Optical Heating Controlled With a Thermoplasmonic Metasurface

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Abstract. We develop a photothermal technology to control optical heating of polymer and liquid crystal films through a refractory titanium nitride (TiN) metasurface. The metasurface represents an array of identical square-shaped TiN nanoantennas on a Si substrate. Upon CW laser illumination, a TiN nanoantenna experiences anomalous Joule heating at a plasmon resonance. A temperature rise provides a unique opportunity for locally probing phase transitions. In the case of heterogeneous PMMA thin films or polymeric blends, a controlled optical heating is needed to probe the glass transition temperature ($T_g$) of their constituents. Here, we model a controlled thermal response originating from the TiN nanoantenna under CW laser illumination by using FDTD/FEM methods.

1. Introduction

Localized heat generation using optical excited plasmonic nanoparticles is currently an active area of research. Under optical illumination, noble metal nanoparticles can play the role of an effective nanosource of heat. It has been demonstrated that the heating effect becomes especially strong when nanoparticles are illuminated under plasmon resonance conditions. This behavior became the basis for development of such areas as photothermal cancer therapy [1], drug release [2], nanosurgery [3], nanothermometers [4], thermophotovoltaics [5], nanotechnology [6], nanotechnology [7], and nanotechnology [8]. The Covid-19 pandemic has also driven new developments in thermoplasmonics. In particular, the Qiu group proposed a version of plasmonic photothermal biosensors for accurate detection of Coronavirus [7]. Traditionally, Au and Ag have been preferred materials for demonstrating various plasmonic phenomena. However, their low melting points do not allow the implementation of practical plasmonic and photonic devices for technologically important high-temperature applications. Titanium nitride (TiN) has become a promising alternative plasmonic material due to its refractory property, chemical stability and good conductivity. In addition, TiN is biocompatible among many others plasmon materials.

The localized heat generated by nanoparticles can reach temperatures up to tens or hundreds degrees (K) while the temperature of the entire sample remains unchanged. This phenomenon can
become the basis for creating plasmon sensors for nanoprobng of such processes as phase transitions in polymer and liquid crystal films. F.A.A. Nugroho et al. have demonstrated for the first time a 3D plasmonic sensor for determination glass transition temperature. The plasmon sensor represents a metasurface consisting of an array of truncated nanocones. The nanocone represents two silver disks of different diameters, separated by a SiO$_2$ truncated nanocone [8]. Thus, two localized surface plasmon resonances (LSPR) can be recorded. Upon heating the local refractive index decreases due to thermal expansion and thus the LSPR peak is shifted. The glass transition temperature was determined from the kink in the temperature dependence of the shift of the plasmon resonance of the disk. However, in this way, the glass transition temperature is only probed in one direction.

In connection with the aforementioned, we present a study of the controlled local heating of a poly(methyl methacrylate) (PMMA) film using a refractory TiN plasmonic metasurface which is a regular array of parallelepipeds of an identical shape on a silicon substrate using numerical simulation.

2. Simulation details

The design of our metasurface is an array of TiN parallelepipeds of size 200x200x50 nm$^3$ (Figure 1(a)) located on a silicon substrate. Nanoantennas are far enough that they can be considered optically independent. Therefore, further all analysis and calculations will be regarded in the context of one nanostructure. In our simulations, we used rounded edges and corners (10 nm) to avoid anomalous electric fields near them. Simulation of electric and magnetic fields around TiN nanoantennas was carried out using the Lumerical FDTD solver. The spatial cell size was set to 1 nm and perfectly matched layers (PML) were boundaries. A TiN parallelepiped was irradiated with a linearly polarized focused CW Gaussian light source (N.A. = 0.9) with a wavelength of 633 nm and an input intensity of 5 MW/cm$^2$, which corresponds to a power 16 mW. This size of parallelepiped is explained by the fact that the absorption and scattering cross sections at our wavelength are close to each other, which provides good field amplification (Figure 1(b)). In our simulations, the complex dielectric constant of TiN was determined by spectroscopic ellipsometry at room temperature.

![Figure 1](image-url)

**Figure 1.** a) Scheme of a TiN metasurface on a Si substrate; b) FDTD calculated absorption $\sigma_{abs}$ (nm$^2$) and scattering $\sigma_{sca}$ (nm$^2$) cross section of a TiN antenna with a size: 200x200x50 nm; c) Schematic of the system simulated in the DEVICE Lumerical;

Simulation of steady-state heat propagation was carried out using the Lumerical FEM solver. The schematic geometry of thermal simulation is shown in Figure 1(c). A thermal boundary condition with a fixed temperature of 300 K was applied at the bottom of the simulation area. The upper part of the simulation region was covered with a PMMA film. The conditions of convective boundaries were defined at the interface with TiN and PMMA, PMMA and Si to model the heat losses of the structure through convection. We used the following thermal conductivities: $k_{TiN} = 29$ W/mK, $k_{PMMA} = 0.19$ W/mK, $k_{Air} = 0.026$ W/mK, $k_{Si} = 148$ W/mK. The optical and thermal properties of all materials were taken from the Lumerical material database. It was assumed that the thermal conductivity of all
components is temperature-independent. The heat power density was calculated in the FDTD simulation.

3. Result and discussion

Heat generation in a metal nanostructure under illumination arises due to the Joule effect. The power of light absorbed by the TiN parallelepiped is a heat source inside the nanostructure and reads

\[ P = \frac{1}{2} \text{Re} \left[ \int J'(r)E(r) dV \right] = \sigma_{\text{abs}} I, \]

where \( p(r) \) is a power density, \( J \) is a current density, \( \sigma_{\text{abs}} \) is an absorption cross-section, 
\( I = c \varepsilon_0 n_i |E_0|^2 / 2 \) (\( c \) is the speed of light, \( n_i \) is a refractive index of the environment and \( E_0 \) is intensity of internal electric field). Thus, optical absorption is proportional to the square of the internal electric field intensity.

We solve Maxwell’s equations by the FDTD solver to obtain \( P \), which we enter into the diffusive equation to determine the heating temperature of the TiN parallelepiped and PMMA film using the FEM solver. Figure 2 illustrates the profile of electric field around a TiN antenna in the case of air (a) and PMMA (b). The maximum intensity in the upper part (50 nm) of the TiN structure in air is 11 and we conclude that the electric field, although insignificant, is amplified due to the excitation of plasmon resonance. The maximum electric field intensity falls more than twofold when TiN is coated with PMMA, while the magnetic field intensity behaves exactly the opposite (more than twofold increase) (Figure 2 (d,c)). This effect is explained by the fact that the refractive index of PMMA is higher than that of air.

In the stationary mode, the thermal diffusion equation has the form:

\[ \nabla[(k(r)V T(r))] = -p(r), \]

where \( k \) is the thermal conductivity of the medium and it is assumed that it does not depend on temperature. For a TiN parallelepiped dressed in PMMA we obtain the temperature increment:

\[ \Delta T = \frac{\sigma_{\text{abs}} I}{4\pi k_{\text{PMMA}} \beta L}, \]

where \( \beta \) is the geometric form factor and \( L \) is the lateral size of the TiN parallelepiped.

The maximum heating temperature of TiN was 630 K in air (Figure 2(e)) while it was 476 K when TiN was coated with PMMA (Figure 2(f)). Such heating is sufficient to achieve the glass transition of a polymer PMMA film (\( T_g = 383 \) K). For polymers with a higher glass transition temperature, this heating will be insufficient. In this regard, we propose a following approach to solving this problem. We offer the addition to enhance the conversion of light to heat. This can be achieved through a confined substrate effect, for example by forming c-Si pillars of some height.

Let us consider a new geometry of the experiment (inset on Figure 2(g)), where a parallelepiped is located on a silicon column with a height \( h \). We use the same incident light conditions. Solving the thermal diffusion equation in the steady state, we get:

\[ \delta T = \frac{\sigma_{\text{abs}} I}{4\pi k_{\text{PMMA}} \beta L} \cdot \frac{1}{r}. \]

Inside the TiN parallelepiped, the temperature increment corresponds to the parabolic expression:

\[ \delta T = \delta T_{\text{TIN}} + \frac{\sigma_{\text{abs}} I}{6 k_{\text{TIN}}} (L^2 - r^2). \]

FEM simulation of the heating temperature is shown in Figure 2(g) for three cases of Si column heights (no column, 150 nm and 300 nm). The upper surface of the TiN parallelepiped heats up to 176 K in the absence of a column. However, as the column height increases, we observe much larger temperature increments, namely 232 K and 329 K on the top surface, respectively, for 150 nm and 300 nm in height. This means that this design and this approach are quite suitable for heating polymer
films to higher temperatures. Thus, the higher the Si column, the greater the temperature rise is achieved.

4. Conclusion
Summing up, in this work we have demonstrated photo-induced heating of a polymer PMMA film on a plasmonic refractory TiN metasurface under CW illumination in a steady state using FDTD/FEM simulation. We show that polymer heating can be controlled by confined Si pillar under TiN pad. We observe that the higher the Si column is, the greater the temperature rise is achieved. Thus, the idea of achieving higher temperatures using a larger column height has the prospect of creating a system of distributed heat sources with different heating temperatures under CW illumination.

5. Acknowledgments
This work was supported by grant No. 19-12-00066 of the Russian Science Foundation. E.A.C. acknowledges the help from the Russian Foundation for Basic Research (grant No. 20-32-90090) for conducting numerical FDTD simulations.

6. References
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