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Research paper

Surface enhanced thermo lithography

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ABSTRACT

We used electroless deposition to fabricate clusters of silver nanoparticles (NPs) on a silicon substrate. These clusters are plasmonics devices that induce giant electromagnetic (EM) field increments. When those EM field are absorbed by the metal NPs clusters generate, in turn, severe temperature increases. Here, we used the laser radiation of a conventional Raman set-up to transfer geometrical patterns from a template of metal NPs clusters into a layer of thermo sensitive Polyphthalaldehyde (PPA) polymer. Temperature profile on the devices depends on specific arrangements of silver nanoparticles. In plane temperature variations may be controlled with (i) high nano-meter spatial precision and (ii) single Kelvin temperature resolution on varying the shape, size and spacing of metal nanostructures. This scheme can be used to generate strongly localized heat amplifications for applications in nanotechnology, surface enhanced thermo-lithography (SETL), biology and medicine (for space resolved cell ablation and treatment), nano-chemistry.

1. Introduction

Differently from their macro-scale counterparts, nanomaterials are characterized by lengths that span different scales to the nanometer size. The complexity in extended dimensions brings about advantages and new functionalities that may be exploited in materials science, biomedical sciences, bioengineering [1,2]. In Surface Enhanced Raman Scattering (SERS), silver or gold nanoparticles, with a regular rather than periodic motif, interact with an electromagnetic field to yield site specific increments of that field [3–6]. This in turn allows obtaining the Raman signature of biological molecules with unprecedented sensitivity and thus to diagnose a disease at the very early stages of its progression. SERS effect occurs because of the collective/resonant oscillations of electrons on the surface of a rough metal, where the roughness of the surface has to be a fraction of the wavelength of the incident electromagnetic (EM) field [7]. Similar oscillations are named localized surface plasmons (LSPs) and the study of the generation, propagation, and dependence of LSPs on the geometry of a metal substrate is at the basis of a new revolution in optics. For certain combinations of physical characteristics of the metal, wavelength and nano-topography, LSPs are responsible for enhanced EM absorption in lieu of EM scattering. Enhanced EM absorption in turn generates heat and the nanomaterial itself may be regarded as a nano-heat generator remotely controlled by light [8,9]. Differently from SERS, the described thermo-plasmonics effect depends on the square (and not to the power of 4) of the EM field intensity [8,9]. Thus the EM distribution on a metal substrate indicates how power density propagates on that substrate. A similar thermos-plasmonic effect has been used in a variety of applications including drug delivery [10], plasmonic photo-thermal therapy [11], nano-surgery [12], photo-thermal imaging [13], plasmon-assisted nano-chemistry [14], plasmon-assisted opto-fluidics [15].

Here, we used an electroless deposition approach [16–18] to achieve the large-scale assembly of silver nanoparticles clusters (Fig. 1) for localized and site specific temperature increment. Computer simulations (Fig. 2) show that the temperature T on the device can be increased up to ~180 K above room temperature for an initial power density $P = 5\ mW/\mu m^2$ and wavelength $\lambda = 532$ nm. The temperature profile is strongly influenced by the particle distribution on the substrate. T attains a maximum at the metal/air interface and rapidly decays moving away from the particles cluster. This allows a tight control of the

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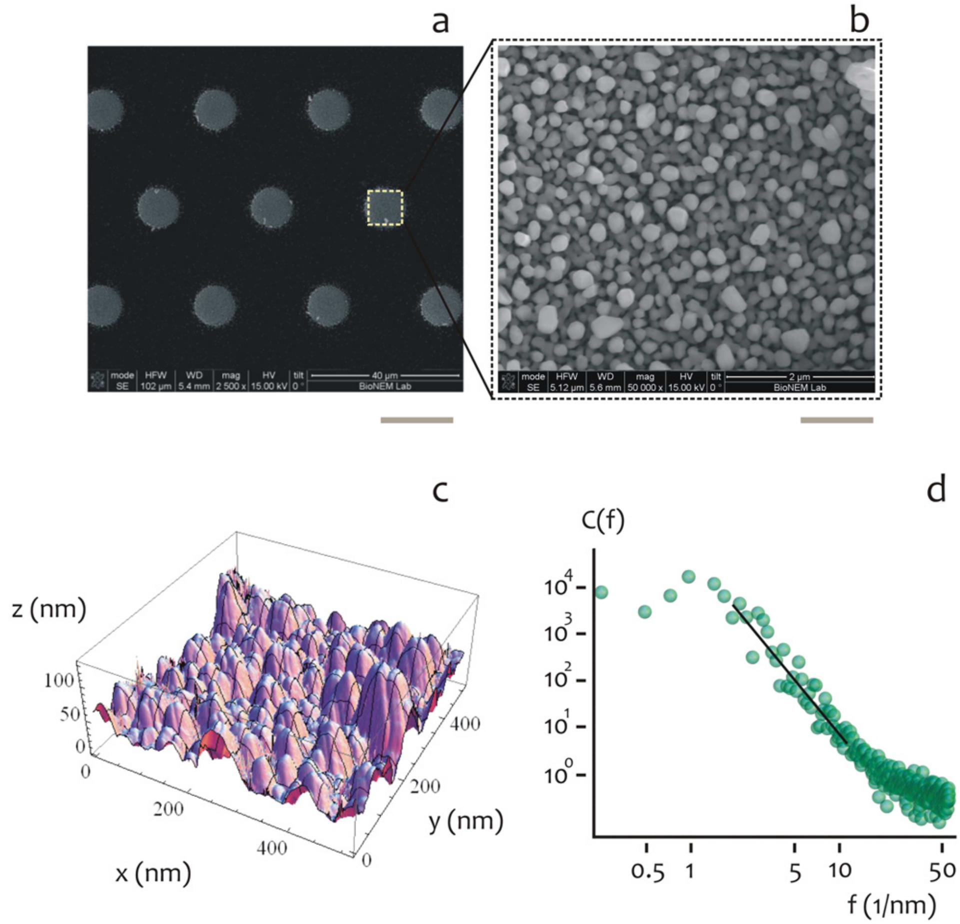

Fig. 1. Clusters of silver nanoparticles arranged in a hexagonal lattice in the plane over extended regions of a silicon substrate, the size of each cluster is 10 μm and the cluster to cluster distance measured from the border is 20 μm (the size bar in the inset is 20 μm, a); high magnification SEM micro-graphs of the upper surface of the pillars reveal the morphology of the silver nanoparticles, where the average diameter of the particles is 50 nm (the size bar in the inset is 1 μm, b). AFM profile of the silver nanoparticles in a cluster (c); a similar AFM profile can be elaborated to derive the fractal dimension of the structures that for the present configuration reads as $D_f = 2.4$ (d).

temperature in the planar coordinates and on changing the size, shape and spacing of the particles one may obtain specific, highly confined temperature fields on a planar surface.

To demonstrate the device, we used a conventional Raman set-up described in the methods to modify a bi-dimensional layer of thermo-sensitive Polyphthalaldehyde (PPA) polymer. The geometries corresponding to the silver nano-particle clusters were transferred from the device to the polymer layer with sub-micrometric resolution that can be as high as the smallest photonics devices that form the substrate and are theoretically limited by surface plasmon resonance. Let's comment on this assertion even further.

Plasmon resonance is an effect where the electromagnetic field is locally enhanced by the resonant interaction of light with the surface plasmons polaritons in a metal [17,19,20]. Surface plasmons polaritons (SPPs) are collective oscillations of conduction electrons excited by an electromagnetic field. The electromagnetic (EM) field enhancement

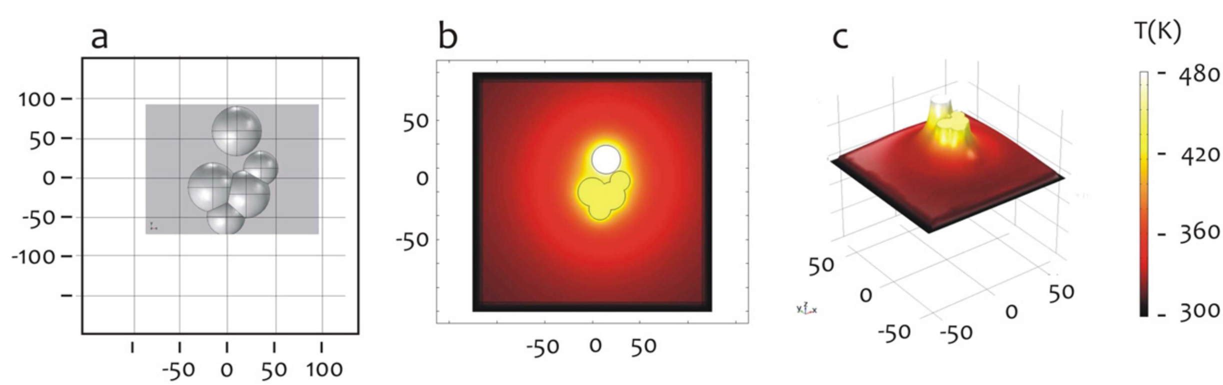

Fig. 2. simulations of the temperature maps around the silver nanoparticles generated by an incident EM radiation. Nanoparticles are represented as partially overlapping spheres (a), where the diameter of the spheres ranges from 50 to 60 nm. Calculated temperature profiles reach a maximum at the particle-particle interfaces and the temperature in the cluster rises up ~180 K above room temperature (b, c).