

# Fabrication techniques towards large area metamaterial devices

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## Abstract

Fabrication of samples showing plasmonic properties is a fundamental step towards the realization of devices exhibiting peculiar electromagnetic properties. Theoretical studies demonstrate that assemblies of Gold or Silver nanoparticles can be considered as building blocks (or meta-atoms) of a metamaterial; in this work we illustrate some fabrication techniques that can reveal useful for the realization of this kind of sample. In our experiments we used PDMS materials (and other photo-patternable polymers) in combination with Gold or Silver nanoparticles for realizing micro/nano structured devices. Field of application of such devices can include novel solar applications.

## 1. Introduction

Wide interest is actually devoted to the realization of structures with metamaterial properties [1]. Main results have been achieved, until now, in the microwave range and in the far infrared but the trend is to scale down structures in order to obtain functionalities also at optical frequencies. In this direction, some prototypes, have already been realized [2], but difficulties to accomplish this objective are encountered, which are related to the necessity of fabricating structures, whose unit cells are much smaller than the probing wavelength; then [3], nanostructuring is necessary. There are several ways to obtain nanoscale fabrication but, in most cases, the involved process is time consuming and the obtained structures have very small sizes (few square millimeters) [4]. A solution of this issue could be in the use of replication techniques: e.g. fabricating a master structure and make a reliable replica of it by using suitable materials. In this regard, Polydimethylsiloxane (PDMS) material is a good candidate. This elastomer is very easy to use and allows the realization of excellent morphological results (resolution up to 10 nm) [5]. In such a way, the use of PDMS can represent the basis for the realization of a new kind of metamaterial devices. In fact, it could be very convenient to combine the plasmonic resonances, shown by noble metal nanoparticles at optical wavelengths, with a flexible and manageable support as offered by this elastomer. Results would be large area, micrometer thick structures including Gold or Silver nanoparticles. The filling factor of these nanoparticles incorporated in the structures could constitute a driving parameter for tuning their metamaterial properties. The obtained new thin-films could be involved in novel high content applications, e.g. as absorbers for achieving efficient light trapping in solar cells.

## 2. Resonant nanoparticles as fundamental property of metamaterials

Metamaterials can be considered as a new kind of matter, in which electromagnetic properties like electrical permittivity, magnetic permeability, diffraction coefficient and so on, are optimized [1]. When functionalities at optical frequencies are required, the most important feature, at the basis of these materials, is the use of gold or silver nanoparticles (NPs). In fact, when nanoparticles are irradiated with visible light, the interaction of light quanta of specific wavelength with surface particle electrons produces a resonance phenomenon: the plasmon. In this framework, a fundamental requirement is that the typical dimension of the unit cell is much smaller than the wavelength of incident light [3]. Application of these concepts is very important for possible devices; as an example, by utilizing plasmonic structures, it would be possible to reduce the physical thickness of a photovoltaic absorber layer [6]. As reported in [6], metallic nanoparticles can be used as subwavelength scattering elements to couple and trap freely propagating plane waves from the Sun into an absorbing semiconductor thin-films (fig. 1a). Furthermore, metallic nanoparticles can be used as subwavelength antennas in which the plasmonic near-field is coupled with the semiconductor, increasing its effective absorption cross-section (fig. 1b); finally, a corrugated metallic film, on the back surface of a thin photovoltaic absorber layer, can couple sunlight into surface Plasmon resonance (SPP) modes supported at the metallic/semiconductor interface, as well as guided modes in the semiconductor slab, whereupon the light is converted to photocarrier in the semiconductor (fig. 1c).

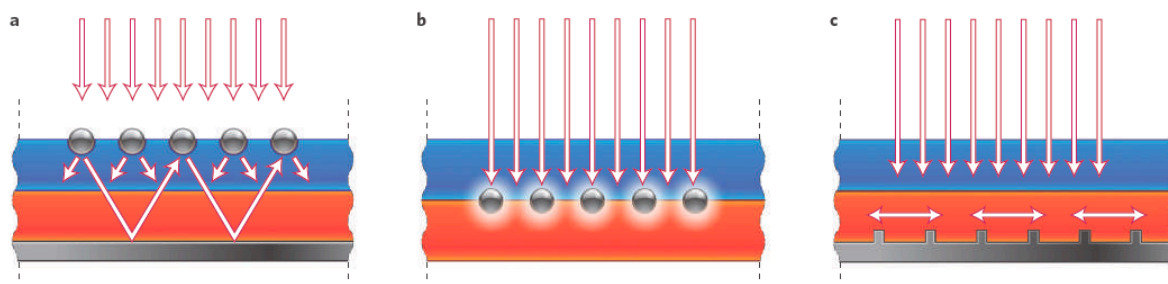


Figure 1. Plasmonic light-trapping geometries for thin-film solar cells [6].

## 3. PDMS support

In this work, we report our first attempts to realize micro/nano structured samples, including Gold or Silver NPs, by using PDMS materials. The PDMS pre-polymer can be directly combined with Gold or Silver NPs (diluted in Chlorofom) in order to obtain a chemical mixture exhibiting a plasmonic response. The high viscosity of the obtained sample prevents the clustering of nanoparticles and, hence, any modification of their plasmonic resonance frequency. Once the mixture of PDMS doped with NPs is ready, it can then be poured into a stamp in order to replicate already existing master structures. A hot baking step is necessary for solidifying the material; depending on the used temperature and oven time, the hardness of the obtained support can be modified at will, passing from a gel-like condition to an almost solid rubber one. Spectroscopical properties of the material are very suitable for possible devices: PDMS is optically transparent from 240 to 1100 nanometers; its thermal stability (up to 300°C) is also a noticeable advantage (especially for solar applications); another advantage of PDMS is the possibility to combine it with other polymer systems that can be processed in further steps. We performed some attempts, by using the NOA61 (from Norland) pre-polymer, in order to obtain photo-patternable structures. Every obtained result can be reproduced on large areas samples (wafer size) by means of semi-industrial procedures [7].

#### 4. Conclusion

Nanoscale fabrication on large areas is fundamental for realizing devices with metamaterial properties. In order to achieve this aim, we propose the combination of easy-to-use materials and metallic nano-inclusions showing plasmonic resonances. Results confirm that replication and photo-patterning techniques can be usefully adopted with PDMS materials doped with Gold or Silver NPs. The filling factor of these NPs represents a control parameter of the obtained sample functionalities.

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#### References

- [1] V.G. Veselago, "The electrodynamics of substances with simultaneously negative values of  $\epsilon$  and  $\mu$ ", *Sov. Phys. Usp.*, vol. 10, 4, 509 (1968).
- [2] J. Valentine, S. Zhang, T. Zentgraf, E. Ulin-Avila, D.A. Genov, G. Bartal and X. Zhang, "Three Dimensional Optical Metamaterial Exhibiting Negative Refractive Index", *Nature*, vol. 455, 376 (2008).
- [3] U. Kreibig, M. Vollmer, "Optical Properties of Metal Clusters", Springer-Verlag, Berlin, Germany (1995).
- [4] M. A. McCord and M. J. Rooks, in *Handbook of Microlithography, Micromachining and Microfabrication*, edited by P. Rai-Choudhury (SPIE and The Institution of Electrical Engineers, Bellingham, WA, 1997), Vol. 1, Chap. 2, pp. 139–249
- [5] Y. Fainman, L. P. Lee, D. Psaltis, C. Yang, "Optofluidics: fundamental, devices, and application"; McGraw-Hill (2010).
- [6] Harry A. Atwater and Albert Polman, "Plasmonics for improved photovoltaic devices", *Nature Mat.*, vol. 9, 205 (2010).
- [7] M. Verschuuren and H. van Sprang, "3D photonic structures by sol-gel imprint lithography", *Mater. Res. Soc. Sym. Proc.* 1002, N03–N05 (2007).