Laser-induced backward transfer of gold nanodroplets

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Abstract: It is demonstrated that femtosecond laser-induced processes can be applied for controllable transfer of spherical gold nanodroplets from a thin gold film towards a glass substrate. The size of the transferred droplets depends on the volume of laser-molten gold and can be varied by changing the laser beam focus on the sample surface and the film thickness. Single- and multi-pulse fabrication of microstructures consisting of spherical gold nanodroplets is demonstrated. Mechanisms of these laser-induced backward transfer processes are discussed.

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1. Introduction

Fabrication of metallic micro- and nanostructures is important for application in many fields including optics, microelectronics, metamaterials, etc. One of the fabrication approaches is laser-induced forward transfer (LIFT). LIFT is a method for additive micropattering, which allows deposition of diverse material microstructures onto different substrates by a simple fast one-step process under ambient atmospheric conditions. Typically the size of LIFT-transferred structures is of the order of the laser beam focus and can be decreased down to micrometer or even sub-micrometer range [1,2]. Recently, it has been demonstrated that some materials (aluminum and nickel [3], chromium [4], copper [5], and $FeSi_2$ [6]) can be controllably transferred in the molten phase in a form of small droplets, which size can be significantly smaller than the laser beam focus. Such kind of transfer can be realized in a

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narrow laser pulse energy range close to the ablation threshold. The smallest size droplets of 330 nm diameter have been transferred by a femtosecond laser from a 30 nm Cr film [4].

Our recent studies have shown that by femtosecond laser irradiation of thin gold films melting of these films and redistribution of the molten material from the edges towards the center of the irradiated region are induced [7]. These processes lead to the formation of microbump and nanojet-like structures on the gold surface [7–9]. Examples of such structures formed by single 30 fs laser pulses with the Gaussian intensity distribution are shown in Fig. 1. Laser beam with a diameter of 8 mm was focused onto the sample surface by a 20 mm focus lens. Laser pulse energy E_p is varied between 65 and 75 nJ. A distinct feature of these structures is a droplet, which is formed on the top of a jet-like structure in the center of irradiated region (see Fig. 1(a) and 1(b)). At slightly higher laser energies this droplet detaches from the jet living a needle-like protrusion on the film surface (Fig. 1(c)).

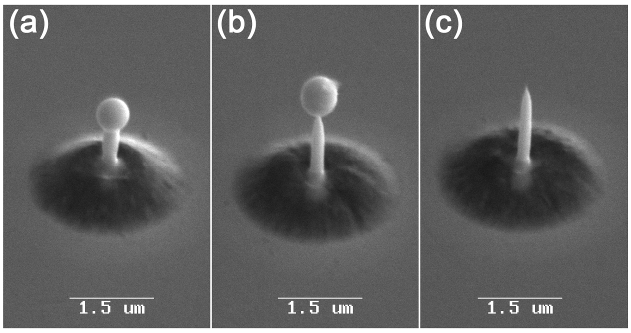

Fig. 1. Structures fabricated on the surface of a 60 nm gold film by a single 30 fs laser pulse with the Gaussian intensity profile. Laser beam with a diameter of 8 mm was focused onto the sample surface by a 20 mm focus lens. Laser pulse energy E_p is 65 nJ (a), 70 nJ (b) and 75 nJ (c), respectively.

In this paper, it is shown that femtosecond laser-induced processes can be applied for liquid phase material transfer in the form of nanodroplets. In contrast to previously reported studies on laser-induced forward transfer of metal droplets [3–5], the nanodroplet transfer is performed in opposite direction backwards to the laser beam. It is shown that in the case of laser-induced backward transfer (LIBT) the size of the transferred droplets is directly related to the volume of laser-molten gold region and can be controlled by the laser beam spot size and film thickness. Controllable transfer of different size droplets is demonstrated.

2. Experimental details

In our experiments, we use a commercial 1 kHz femtosecond laser system (Femtolasers Produktions GmbH Femtopower Compact Pro) delivering 0.9 mJ, 30 fs laser pulses at average wavelength of 800 nm. Gold films with thicknesses of 10, 20 and 60 nm coated onto quartz glass substrates were fabricated by Layertec GmbH using magnetron sputtering.

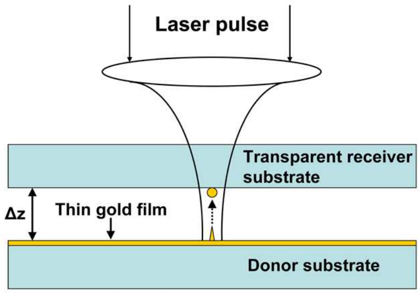

Fig. 2. Experimental scheme.

Laser irradiates the front side of the gold films through a transparent (glass) receiver substrate placed on the top of the sample in close contact: $\Delta z < 10$ µm (Fig. 2). Laser-induced gold structures on both donor and receiver substrates have been analyzed by Scanning Electron Microscopy (SEM).

3. Results and discussion

Femtosecond laser irradiation of a thin gold film induces a flow of molten material from the edges towards the center of the irradiated region and out of the substrate [7,10]. This flow is affected by strong surface tension forces leading to the formation of jet-like structures with droplets on the top. If the laser energy is low enough these structures solidify on the film surface without any ablation (see Fig. 1(a) and 1(b), and [7]). However, when the energy becomes higher than some threshold value (75 nJ for the irradiation conditions described in Fig. 1) the droplet detaches from the top of the jet and flies away from the surface (Fig. 1(c)). In this case, if one puts an additional transparent substrate above the sample, these droplets can be either attached to this substrate or reflected from it, falling back onto the gold film surface. Both of these processes have been observed in our experiments. If the distance between the donor and the receiver substrates is high enough (typically $\Delta z > 10$ µm) most of the droplets are reflected from the receiver and fall back onto the donor substrate. However, if the distance is low enough ($\Delta z < 10$ µm) most of the droplets are attached to the receiver. This method can be applied for the fabrication of ordered microstructures consisting of gold nanodroplets (Fig. 3(a)). The attached droplets have a spherical shape, as can be seen from the SEM images (see an example shown in Fig. 3(b)). The diameter of the droplet shown in this figure is about 800 nm and is smaller than the diameter of the laser beam focus on the sample surface (about 3 µm). This difference is explained by the movement of the molten material towards the center of the irradiated area before the detachment. It is likely that all the material from the disk-shape laser-melted region partially contributes to the formation of a spherical droplet and a jet-like structure in the center. According to this scenario, one can expect that changing the volume of the molten material by varying laser focusing conditions or the film thickness will strongly affect the size of transferred droplets. Results of this experiment are shown in Fig. 4(a). One can see that the size of transferred droplets can be varied in a wide range and can be decreased down to 300 nm when 20 nm gold films are used. Even smaller sizes down to 220 nm can be obtained with 10 nm gold films (Fig. 4(b)). Solid curves in Fig. 4(a) show calculated dependences of the droplet diameter on the size of molten region under assumption that all the material in this area redistributes into the center and forms a spherical droplet (for a cylindrical molten region and a spherical droplet $d_{droplet} \sim d_{molten\ region}^{2/3}$). These results show that in case of 60-nm gold films only a part of the molten material transforms into a droplet, while another part contributes to the formation of a jet-like structure.

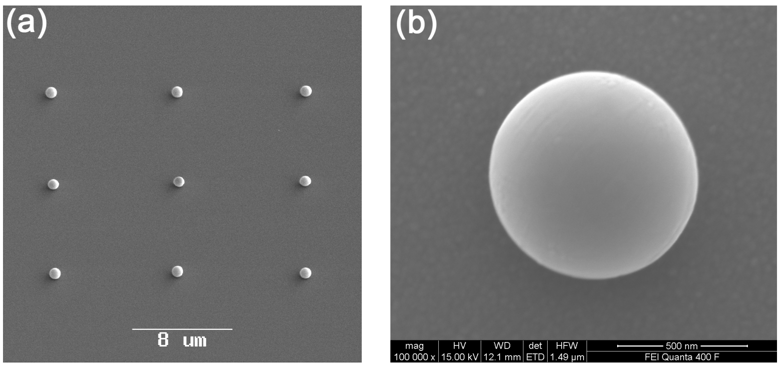

Fig. 3. (a) Array of gold nanodroplets transferred onto a glass substrate by subsequent 30 fs laser pulses. Laser focusing conditions are the same as in Fig. 1, $E_p = 75$ nJ. (b) Magnified view of a droplet from Fig. 3(a).

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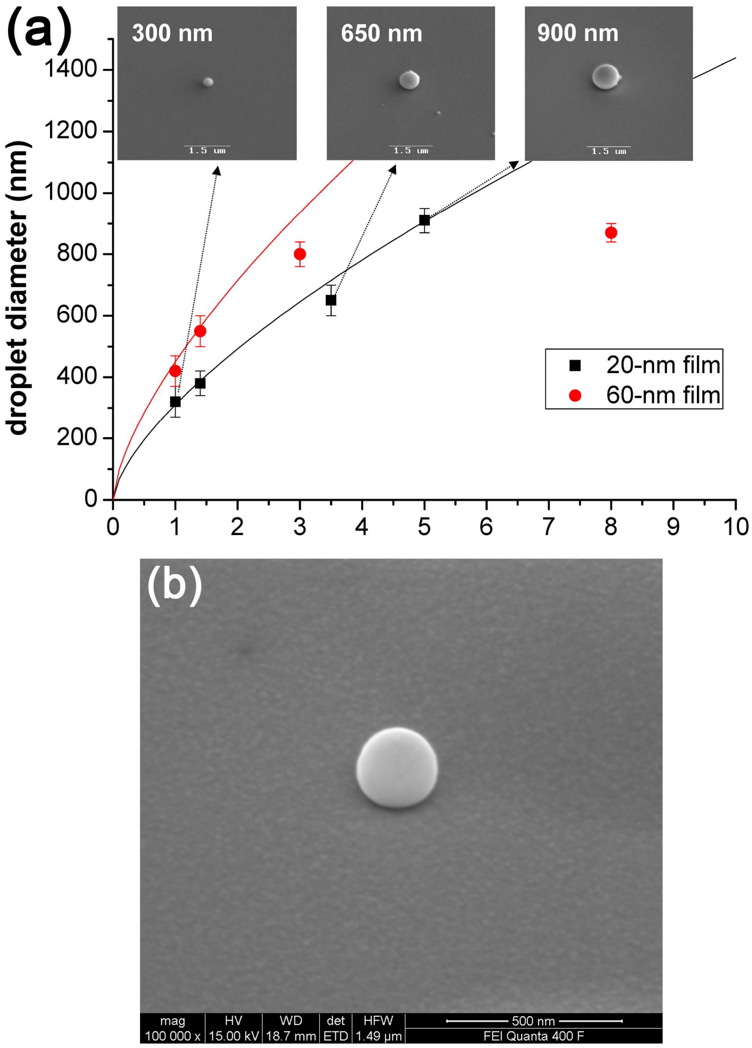

Fig. 4. (a) Size dependence of the transferred droplets on the focusing conditions and gold film thickness. Diameter of the laser-melted region was defined as a diameter of a modified area on the donor substrate by SEM imaging. (b) A 220 nm gold droplet generated by LIBT using a 10 nm gold film.

On the other hand, in case of 20-nm gold films almost all the molten material transforms into a droplet transferred towards the receiver substrate. These findings were supported by SEM observations of the structures remained on the gold film after the transfer process: (i) the jet-like structures in case of 60 nm gold film (Fig. 1(c)) and (ii) holes in case of 20 nm gold film (not shown here).

In contrast to previous observations [4], the shape of transferred gold droplets is always close to spherical, independent of laser fluence. On the other hand, the number of transferred droplets by single laser pulse changes with the laser pulse energy. For the experimental conditions described in Fig. 1 and laser pulse energies close to the droplet transfer threshold (75nJ $\leq E_p \leq$ 90 nJ), single droplet transfer is observed. At somewhat higher laser pulse energies, backward transfer of two droplets by single laser pulse is detected. At much higher laser pulse energies one could observe transfer of multiple droplets of smaller sizes. In case of multiple droplet transfer the size and position of droplets cannot be controlled anymore.

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The mechanism of such liquid phase laser-induced backward transfer (LIBT) of gold nanodroplets is different from that proposed earlier for explanation of LIFT experiments [3]. In case of LIFT, a donor film is melted first on the inner interface between the metal film and the substrate. It is supposed that the transfer of small droplets in the liquid phase becomes possible when the melted region expands up to the free surface of the metal film. After that the melted material is ejected from the free surface [3–6]. In case of LIBT, gold film is first melted on the free surface. The fast heating and melting processes lead to material expansion since the density of the liquid gold is lower than that of the solid gold. The increase in pressure due to the confined material expansion generates initial compressive stress in the film. This compressive stress induces an unloading tensile wave, which is reflected from the substrate and solid walls around the melted region. The reflected unloading wave generates movement of the melted material towards the center of the irradiated region and out of the substrate [7,10]. This movement, in competition with strong surface tension forces, leads to the formation of a spherical droplet and, depending on laser energy, its solidification or ejection from the surface. Formation of multiple droplets at higher laser fluences can be explained by a surface tension-induced breakage of a liquid jet into several droplets calculated for example in [11].

Figure 3(a) demonstrates an array of gold nanodroplets obtained by successive laser pulses. This approach requires sample positioning for a transfer of each droplet and a modification of focusing conditions in order to vary the droplet size. Another interesting approach, which can allow single-pulse controllable fabrication of multiple droplets of varied sizes, is provided by the image transfer technique based on the projection of different masks onto the gold film surface [7]. Two examples of structures formed by single laser pulses in the case of grid-like hole mask are shown in Fig. 5. The laser beam diameter before the mask is 8 mm and the laser pulse energy is 70 μJ. One can see that the fabrication of multiple nanodroplets of controllable size is possible in this case. Small variations of the droplet shape appear due to inhomogeneities of the laser beam profile.

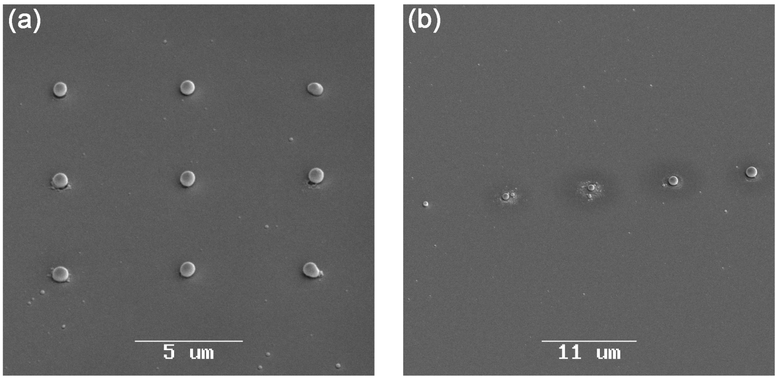

Fig. 5. Arrays of gold nanodroplets transferred by single femtosecond laser pulses through the grid-like hole mask. These results are obtained by the image transfer of the grid-like hole masks with 100 μm holes (a), and 100, 150, 200, 250, and 300 μm holes (b) using 50 × demagnification. Laser beam diameter before the mask is 8 mm, laser pulse energy is 70 μJ.

4. Conclusion

In conclusion, femtosecond laser-induced backward transfer (LIBT) of gold nanodroplets is demonstrated for the first time. Droplets are formed and ejected from the surface of a thin gold film towards a glass substrate due to laser-induced thermal expansion of the molten layer affected by strong surface tension forces. Size of the droplets depends on the volume of laser-melted material and can be varied by changing laser focusing conditions and the gold film thickness. Controllable transfer of gold droplets with a minimum size of 220 nm has been demonstrated using a 10 nm gold film. This approach should also work with other metals. It

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can be used for the fabrication of complex microstructures composed of spherical metal nanodroplets which can find interesting applications in plasmonics.

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