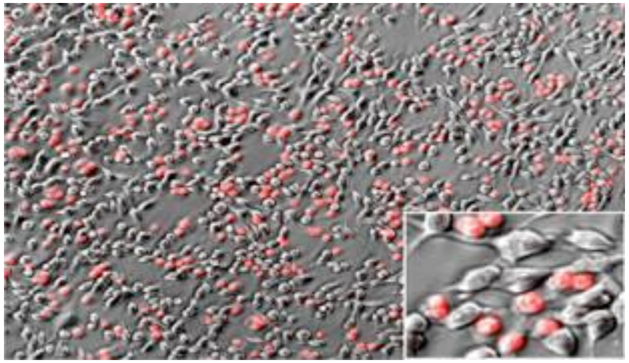
NP-basierte Therapie von Tumozellen im Blut



Drucksignal (PVDF Folie + Verstärker) von Au NP in H_2O nach 6ns Laserpuls bei 532 nm

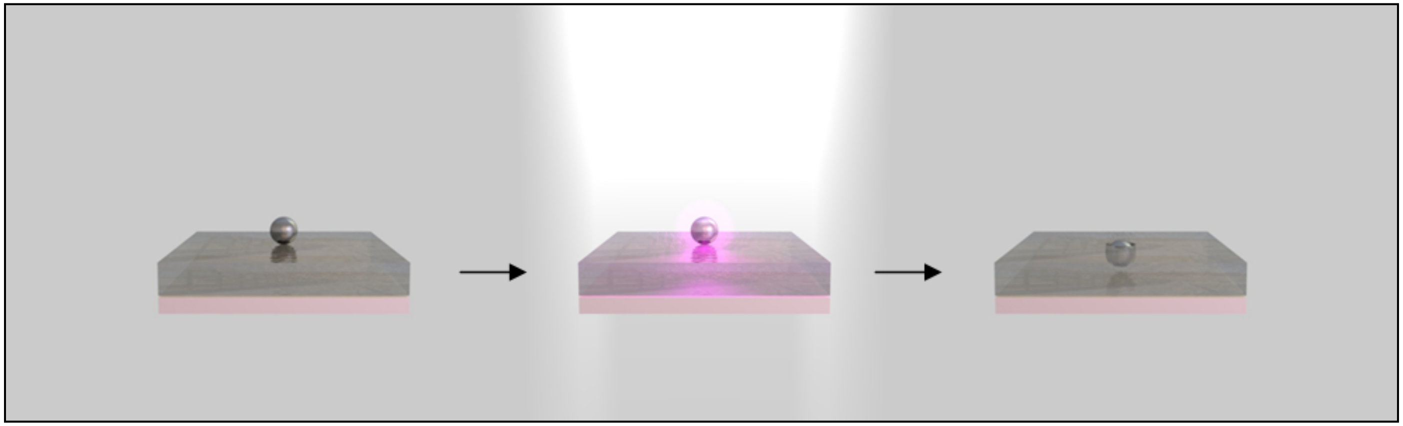


80nm Au NP auf adherenten Zellen

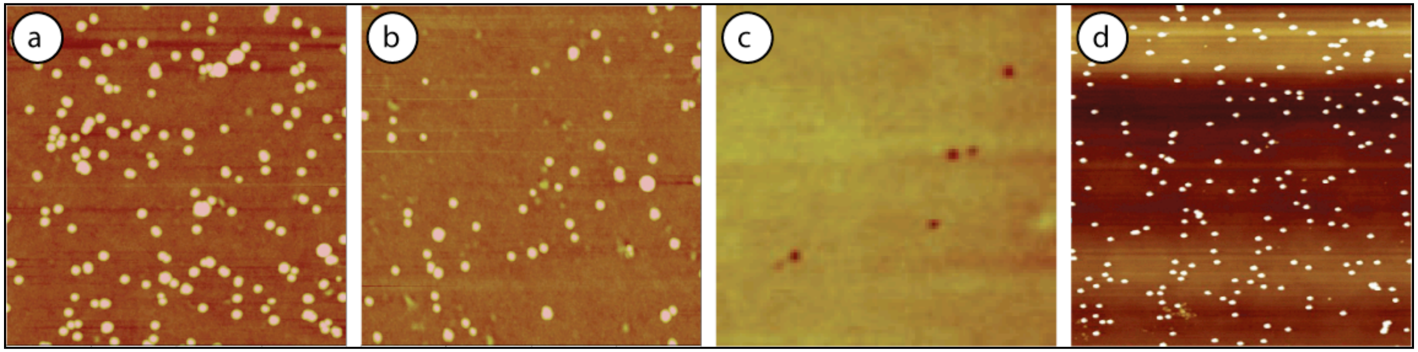


selektive Zerstörung von adhärenten Zellen in einer Mischkultur mittels laserbestrahlter Au NP

F. Levold, E. Endl, IMMEI, Universitätsklinik Bonn



several laser parameters on 30 nm Au NP



F = 2,8 mJ/cm2 t = 100 µs cw no sinking	F = 2 ,8 mJ/cm2 t = 3 ps f = 76 MHz no sinking	F = 2,8 mJ/cm2 t = 100 fs f = 76 MHz **sinking** (dark regions)	F = 2,8 mJ/cm2 t = 100 fs f = 76 MHz **no ablation** (section analysis)

c) warming of Au NP - surrounding near to T_g so viscosity changes, particles sinking ???

relaxation dynamics of the electron temperature

electron-phonon coupling model

thermal diffusion — electron-phonon coupling — optical excitation

$$c_e(T_e)\frac{\partial T_e}{\partial t} = \kappa\,\Delta T_e - G\,(T_e - T_l) + P(t)$$

$$c_l\,\frac{\partial T_l}{\partial t} = G\,(T_e - T_l)$$

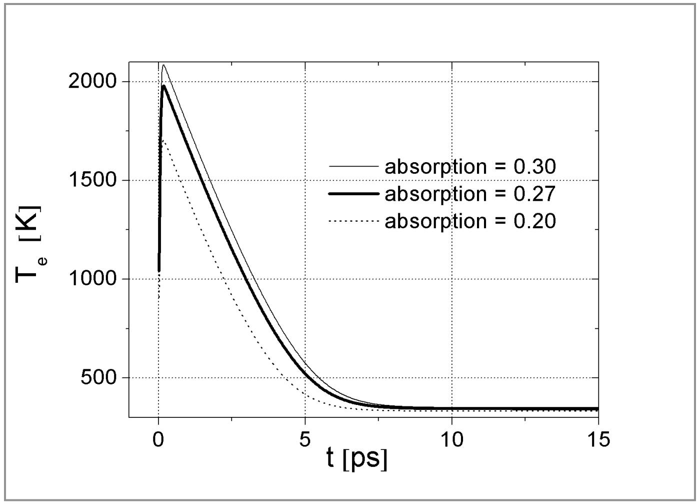
electronic heat capacity	$c_e = c_0 T_e$, $c_0 = 66 J/m^3K^2$	[1]
lattice heat capacity	$c_l = 3x10^6 J/m^3K$	[2]
electron-phonon coupling constant	$G = 3x10^4 J/psm^3K$	[2]
transient absorption	A = 27%	[3]
thermal conductivity losses to matrix	$\kappa\Delta T_e = 0$	
excitation energy density per unit time and unit volume	P(t)	

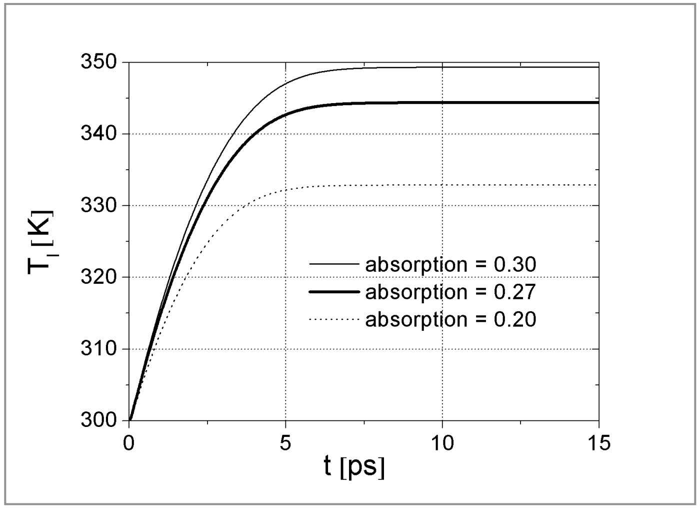
-> absorption of photons by electrons (100 fs), electron-phonon relaxation (10 ps) and phonon-phonon relaxation (100 ps) are separated in time

-> during fs-pulse: no time for plasma development, heating diffusion into material is negligible

[1] K.L. Kelly et al. J.Phys.Chem. B **107** p668 (2003)
[2] R. Groeneveld et al. PRB **51(17)** p11433 (1995)
[3] S.L.Logunov et al. J.Phys.Chem. B **101** p3713 (1997)

results: electron-phonon coupling model





- electron temperature very high (2000 K, 5 ps relaxation time)
- lattice temperature increase to 344,5 K in 5 ps

+ heat of electrons in nanoparticle is fast and effective (cold ions can absorb more photons)
- reduced ablation threshold (3 mJ/cm^2)

F.Garwe, Nanotechnology **19**, p.55207,(2008)

heat equation

$$\rho\, C_p \frac{\partial T}{\partial t} + \nabla\cdot(-k\nabla T) = q$$

domains: gold np (truncated sphere with r=15nm without a cup of 5nm)
PMMA matrix as cuboid of 200 by 200 by 100 nm

boundary between the two subdomains

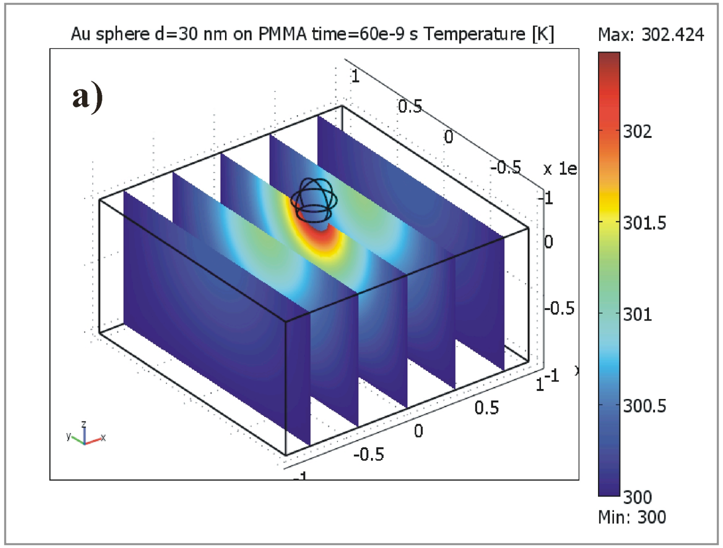
$$-\mathbf{n}_{Au}\cdot(-k_{Au}\nabla T_{Au}) - \mathbf{n}_{PMMA}\cdot(-k_{PMMA}\nabla T_{PMMA}) = 0$$

top boundaries: external natural cooling conditions

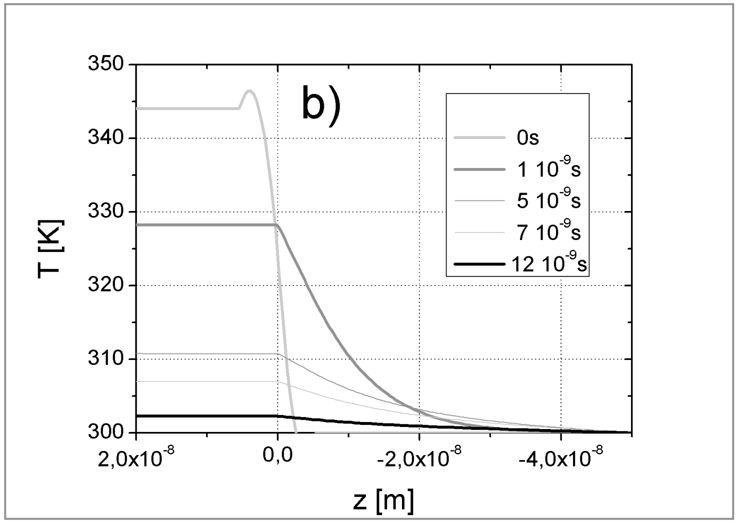
$$-\mathbf{n}\cdot(-k\nabla T) = h(T_{\inf} - T)$$

$$h = 0.54\, F_{lam}\left(\frac{\Delta T}{L}\right)^{0.25} \qquad F_{lam} = k\left(\frac{Ra}{L^3\Delta T}\right)^{0.25}$$

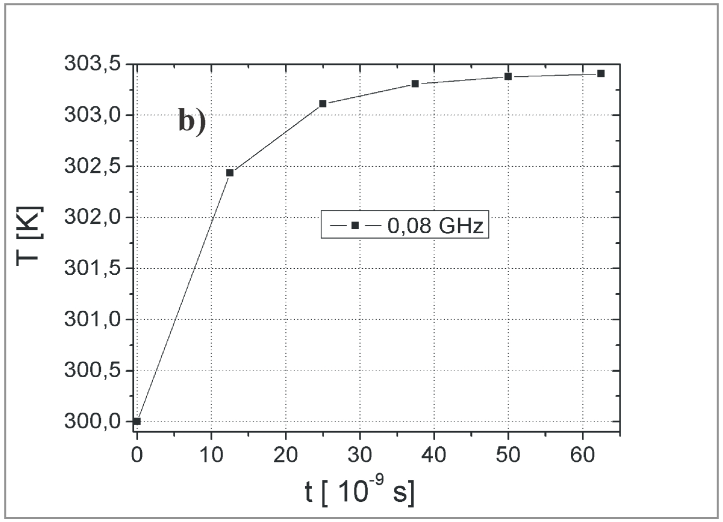
h = horizontal surface Ra = Rayleigh number L = characteristic length



conductive heat transfer from gold np -> PMMA starts after equilibrium of electron gas with lattice



temperature increase of PMMA is very local (40 nm), caused by low heat capacity of nanoparticle



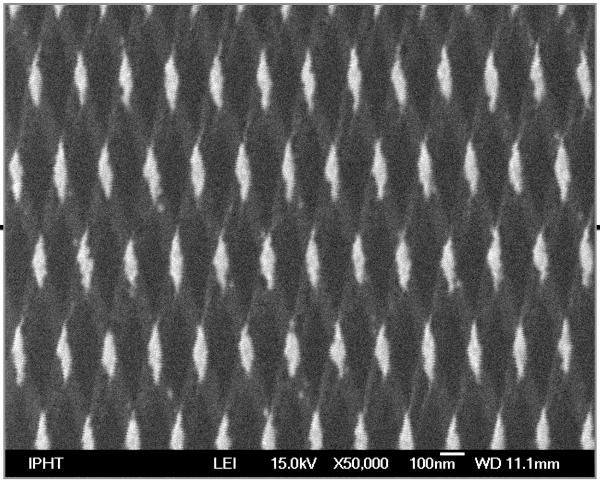
at the end of the period between two fs-laser pulses (12 ns) is a small temperature increase of PMMA and nanoparticle

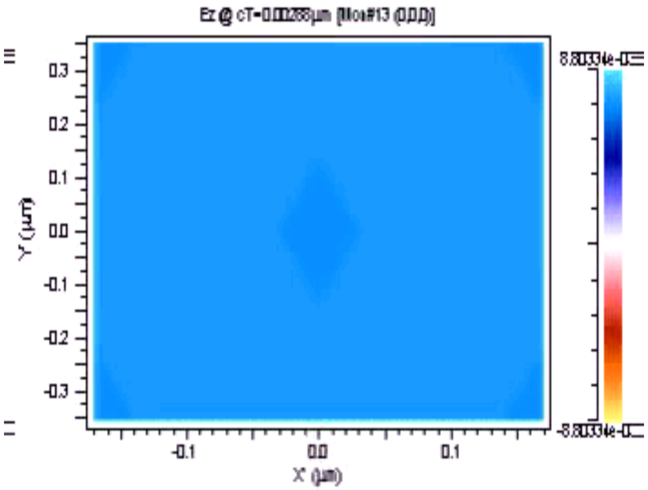
3. TEIL: Wirkungen hoher Feldstärken in dielektrischer Umgebung von NP

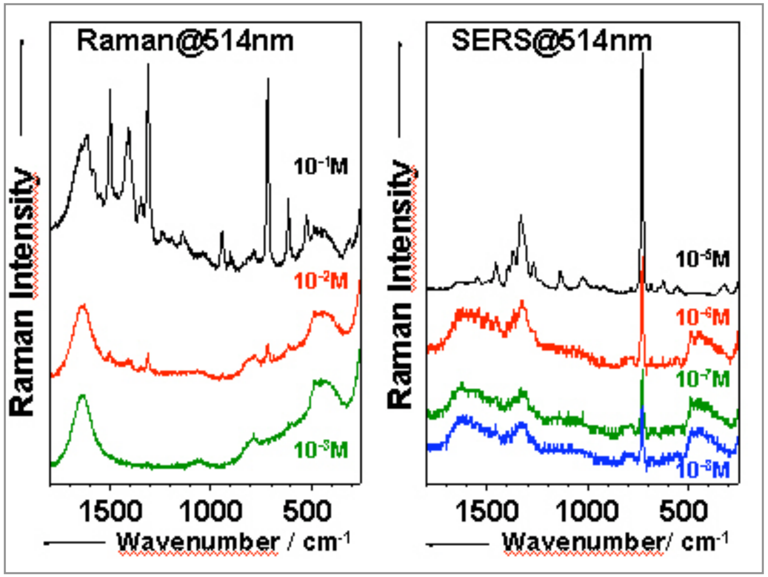
(eine Folge der Anregung von Metall NP mit fs Laserpulsen)

FDTD:

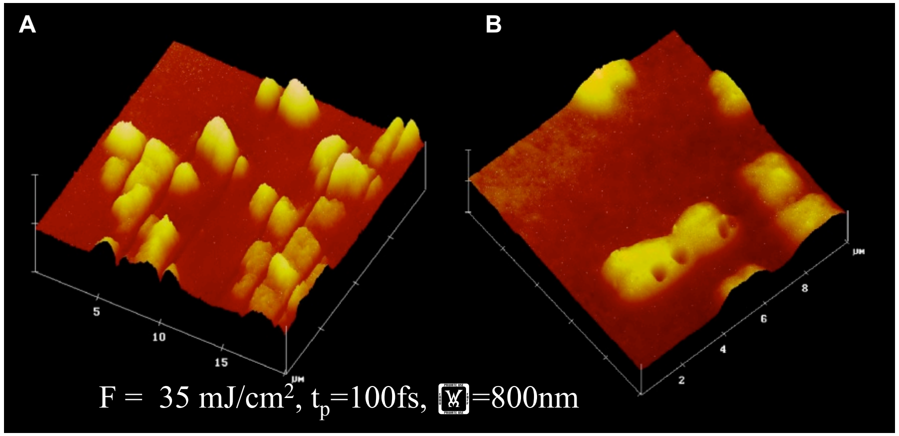
Routenstrukturen (r=5nm) $\boxed{f = \frac{\vec{E}}{\vec{E}_0}}$ = 13





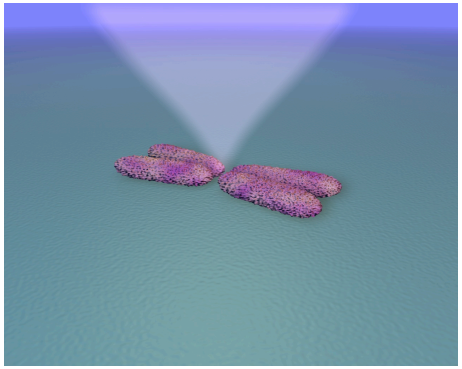


D. Cialla, CemPhysChem 4,9(5), p758 (2008)

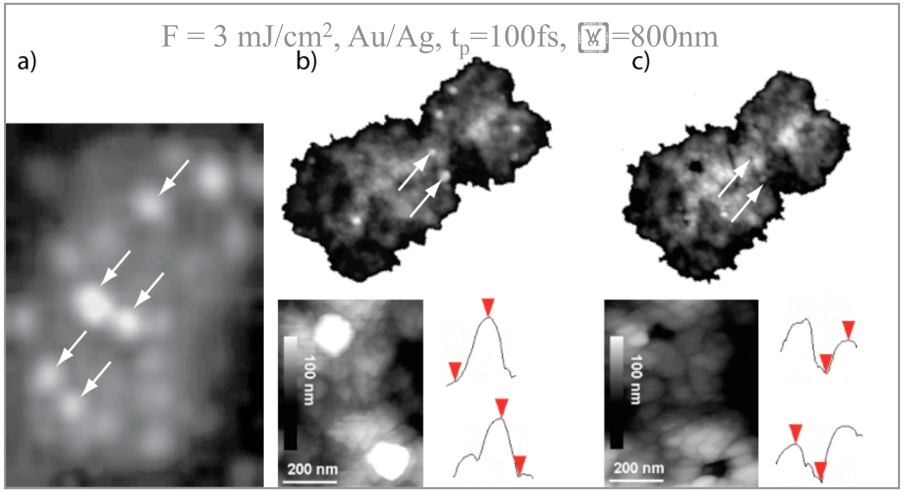


$F = 35\ \mathrm{mJ/cm^2}$, $t_p=100\mathrm{fs}$, $\lambda=800\mathrm{nm}$

destruction of chromosomes without NP in an unspecific way

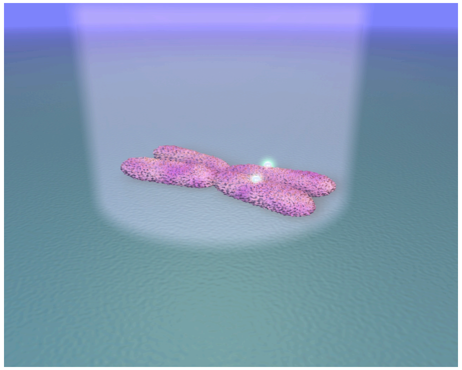


multiphoton excitation of electrons
in molecules takes place,
minimal destruction 100nm



$F = 3\ \mathrm{mJ/cm^2}$, Au/Ag, $t_p=100\mathrm{fs}$, $\lambda=800\mathrm{nm}$

destruction of chromosomes nearby the NP in a specific way

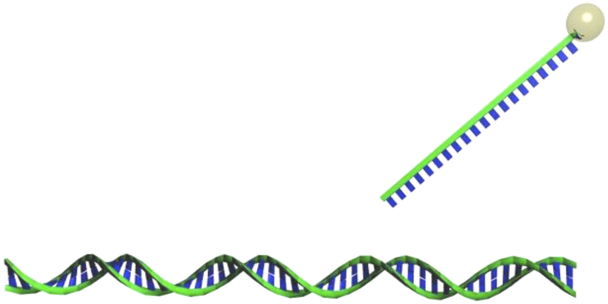


reduction of the laser pulse fluence
below the unspecific destruction limit
of chromosomes
using chromosomes with specific
bound NP

F.Garwe et. al., Nanotechnology **19**, p.55207,(2008)

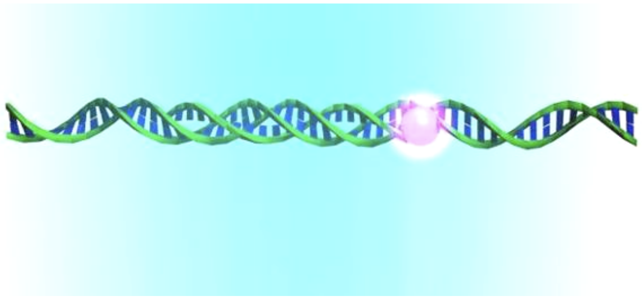
ZIELSTELLUNG

1 Konjugation von Nanopartikel an sequenz-spezifische Oligonukleotide

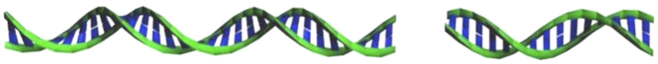


2 Hybridisierung der modifizierten Oligonukleotide an die Zielsequenz

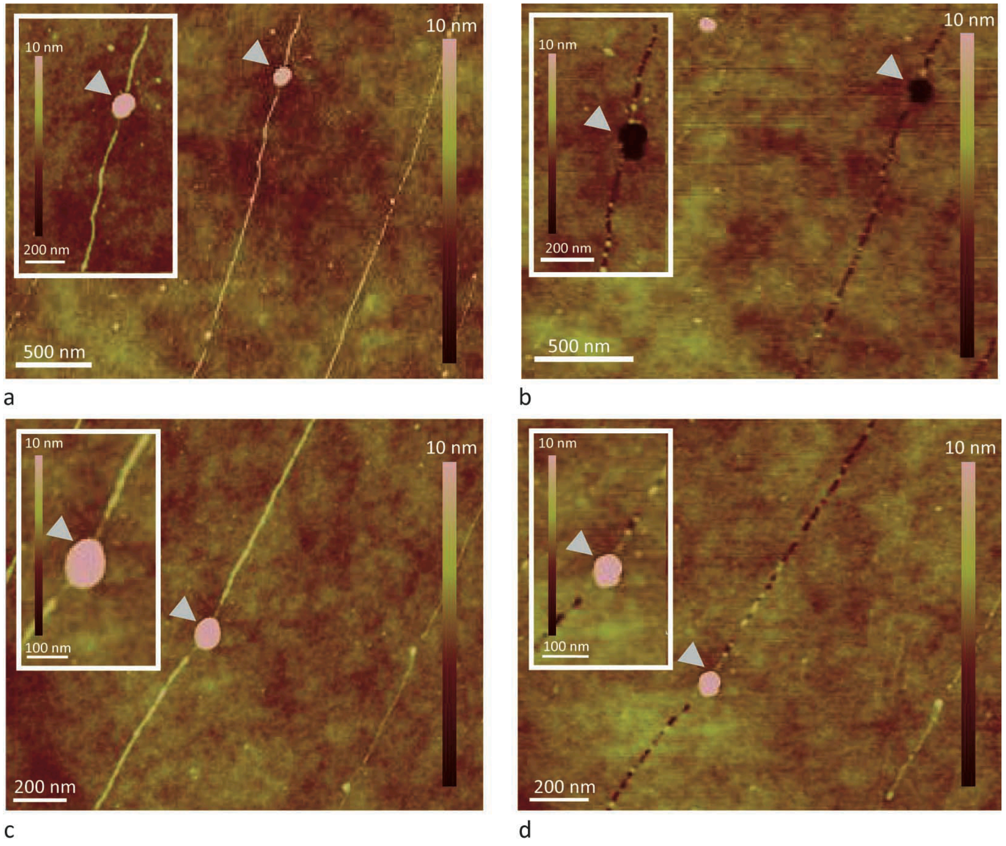
3 Sequenzspezifisches Schneiden der DNA an den markierten Stellen durch Laserstrahlung



4 Ergebnis: Geschnittenes DNA-Molekül

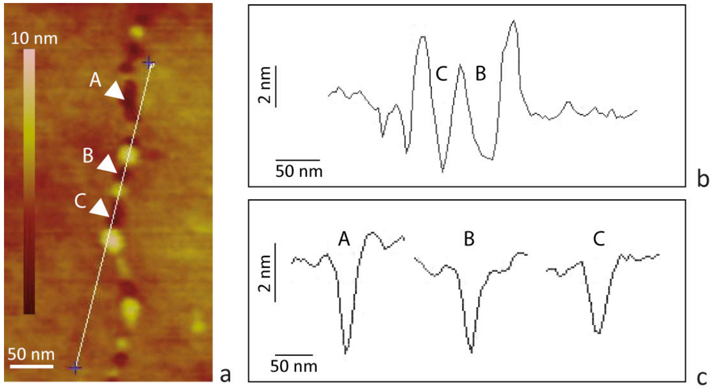


Ist es möglich DNA-Moleküle spezifisch an den markierten Stellen zu schneiden?



Zerstörung PMMA um NP
PMMA Zerstörung entlang DNA
DNA Zerstörung d = 90 nm

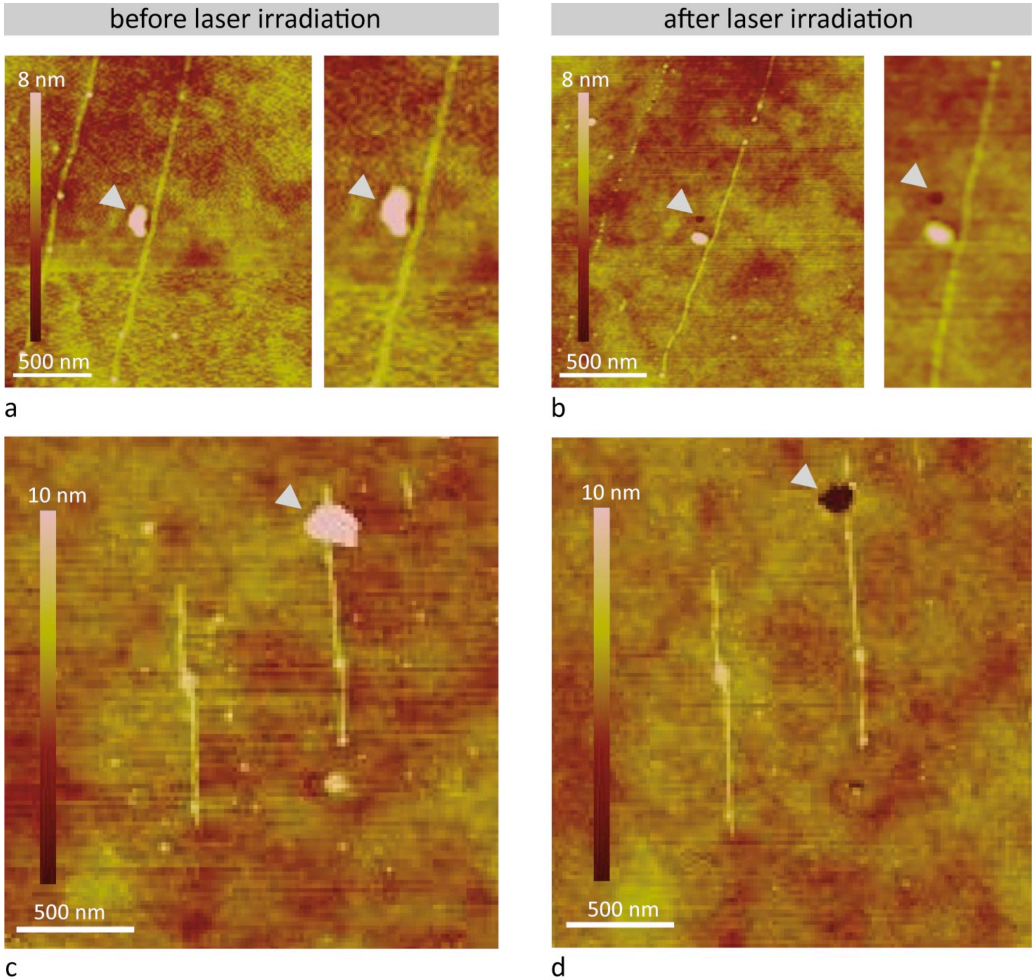
PMMA Zerstörung entlang DNA
DNA Zerstörung d = 90 nm



DNA Bündel
Tiefe 3 nm
Höhe 3 nm
Breite 15 nm

Ergebnisse reproduzierbar !

J. Wirth et. al. Nano Lett. submitted

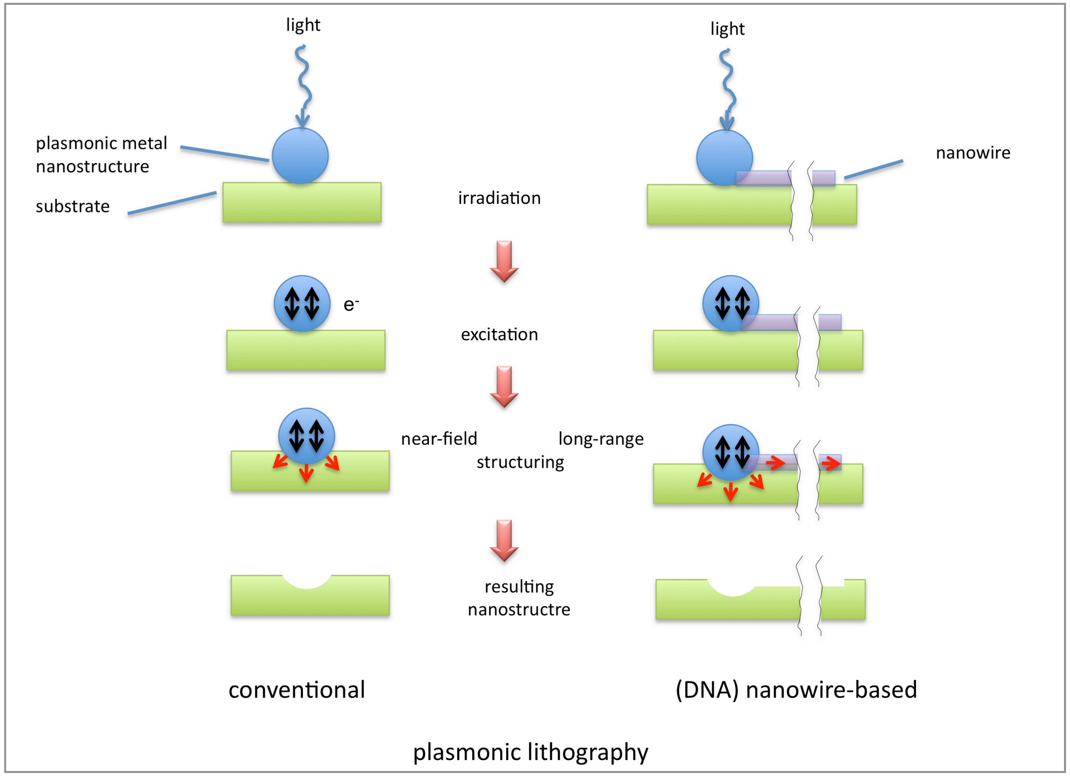


D (NP-DNA) > 100 nm

D (NP-DNA) < 30 nm

-> keine PMMA Zerstörung entlang der DNA
-> Kopplung an DNA sehr Abstands sensitiv

J. Wirth et. al. Nano Lett. submitted



plasmonic lithography

Hypothese:

a) e^- des NP überwinden Austrittsarbeit oder hohen Felder an NP bewirken Zerstörung umgebender PMMA Moleküle und Übertragung e^- Impuls auf DNA Basen Paare, wo Impuls weitergeleitet wird und umgebende PMMA Moleküle ebenfalls zerstört werden

b) nichtlinear angeregte e^- im NP kann man als Licht auf der Nanoskala sehen, dieses koppelt in die DNA, wo es dann propagiert. Das UV Licht zerstört PMMA Molekülbindungen

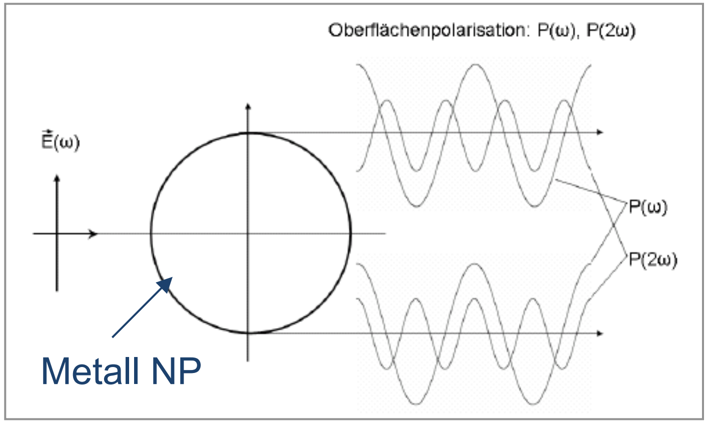
-> **neues Projekt, wo unter anderem dieses Phänomen auf der molekularen Ebene beschrieben werden soll**

4. TEIL: Plasmon Polariton Resonanz unterstützte **S**econd **H**armonic **G**eneration (SHG)

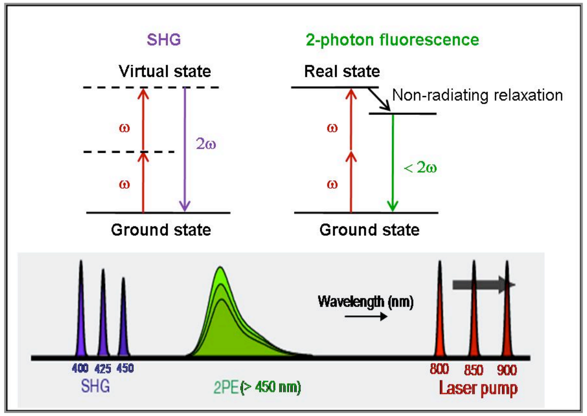
(wenn die Laserfelder in den Bereich der Feldstärken für die Atombindungen kommen)

$$\vec{P} = \varepsilon_0(\chi^{(1)}\vec{E} + \chi^{(2)}\vec{E}^2 + \dots$$

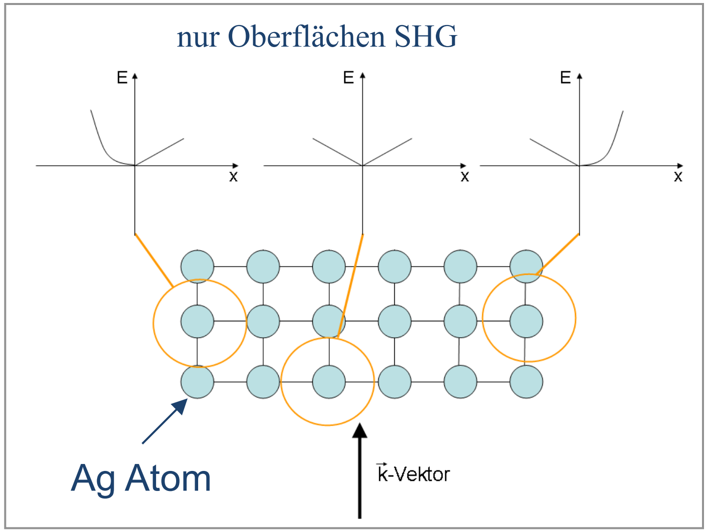
aber: $c^{(2)}_{36}{}^{KDP} = 1.1 \cdot 10^{-23}$ [As/V^2], → E muss groß



da der NP Durchmesser << λ → asym. NP

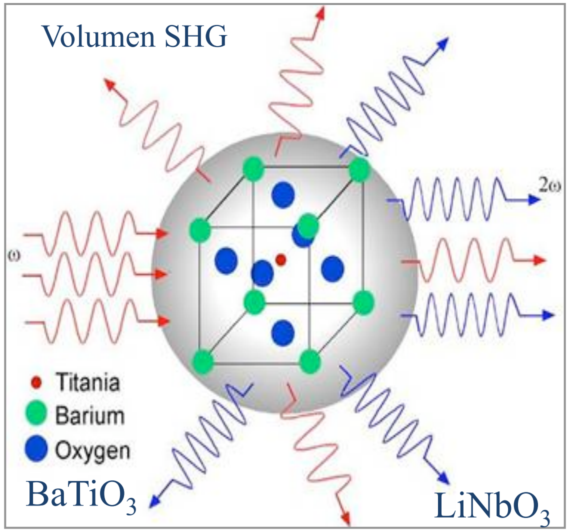


SHG und Fluoreszenz möglich



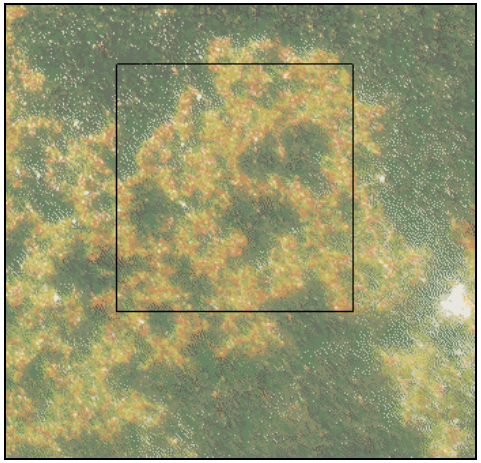
$$I(2\omega) \propto |f(2\omega)|^2 |f(\omega)|^4 I(\omega)^2 \rightarrow f = \frac{\vec{E}}{\vec{E}_0}$$

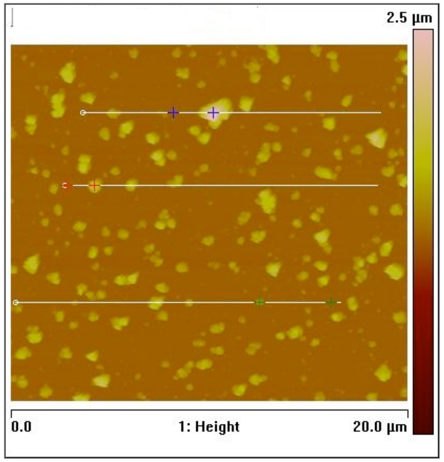
aber: Plasmonenresonanzverstärkung der SHG



$$I(2\omega) \propto I(\omega)^2$$

aber: Volumen SHG





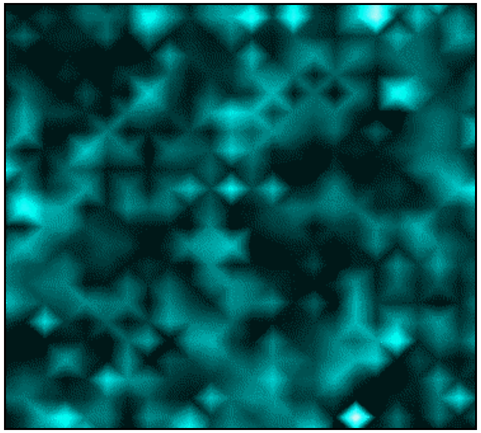
Parameter:

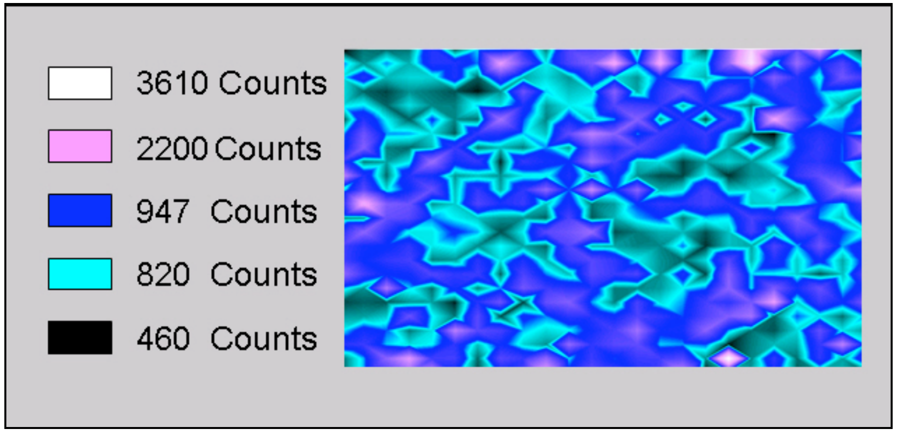
- λ=800nm, f=76MHz,
- 40iger Objektiv -> d = 3 µm
- F=5,6mJ/cm^2

- 26 x 26 Pixel Tischscanning
- Interferenzfilter 400 nm
- Kurzpassfilter 800nm OD8
- 500 µm Blende
- (konvokales Mikroskop)
- APD, SEV + Counter

Dunkelfeldmikroskopie:

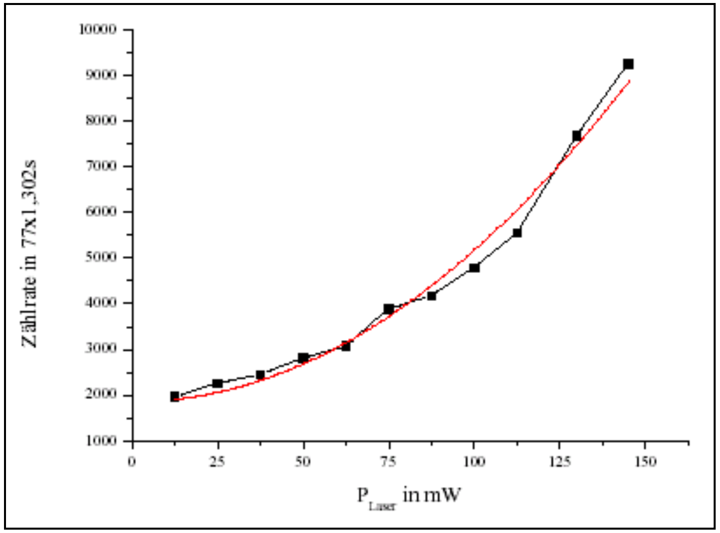
AFM: Nanocluster aus 25nm Ag
Clustergröße: 100 nm – 500 nm



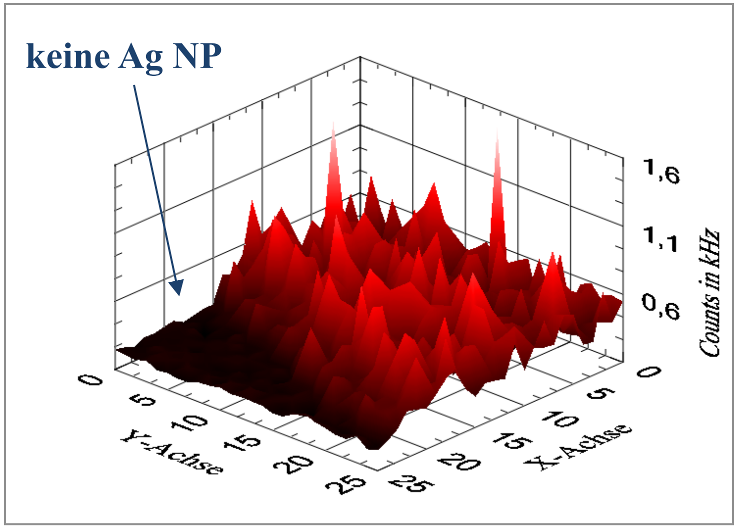


SHG Signal (Schwellwert 947 counts)

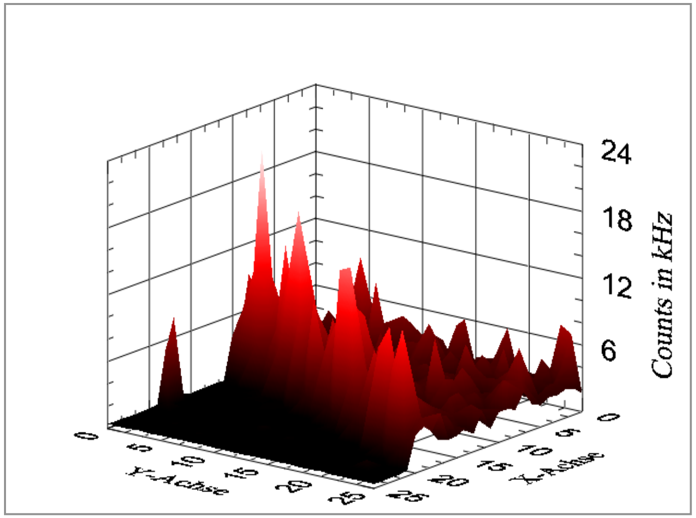
Mehrfalschfarbendarstellung SHG Signal



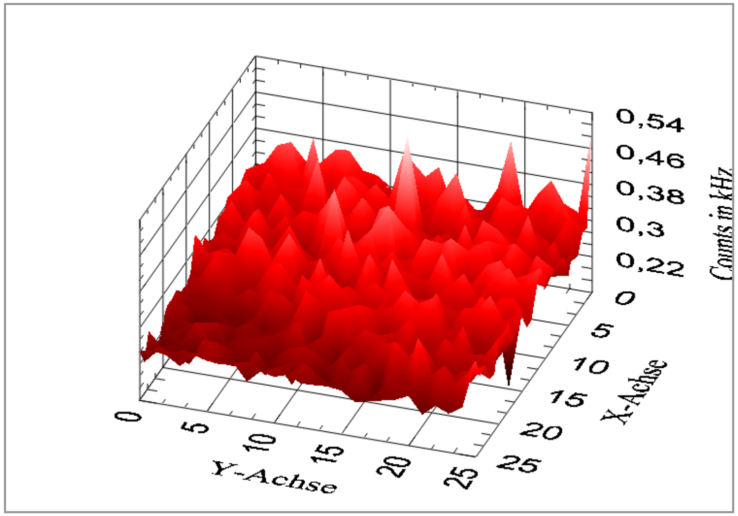
quadratische Abhängigkeit der Zählrate von Laserleistung


keine Ag NP

SHG nach der Herstellung

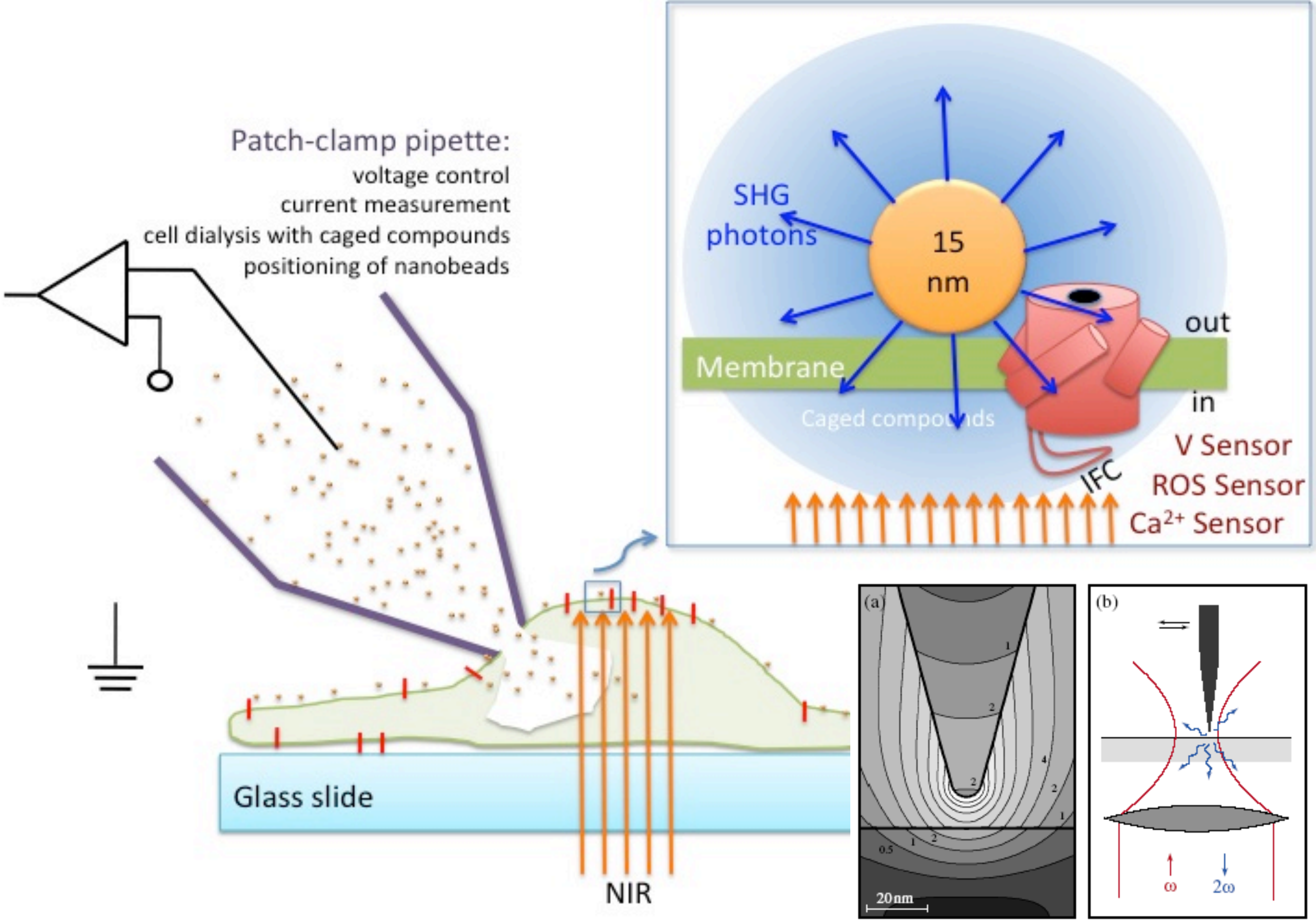


Fluoreszenz nach 24 h



SHG nach 7 Tagen

UV Nanoemitter

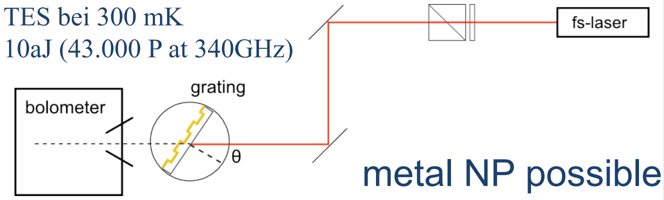


Patch-clamp pipette:
voltage control
current measurement
cell dialysis with caged compounds
positioning of nanobeads

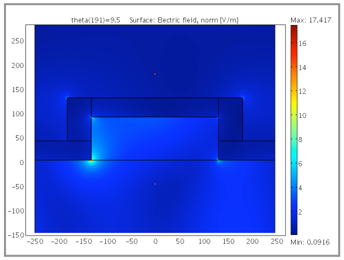
5. TEIL: Terahertz Abstrahlung von metallischen Nanostrukturen

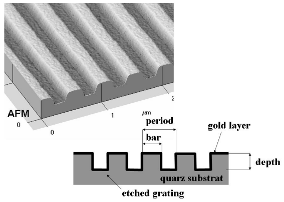
(eine Folge der Beschleunigung von freien Elektronen im evaneszenten Feld, oder?)

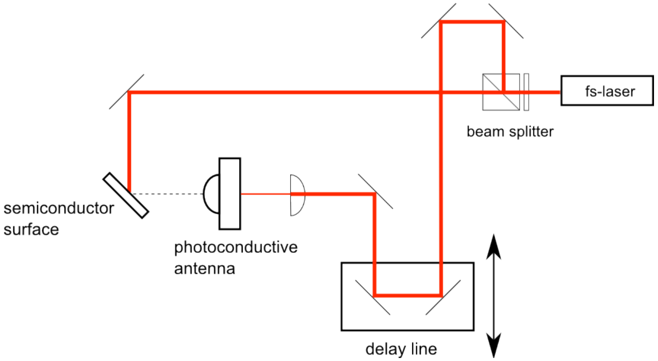
TES bei 300 mK
10aJ (43.000 P at 340GHz)

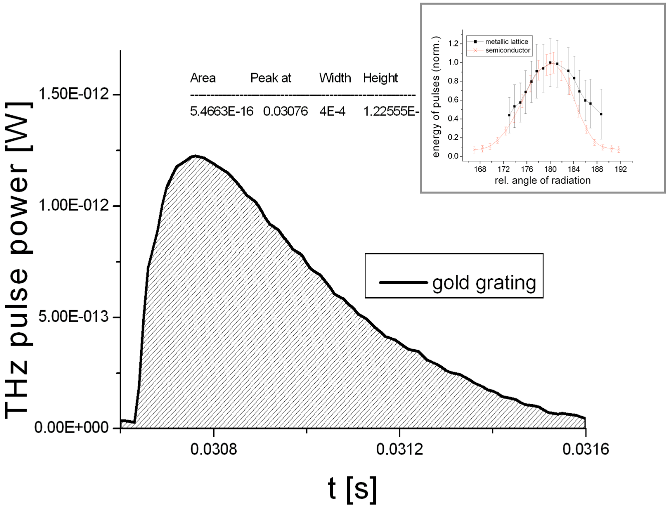


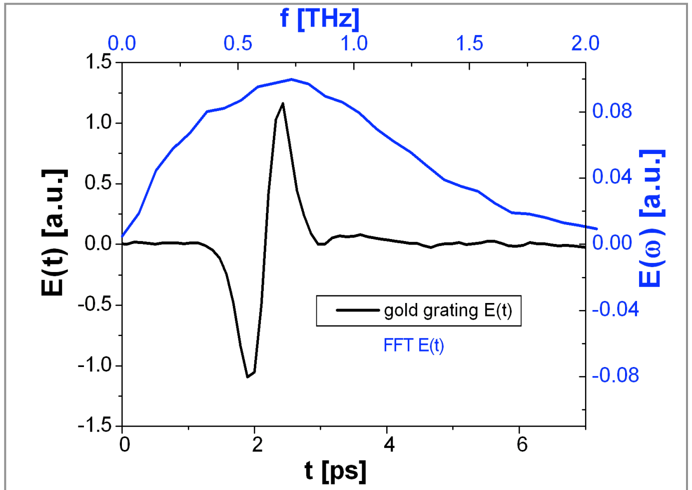
metal NP possible











auch für NP gemessen

Integration over angle:

$E_P = 1.7 * 10^{-15}$ J

Integration over spectrum:

$E_P = 170*10^{-15}$ J

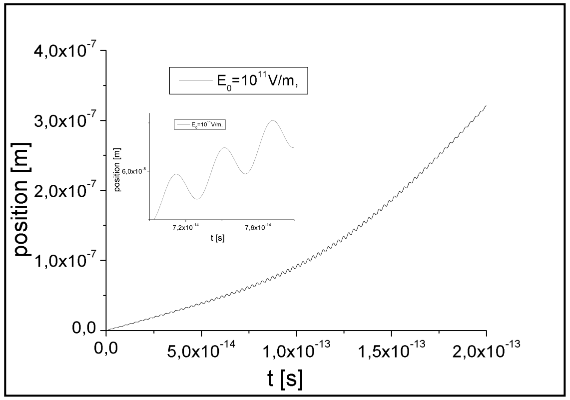
$P_p =$ **56 mW**

Modell

- freie e^- über Au Oberfläche werden durch Laserfeld beschleunigt
- e^- in evaneszenten Feld sieht in verschiedenen Richtungen unterschiedliche starke Felder (ponderomotive Kraft)

oscillation of Laser field | evanescent field | Gauss-envelope

$$m*\ddot{z} = eE_0\cos(\omega t+\phi_0)*e^{-z(t)/\lambda_{ev}}*e^{-2*\ln 2\left(\frac{t-\sigma\sqrt{0,5\frac{\log\frac{E_0}{E_S}}{\log 2}}}{\sigma}\right)^2}$$



Lösung

- 1d, klassisch, numerisch, - durch Berechnung von Position und Energie Schritt für Schritt mit Δt=1as

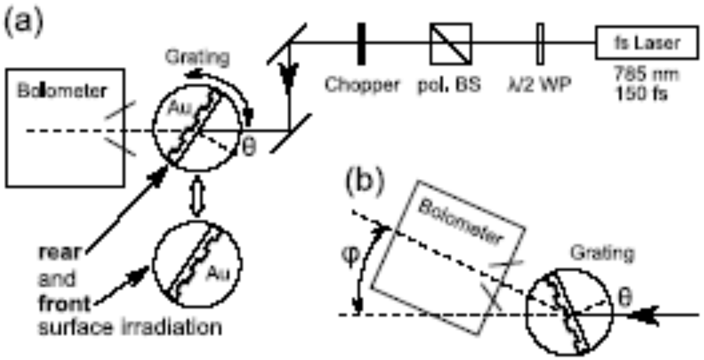
beschleunigte Bewegung einer Ladung strahlt ab

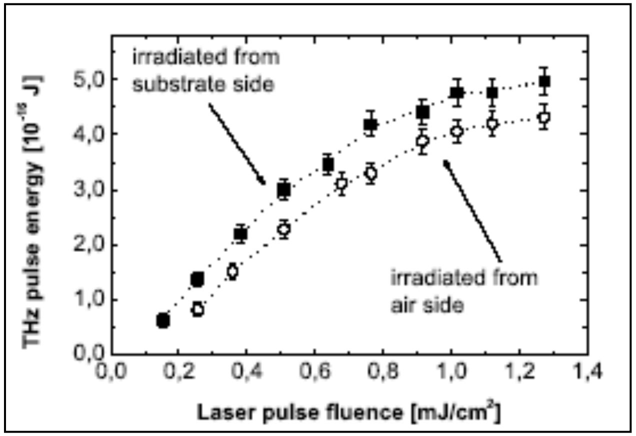
aber: nur 250 fs

el-ph Relaxation (2 ps) bestimmt THz Pulslänge

aber: erst ab E = 10^{10} V/m e^- Austritt

Experiment





Das bisherige Model kann diese Experimente nicht erklären -> neues Model notwendig

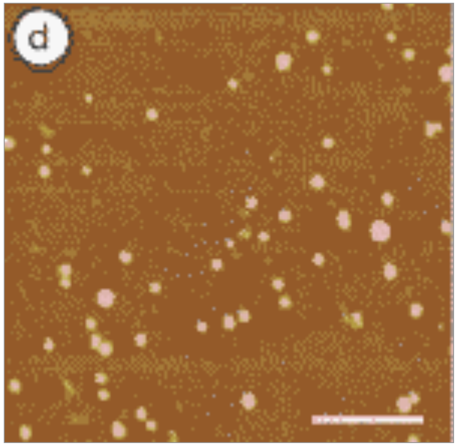
F. Garwe Appl. Phys. B accepted

Abspann: Coulomb Explosion – Ablation der NP

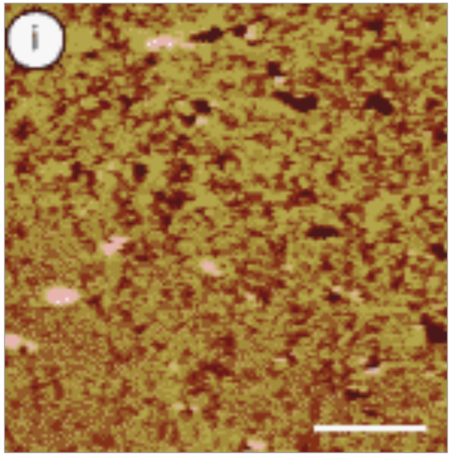
(eine Folge von zu hohen Feldern und damit Austritt von Elektronen aus der Oberfläche (Plasma))

F = 3 -7 mJ/cm^2 = 1 GO niedriger als bei dielektrischen Materialien

AFM picture bevor laser radiation:



300 fs, 90mJ/cm^2



d) 30 nm Au NP on top of a 50 nm e$^-$ sensitive PMMA layer

i) cold fragments do not sink into PMMA,
multiphoton excited e$^-$ override the work function
NP has positive ions, which reject each other

SUMMARY:

lange Laserpulse auf Metall NP

- schnelle und nanoskalige Wärmequellen (Krebstherapie/Nano Sensoren)

hohe Laserfelder auf Metall NP

- Transport von Licht auf Nanometerskalen (Plasmonik/Optoelektronik)
- Nano UV-Lichtquellen (Nano Biochemie)
- Nano THz Quellen (???)

Hier wird professionelle theoretische Beschreibung notwendig

DANKSAGUNG

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