Fabrication of porous metal nanoparticles and microbumps by means of nanosecond laser pulses focused through a fibre microaxicon

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Abstract

We present a novel optical element: a fibre microaxicon (FMA) for laser radiation focusing into a diffraction-limited spot with a Bessel-like profile as well as for precision laser nanostructuring of metal film surfaces. Using the developed FMA for single-pulse irradiation of Au/Pd metal films on a quartz substrate, we demonstrated the formation of submicron hollow microbumps, each with a small spike atop it as well as hollow spherical nanoparticles. The experimental conditions for the controllable and reproducible formation of ordered arrays of such microstructures were defined. The internal structure of the fabricated nanoparticles and nanobumps was experimentally studied using both argon-ion polishing and scanning electron microscopy. These methods revealed a porous inner structure of laser-induced nanoparticles and nanobumps, which presumably indicates that a subsurface boiling of the molten metal film is a key mechanism determining the formation process of such structures.

Keywords: Laser-assisted nanostructuring; Nanosecond laser pulses; Fibre microaxicon

Introduction

Nanostructuring using short and ultra-short laser pulses provides opportunities for the fabrication of different micro- and nano-scale structures (nanojets [1,2], nanowhiskers [3], bumps [4], spherical nanoparticles [5,6], through nanoholes [7], nanocrowns [8], etc.) on sample surfaces. Single or periodically arranged laser-induced nanostructures can exhibit the desired properties of local field enhancement and strong plasmonic response [9] and high electron emission [10], which make such nanostructures promising candidates for use in different sensors as well as in nanophotonic and plasmonic devices [11]. Research interest in this area has continued unabated for several decades, largely due to the versatility, non-contact nature, high efficiency and relatively low cost of the laser nanostructuring methods compared with electron- and ion-beam milling methods as well as the
possibility to fabricate unique types of nanostructures via laser—matter interaction.

The fabrication of nanostructures onto the sample surface is mainly performed by using nano-, pico-, and femto-second laser pulses focused using classical high-NA focussing optics [1,2,5,6]. The minimal lateral size of the focal spot in this case is limited by a fundamental diffraction limit, which, under ideal conditions, is equal to $\lambda/2$ ($\lambda$ — laser wavelength), i.e., $\sim$200 nm for visible light. Fabrication of sub-100-nm structures using focussing optics is still possible and can be performed despite the diffraction limit effect by using a non-linear threshold response of the modified sample. However, in this case, the requirements for homogeneity and intensity distribution in the focal spot are very high, which often necessitates the use of additional diffraction optical elements. In practice, the achievement of such extreme light localisation with the high-NA optics is a difficult task and requires expensive high-quality focussing lenses. However, several papers [7,12−14] report that the high spatial focussing of the laser radiation into a high-quality focal spot as well as precise positioning of the focal spot on the sample surface can be achieved by using a single optical element — a bare fibre taper (BFT). This element is similar to a standard aperture-type probe of a scanning near-field optical microscopy (SNOM) but differs due to the absence of a metal coating and a nanosized aperture. Such BFTs, despite the reduced focussing capabilities compared with conventional SNOM probes, exhibit a significantly higher throughput and damage threshold and are widely used in precision laser nanostructuring [7], laser-induced breakdown spectroscopy [12], local spectroscopy of quantum objects [13], reflection-mode SNOM [14], etc. To achieve the maximal lateral localisation of the laser radiation by using the BFT, its tip must be shaped into a truncated cone with an upper cone base diameter $\sim\lambda/2$ [15]. However, such geometric shape optimisation of the probe tip requires not only an expensive and the time-consuming ion-beam milling, which significantly complicates the fabrication process of probes, but also causes the focussing element to be tied to a specified wavelength of the input laser radiation.

In our previous work [16], we demonstrated that near-$\lambda/2$ lateral localisation of laser radiation can be achieved by using a fibre microaxicon (FMA) fabricated on the flat endface of a single-mode optical fibre (OF) that is axially symmetric to its core. We also modified a chemical etching method to fabricate the FMAs [16] using different commercial OFs. In this paper, we will use for the first time the FMA as a compact, universal and highly efficient optical element for the spatial filtering and focussing of nanosecond laser pulses into a diffraction-limited spot with a Bessel-like spatial distribution as well as demonstrate the single-pulse laser-assisted fabrication of various nanostructures on the surfaces of metal films. We also report the fabrication of submicron bumps through holes and porous spherical nanoparticles as well as discuss the possible underlying formation mechanisms of such micron- and nano-scale structures.

Experimental details

Linearly polarized third-harmonic ($\lambda = 355$ nm) pulses of a Nd:YAG-laser with the pulse width $\tau_p \sim 7$ ns, maximum energy $E \sim 10$ mJ and energy stability $\sim 10\%$ were used for surface nanostructuring (Fig. 1(a)). Spatial filtering of the output laser beam and its focussing into the diffraction-limited spot were performed by means of the FMA (Fig. 1(b))
fabricated using modified chemical etching [16] on the flat endface of the OF (optical core diameter \(\sim 1.7 \, \mu m\)). The FMA's geometric shape (full cone angle \(\theta \approx 90^\circ\) and cone base diameter \(D = 2 \, \mu m\)) was optimised to achieve the smallest laser spot [16] (Fig. 1(b)). The resulting laser beam at the FMA focal plane represents a central spot surrounded by additional maxima of significantly lower intensity than the central spot; these additional maxima do not influence the laser nanostructuring process. A typical laser intensity distribution at the FMA output measured by using the aperture-type collection-mode SNOM indicates the spatial localisation of laser radiation is in a highly symmetric focal spot with a FWHM diameter of \(\sim 180 \, nm \) (\(\lambda/2\) at \(\lambda = 355 \, nm\)) (Fig. 1(c)).

To measure the pulse energy at the FMA output, the Bessel-like beam is filtered to remove additional maxima and is then focused using a lens onto the sensitive photodetector (J-10SI-HE Energy Sensor, Coherent EPM2000). We used Au/Pd (80/20 wt.\% ) films of different thicknesses deposited using a magnetron sputter coater (Quorum Technologies) on the smooth OF endface. During the laser nanostructuring process, the FMA was placed normally to the sample surface (inset in Fig. 1(a)). The probe-to-sample distance was controlled at a constant level (\(\sim 0.3 \lambda [16]\)) using tuning fork feedback. Visual control of the FMA movement was performed using a high-resolution optical microscope (Hirox KH7700). All laser-induced structures were fabricated using single-pulse irradiation under ambient conditions and were then characterised using a scanning electron microscope (SEM, Hitachi S3400N) and an atomic force microscope (AFM, NanoDST Pacific Nanotechnology).

**Results and discussions**

Fig. 2 shows the main types of laser-induced structures fabricated on the 40-nm thick Au/Pd film using single-pulse irradiation for the pulse energy \(E\) ranging from 1 to 4 nJ. Visible modification of the metal film is observed at \(E > 1 \, nJ\) and represents a 400-nm wide microbump with a height \(h_{bump}\) up to 30 nm (see inset in Fig. 2(a)). Note that the minimum lateral size of the microbump is approximately 2 times larger than the initial optical spot (\(\sim 180 \, nm\)) on the Au/Pd film surface, presumably indicating lateral heat transfer. As the pulse energy increases, the lateral size \(D_{bump}\) and the height \(h_{bump}\) of the microbump grow, reaching their maximum values (\(D_{bump} = 600 \, nm\) and \(h_{bump} = 60 \, nm\)) at \(E \sim 2 \, nJ\) (Fig. 2(b)). Both darker areas in the SEM images (marked by the red arrows in Fig. 2(b)) and the absence of any local convexities or dents in the corresponding AFM images presumably indicate a local thinning of the Au/Pd film and formation of nanoscale cavities inside the microbump, indicating the occurrence of a subsurface boiling process at the “film – substrate” interface.

When the pulse energy reaches approximately \(E \approx 2.3 \, nJ\), one of the inner cavities inside the
microbumps was observed to collapse, thereby forming a through (in accordance with a high SEM images contrast) nanohole (Fig. 2(c)). The diameter of the fabricated nanohole may be very small, reaching ~35 nm [7]. However, the formation mechanism of the through nanohole seems to be a result of an increasing vapour recoil pressure, which increases with $E$. Thus, the nanohole can appear randomly at the microbump centre or at the interface of the melted and unmodified film (see Fig. 2(c)). We assume that the fabrication of the sub-100-nm through holes in [7] was also associated with a similar mechanism. Note also that this process can result in the simultaneous formation of several nanoholes in the microbump area (not shown in the figure).

Further increase of the pulse energy up to $E \approx 3.7$ nJ leads to the film break via the vapour recoil pressure and the formation of sufficiently large 600-nm wide through holes, with the molten material tending to form a nanoparticle or to spread in different directions, thus forming frozen edge microstructures (Fig. 2(d)). Note that an attempt to calculate and compare the volumes of the spherical nanoparticles and the corresponding through nanoholes (Fig. 2(d)) leads to some discrepancy. Thus, the average nanoparticle diameter ranges from 350 to 420 nm with its volume being approximately $V_s = 0.03 \text{ \mu m}^3$. Similarly, the volume of the through hole with an average diameter $D_{\text{hole}} = 800$ nm fabricated in a 40-nm thick Au/Pd film (Fig. 2(d)) is approximately $V_{\text{hole}} \approx 0.02 \text{ \mu m}^3$. Thus, even without assuming the small frozen edge microstructures the $V_s$ value is approximately 1.5 times larger than the corresponding through-hole volume, which presumably indicates the hollow internal structure of the nanoparticle. When the pulse energy exceeds $E \approx 4.1$ nJ, almost all of the molten material is ejected from the hole (not shown in Fig. 2).

Note that similar microstructures are also fabricated by single-pulse irradiation of an 80-nm thick Au/Pd film; however, the threshold energies for the formation of the corresponding microstructures are approximately 2 times higher in comparison with the $E$ values measured for the 40-nm thick film. This result is in good agreement with our earlier experiments performed on pure gold films, demonstrating the influence of the film thickness $d$ on the size of the obtained laser-induced nanostructures and the threshold pulse energy $E_{\text{th}}$ required for the fabrication of such structures (“size effect”). The fabrication of microbumps resulted from the subsurface boiling and the vapour recoil pressure was also observed for a 160-nm thick Au/Pd film irradiated by single nanosecond pulses at $E > 10$ nJ. However, at an increasing pulse energy, no nanosized

![Fig. 3. Main types of laser-induced microstructures fabricated on the 160-nm thick Au/Pd film irradiated by single nanosecond pulses at the pulse energy $E$ values of 1 nJ (a), 2.1 nJ (b), 2.5 nJ (c), 3.8 nJ (d).](image)
through-holes were observed. Instead, when the pulse energy reaches $\approx 15 \text{ nJ}$, the microbump walls thinned down, as evidenced by a noticeable darkening in the SEM image, and the formation of the spherical protrusions at the microbump apexes were observed. Apparently, the formation of apexes are associated with both increasing vapour recoil pressure and molten material accumulation caused by the surface tension gradient (Marangoni effect \cite{1,3,5}). Note that these microstructures resemble the initial stage of the formation of nanojets, which involves spherical nanoparticle ejection under the action of a single tightly focused femtosecond laser pulse \cite{1,3,5}. However, at higher pulse energies, no nanojets are observed; instead, the microbumps collapse, forming submicron holes with frozen structures at its edges (Fig. 3(d)). Note that, despite the high uniformity and symmetry of the output FMA beam, the frozen edge structures are poorly reproducible, with the microhole diameter $D_{\text{hole}}$ significantly varying from 400 to 1200 nm.

To confirm the subsurface boiling mechanism leading to microstructure formation, we studied their internal structure using a slow polishing by unfocused Ag$^+$ ions (Hitachi IM4000). This technique allows one to remove layers of a metal film at an average polishing rate $\sim 0.33 \text{ nm/s}$. To minimise the possible melting of the metal film under the action of the heating Ag$^+$ beam, the polishing process was performed for several consecutive irradiation cycles, each of which does not exceed 15 s, followed by metal film cooling for 1 min after each cycle. The result of 160-nm thick Au/Pd film polishing for a total exposure time $\sim 300 \text{ s}$ is shown in Fig. 4 for some selected microstructures (bottom row). The same figure (top row) also shows the corresponding microstructures before their Ag$^+$ beam processing. The laser-induced microbumps are observed to have a highly porous internal structure, with the molten film material being mainly concentrated at the centre of the irradiated laser spot, which confirms the findings discussed in this work. We also note that the appearance of the local thickness inhomogeneities after single-pulse irradiation may be associated with an explosive boiling as well as a formation of cavitation bubbles with a rapid expansion of the molten material under the laser pulse action.

Similar experiments performed for Au/Pd films with thicknesses $d$ of 40 nm and 80 nm also reveal similar porous internal structures of the fabricated spherical nanoparticles and microbumps. To the best of our knowledge, the controllable fabrication of laser-induced hollow nanoparticles is reported here for the first time. Plasmonic properties of such hollow nanoparticles appear to significantly differ from the properties of bulk nanoparticles, demonstrating the local plasmon resonance shifts or even additional resonances \cite{17}.

However, these studies are clearly outside the scope of this paper and will be presented in a forthcoming paper. Dependencies of the geometric dimensions of
the laser-induced microstructure on the pulse energy $E$ for different film thicknesses $d$, which summarise the experimental results of this paper, are shown in Fig. 5(a). The film thickness $d$ is found to be a determining parameter for controllable fabrication of the desired microstructure. Fig. 5(a) Diameter and height of laser-induced microstructures versus pulse energy measured for Au/Pd film thicknesses 40 nm, 80 nm and 160 nm. SEM images in the insets illustrate the main types of the laser-induced microstructures; (b) SEM image of “IACP” letters consisting of microbumps on the 80-nm thick Au/Pd film surface (each microstructure was fabricated using a single-pulse irradiation at $E = 3.2$ nJ); (c) SEM images of the single microstructure — 100-nm wide through-hole formed in the FMA apex coated with the 80-nm thick Au/Pd film.

Conclusions

In conclusion, this paper presents a novel optical element: a fibre microaxicon for laser radiation focussing into a diffraction-limited spot with a Bessel-like spatial distribution as well as for precision laser nanostructuring of metal film surfaces. Using the developed FMA for single-pulse irradiation of Au/Pd metal films on quartz substrates, we demonstrated the formation of submicron hollow microbumps with a small spike atop as well as hollow spherical nanoparticles. The experimental conditions for the controllable and reproducible formation of ordered arrays of the corresponding microstructures were defined. The internal structure of the fabricated nanoparticles and nanobumps was experimentally studied by using accelerated argon ion polishing as well as scanning electron microscopy. These methods revealed a porous inner structure of laser-induced nanoparticles and nanobumps, which indicates that a subsurface boiling of the molten metal film is a key mechanism determining the formation of such structures.

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References

[7] YuN. Kulchin, et al., Through nanohole formation in thin metallic film by single nanosecond laser pulses using...