

# Jumping nanodroplets: a new route towards metallic nano-particles

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**Abstract** The dewetting process, which appears upon laser-induced melting of flat nanostructures and leads to a jumping of the droplets off the surface, is used for deposition of nano-particles onto a second substrate. Limitations in materials and particle sizes are discussed and experimentally verified. The experiments show that a variety of metals can be deposited in a size ranging from tens up to several hundreds of nanometers.

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## 1 Introduction

Due to their potential applications in practical all fields of science and technology, metal, semiconductor or oxide nano-particles are of ever-growing importance [1]. Here, the term “nano-particles” is reserved for 3-dimensional, approximately spherical objects, while other shapes of about the same size would be explicitly addressed as nano-rods, -tripods, -tetrapods etc. or, in case of more 2-dimensional objects, as nano-islands. In the following a subgroup of such nano-objects will be addressed: nano-particles deposited on top of a given substrate. In that case, the particles together with a suitable substrate may form the building blocks and platform for a more complex functional device, where the function results from a combination of the properties of the

individual particles, their mutual interaction in a given geometrical arrangement as well as their contact with the underlying substrate. Obviously, the interparticle as well as the particle-substrate interactions may be strongly influenced by any organic ligands surrounding the particles with immediate consequences on the desired device functions. Such ligands, however, are inevitably present when applying chemical preparation methods like those based on solution-phase synthesis involving colloids or micelles [2–8] as well as copolymer templates [4, 9–12]. Thus, the versatility offered by these chemical synthesis routes is at least partly compensated for by the additional experimental effort necessary to analyze the effect of the organic ligands on the properties of the resulting nano-particles. An example of how dramatic the effect of ligands can be has been reported for Au nano-particles. In that case, by completely removing the stabilizing ligands of Au nano-particles each composed of 55 Au atoms and, thus, forming particles of 1.4 nm diameter, a transition was observed from a nonmetallic into a metallic state [13]. Though meanwhile processes have been developed allowing for such a complete ligand removal by exposing the stabilized nano-particles to oxygen or hydrogen plasmas [14, 15], the chemical preparation of more complex alloys or compounds with more than two components still appears to be difficult. Thus, recipes are still sought to prepare such multicomponent nano-particles. Additionally, if we have a choice, an approach avoiding organic ligands would be preferable.

Possible ways towards this aim are based on appropriate nano-masks applied during a subsequent deposition process like evaporation, laser ablation or sputtering. In this context, ultrathin alumina membranes (UTAMs) are especially promising due to their heat resistance. These masks with pore diameters ranging between about 20 nm and some hundred nm often can be electrochemically prepared directly

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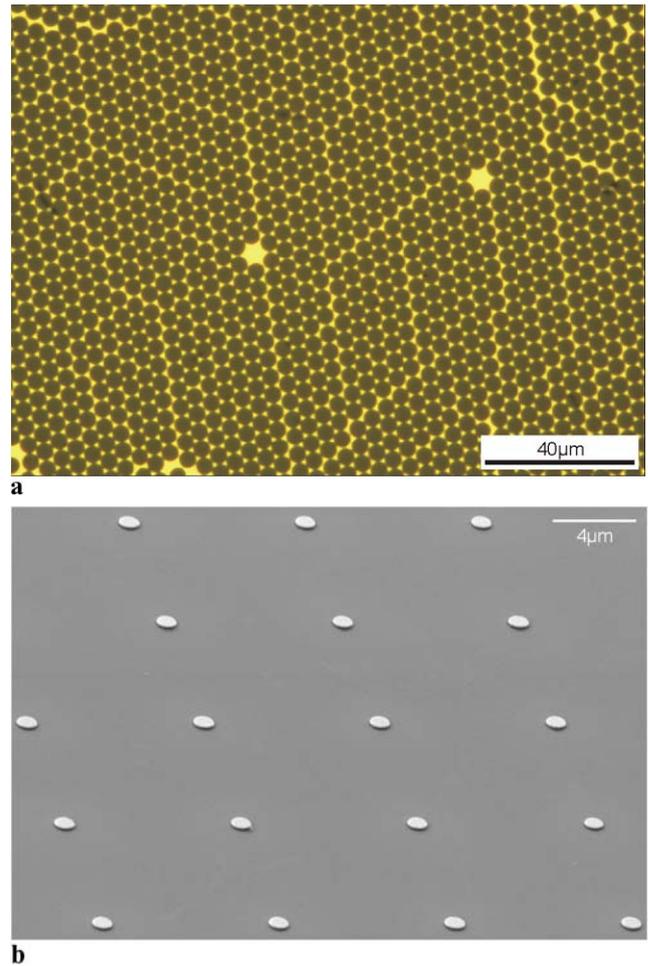
on top of a substrate [16]. In that case, however, an additional mask removal step has to follow after deposition of the chosen material. A specific problem common to all deposition processes performed at ambient temperatures through masks like UTAMs or standard masks prepared by photo or electron beam lithography is the formation of nano-islands rather than nano-particles in the above given sense. This is related to the wetting behavior of the material on a given substrate.

Therefore, in the present work, a completely different approach is introduced to arrive at supported nano-particles. Here, lithographically pre-patterned arrays of metallic nano-islands are exposed to pulsed laser irradiation. As has previously been demonstrated [17], upon laser-induced melting of the metallic structures, dewetting leads to a jumping process from the surface, which can be used for deposition of metallic nano-particles onto any arbitrary nearby positioned surface. Due to the laser-induced ballistic flight of the nano-particles, the present method resembles particle preparation in a gas phase [18].

## 2 Experimental results

As already briefly outlined above, in a first step flat sub-micrometer metallic structures have to be fabricated. This can be done either by colloidal mask lithography, where a monolayer of spherical monodisperse colloidal particles (in the following polystyrene (PS) particles) serves as a deposition mask [19–21], or by standard electron beam lithography (EBL). While the first approach leads to a fast parallel deposition process once the mask is provided, EBL is more elaborate and time consuming. This disadvantage is compensated for, however, by the homogeneity of the resulting metallic structures. In contrast, the colloidal masks form domains separated by dislocation-like extended defects and, though to a lesser degree, additional point-like defects due to missing colloidal particles. Both types of imperfections are clearly visible in the example presented in Fig. 1a. Here, the colloidal mask has been already removed by an adhesive tape and the visible submicron structure in this large scale optical image is due to the evaporation of Au through the colloidal mask of 1.5  $\mu\text{m}$  PS particles (nominal Au thickness 100 nm) onto a glass substrate. Thus, the deviations from perfect periodicity found in the Au structure mirror the various defects of the colloidal mask. In contrast, the flat circular Au disks (thickness 100 nm, diameter 1000 nm) prepared by EBL exhibit a practically perfect periodicity as exemplified by the SEM image shown in Fig. 1b.

The second step, decisive for the present novel approach to fabricate nano-particles, is to expose the above pre-formed submicron structures to an intensive ns-laser pulse (Nd:YAG,  $\lambda = 532$  nm, FWHM = 10 ns) at intensities

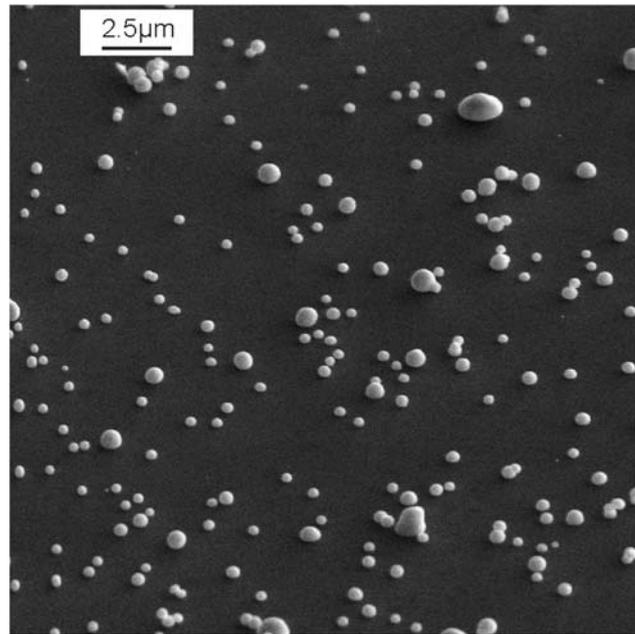


**Fig. 1** (a) Au nano-structures prepared by colloidal mask (5.2  $\mu\text{m}$  PS particles) lithography. While most of the metal structures are triangular and of practically equal size, deviations from periodicity clearly appear due to grain boundaries and missing particles in the mask. (b) SEM image of submicron Au structures prepared by standard electron beam lithography (EBL)

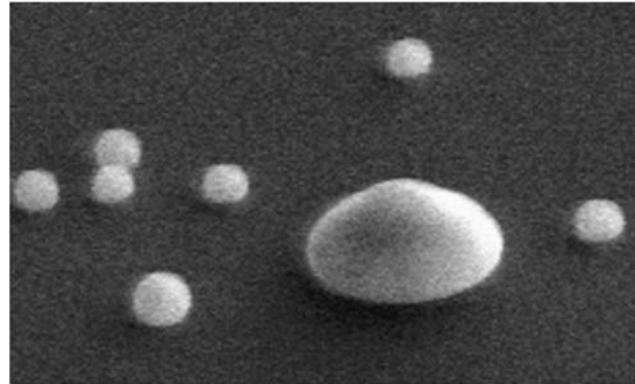
which result in melting of each of those metallic structures. The local liquids produced in this way are far from the equilibrium contact angle on the surfaces used here (e.g. the contact angle of liquid Au on  $\text{SiO}_2$  is  $140^\circ$  [22]) and thus a dewetting process sets in. As a consequence, in order to form a local droplet, the liquid material is transported towards the center of the metallic structure, leading to a vertical movement of the center-of-mass. Finally, the liquid droplet leaves the surface due to inertia. Typically droplet velocities are found to be in the range of tens of m/s. Upon positioning a substrate some mm above the original nano-structures, the droplets will solidify during flight and can be collected there.

As will be demonstrated now, significant differences are observed for the finally obtained nano-particles depending on the degree of order of the pre-formed submicron structures. For this purpose, in Fig. 2 a SEM image of Au nano-

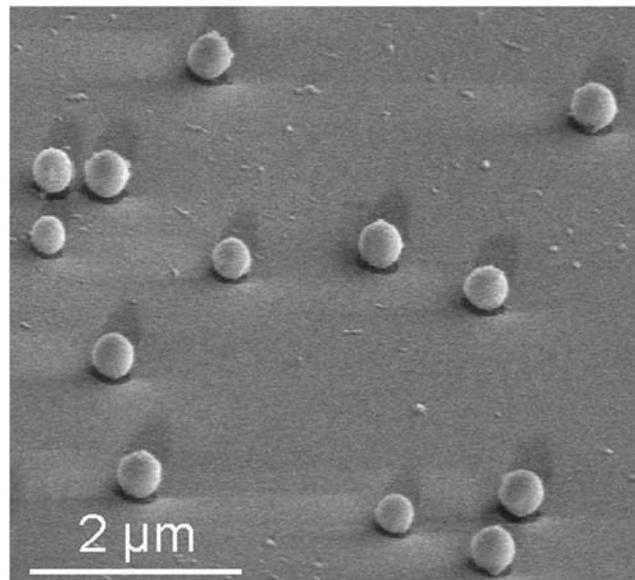
**Fig. 2** (a) SEM image of Au nano-particles collected on a Si wafer after laser exposing the starting Au structure of Fig. 1a, prepared by applying colloidal mask lithography. (b) Magnified image of the bigger particle in the upper right corner of panel (a). (c) SEM image of Au nano-particles collected on a glass surface after laser exposing the starting Au structure of Fig. 1b. In order to facilitate the electron microscopy, a thin gold layer of a few nanometers was applied to the surface



a



b

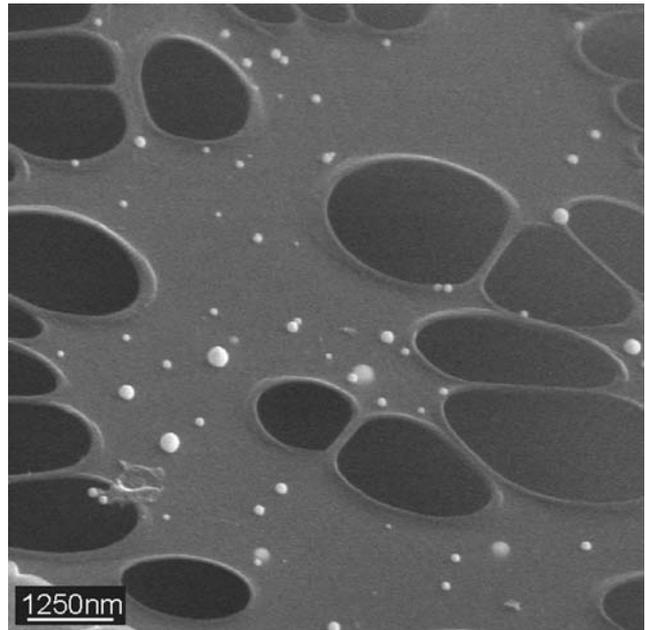


c

particles is shown, collected on a silicon wafer after laser illuminating the nanostructures of Fig. 1a as obtained by colloidal mask lithography. The majority of the particles have identical sizes of 250 nm as calculated from the size of the starting structures and assuming mass conservation. Additionally some bigger particles can be found as well, originating from the disordered part of the starting structure caused by the grain boundaries and missing particles of the colloidal mask. Closer inspection reveals that at the flight distance of the particles used in this experiment (distance between the glass substrate with the starting Au structure and the collecting Si substrate), the biggest particles found on the collecting substrate are laterally spread out, resulting in a spherical calotte shape rather than in a sphere (Fig. 2b). Thus, one concludes that these particles had not solidified during the time of flight but landed in the liquid state followed by splat cooling. This can be expected, as, due to their higher heat capacity, bigger particles would take a longer cooling process. In contrast to the broad size distribution of the Au nanoparticles produced from starting structures obtained by colloidal mask lithography, the particles originating from electron beam lithography exhibit a monodisperse appearance (Fig. 2c). Thus, the degree of order of the primary structure, which is illuminated in a second step by the pulsed laser light, is directly reflected in the size distribution of the resulting nano-particles collected on the second substrate.

It turns out that for collecting the laser-induced nanoparticles arbitrary substrates can be used. An example important for the further characterization of the nano-particles by transmission electron microscopy (TEM) is presented in Fig. 3. Here, the deposition of Au nano-particles on top of a commercial carbon TEM grid along the method outlined above is demonstrated.

The particle diameters that were achieved in the present experiments range from 30 nm to 1000 nm and, thus, cover a technological interesting range for metallic nano-particles. The limits are given by the following experimental constraints. In order to achieve jumping of the nano-droplets their surface energy must be high, which can be realized by an oblate shape with the lateral dimensions larger than the thickness of the structure (typical values of this ratio in the experiments were around 2). The lower size limit of the resulting nano-particles is related to the minimum thickness of the starting structure, which, in turn, experiences restrictions due to roughness. In the present case, where the metal films had to be evaporated onto nonwetting substrates, the roughness of the evaporated films was in the range of several nm. Thus, very thin films will break up into individual patches upon melting, a method which may also be used to create nanostructures [23]. It turned out that a useful thickness to avoid such problems is around 20 nm. Consequently, the lateral size must be at least 40 nm. Assuming conservation of mass, one ends up with particle diameters in the



**Fig. 3** Au nano-particles collected on a carbon TEM grid applying the laser-induced technique described in this work

range of 30 nm. At the other end, the complete film thickness must be molten, thereby limiting the useful thickness to the heat diffusion length of the material, which for typical metals is in the range of several hundred nm. Combining this with lateral dimensions which can be larger by a factor of ten (limited by the homogeneity of the laser) we end up with diameters of the resulting nano-particles in the 1000 nm range.

Regarding the applicable materials, there are only a few conditions which have to be met in order to facilitate the dewetting-induced jumping of metals. (1) The melting point of the metal must be reached. Since typical temperatures lie in the range up to 3500 K, this condition can be fulfilled by an increase of the laser energy density. (2) For the metal used the substrate must provide nonwetting conditions. Therefore, glass or sapphire are good choices for most of the metals [22]. (3) In order to achieve the jumping process, the energy losses during the dewetting process must not be too high. Experimentally it is found that changes in the surface chemistry of nonnoble metals typically lead to a reduction in the detachment velocity. In such cases, a nonmetallic interface layer may be formed due to oxidation resulting in a reduction of the detachment velocity or even suppression of the dewetting process. Despite this complication, successful nano-particle depositions have been performed with Ag, Ni, and Al additionally to the noble metals Au and Pt.

In summary the experiments demonstrate that a large number of metallic materials can be transformed into nanoparticles on top of practically any substrate by laser illumination of oblate metallic structures on a nonwetting sub-

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strate at energy densities sufficient to melt the starting material. The jumping nanodroplets, which are ejected at velocities of several tens of meters, can be landed on a second arbitrary substrate.

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## References

1. G. Schmid, *Nanoparticles. From Theory to Application* (Wiley-VCH, Weinheim, 2004)
2. I.M. Hamley, *Nanotechnology* **14**, R39 (2003)
3. G. Kästle, H.-G. Boyen, F. Weigl, G. Lengl, T. Herzog, P. Ziemann, S. Riethmüller, O. Meyer, C. Hartmann, J.P. Spatz, M. Möller, M. Ozawa, F. Banhart, G. Garnier, P. Oelhafen, *Adv. Funct. Mater.* **13**, 853 (2003)
4. M.J. Misner, H. Skaff, T. Emrick, T.P. Russel, *Adv. Mater.* **15**, 221 (2003)
5. J.P. Spatz, S. Moessmer, C. Hartmann, M. Moeller, T. Herzog, M. Krieger, H.-G. Boyen, P. Ziemann, B. Kabius, *Langmuir* **16**, 407 (2000)
6. S. Krishnamoorthy, C. Hinderling, H. Heinzlmann, *Materialstoday* **9**, 40 (2006)
7. J.L. Wilbur, G. Whitesides, in *Nanotechnology*, ed. by G. Timp (Springer, New York, 1998), p. 331
8. S.I. Yoo, J.-H. Kwon, B.-H. Sohn, *J. Mater. Chem.* **17**, 2969 (2007)
9. J.Y. Cheng, C.A. Ross, E.L. Thomas, H.I. Smith, G.J. Vancso, *Appl. Phys. Lett.* **81**, 3657 (2002)
10. M. Li, C.K. Ober, *Materialstoday* **9**, 30 (2006)
11. M.P. Stoykovich, P.F. Nealey, *Materialstoday* **9**, 20 (2006)
12. T. Thurn-Albrecht, J. Schotter, G.A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C.T. Black, M.T. Tuominen, T.P. Russell, *Science* **290**, 2126 (2001)
13. H.-G. Boyen, G. Kästle, F. Weigl, B. Koslowski, C. Dietrich, P. Ziemann, J.P. Spatz, S. Riethmüller, C. Hartmann, M. Möller, G. Schmid, M.G. Garnier, P. Oelhafen, *Science* **297**, 1533 (2002)
14. G. Kästle, H.-G. Boyen, F. Weigl, G. Lengl, T. Herzog, P. Ziemann, S. Riethmüller, O. Mayer, C. Hartmann, J.P. Spatz, M. Möller, M. Ozawa, F. Banhart, M.G. Garnier, P. Oelhafen, *Adv. Funct. Mater.* **13**, 853 (2003)
15. J.P. Spatz, T. Herzog, S. Mößmer, P. Ziemann, M. Möller, *Adv. Mater.* **11**, 149 (1999)
16. Y. Lei, W.P. Cai, G. Wilde, *Prog. Mater. Sci.* **52**, 465 (2007)
17. A. Habenicht, M. Olapinski, F. Burmeister, P. Leiderer, J. Boneberg, *Science* **309**, 2043 (2005)
18. S. Stappert, B. Rellinghaus, M. Acet, E.F. Wassermann, *J. Cryst. Growth* **252**, 440 (2003)
19. F. Burmeister, W. Badowsky, T. Braun, S. Wieprich, J. Boneberg, P. Leiderer, *Appl. Surf. Sci.* **144–145**, 461 (1999)
20. U.C. Fischer, H.P. Zingsheim, *J. Vac. Sci. Technol.* **19**, 881 (1981)
21. H.W. Deckman, J.H. Dunsmuir, *Appl. Phys. Lett.* **41**, 377 (1982)
22. J.V. Naidich, in *Progress in Surface and Membrane Science*, vol. 14, ed. by D.A. Cadenhead, J.F. Danielli (Academic Press, New York, 1981), p. 353
23. C. Favazza, R. Kalyanaranman, R. Sureshkumar, *Nanotechnology* **17**, 4229 (2006)