Nanostructuring of solids with femtosecond laser pulses

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ABSTRACT

Investigations of possibilities for nanostructuring with femtosecond laser pulses of different materials are reported. The aim is to develop a simple laser-based technology for the fabrication of two- and three-dimensional nanostructures with structure sizes on the order of several hundred nanometers. This is required for many applications in photonics, for the fabrication of photonic crystals and microoptical devices, for data storage, displays, etc. Sub-wavelength structuring of metals by direct femtosecond laser ablation is performed. The band gap dependence of the minimum structure size for transparent materials is identified.

Keywords: material processing, femtosecond lasers, nanostructuring

1. INTRODUCTION

Rapid progress of ultrafast lasers opens up new applications and possibilities for high-precision material processing that can not be realized with traditional laser systems. Femtosecond lasers have established themselves as excellent and universal tools for microstructuring of solid materials by direct ablative writing.[1–8] This technique allows to fabricate large area patterns and high quality microstructures with structure sizes between one and hundred micrometers. Whereas the ability to microstructure is well established, the ability to nanostructure with femtosecond lasers is still in its infancy.

By using tightly focused femtosecond laser pulses it is possible to produce sub-micrometer structures. However, it is still unclear how practicable and reliable this technique could be. At present, the challenge is to develop a simple, reliable and rapid nanofabrication technique.

In this paper we report on investigations of possibilities to use femtosecond lasers for nanofabrication with a resolution (structure size) of the order of several hundred nanometers (100 – 500 nm). This is required for many applications in photonics, for fabrication of photonic crystals, LEDs and laser diodes, microoptical devices, data storage etc.

2. STRUCTURING BELOW THE DIFFRACTION LIMIT

In laser-processing technologies the minimum achievable structure size is determined by the diffraction limit of the optical system and is of the order of the radiation wavelength. However, this is different for ultrashort laser pulses. By taking advantage of the well-defined ablation (in general, modification) threshold one can beat the diffraction limit by choosing the peak laser fluence slightly above the threshold value (see the schematic illustration in figure 1).[1] In this case only the central part of the beam can modify the material and it becomes possible to produce sub-wavelength structures. The minimum structure size is determined by the equation

$$d = d_0 \sqrt{\ln \frac{F}{F_{th}}}, \qquad (1)$$

where F is the laser fluence, F_{th} is the threshold fluence for ablation, and d_0 is the beam diameter.

In principle, this technique allows arbitrary small structure sizes. But in practice, there is a limit due to intensity fluctuations of the laser pulse and beam pointing instabilities. Therefore, the minimum achievable structure size is limited by the stability (and beam profile quality) of the femtosecond laser system and reproducibility requirements.

On transparent materials there is a further possibility to produce sub-diffraction limited structures. It will be discussed in section 4.

Another approach to beat the diffraction limit (witch is not discussed here) is to use femtosecond pulses in combination with a scanning near-field optical microscope (SNOM). Applications of this technique for nanostructuring and direct ablative writing have already been demonstrated.[9]
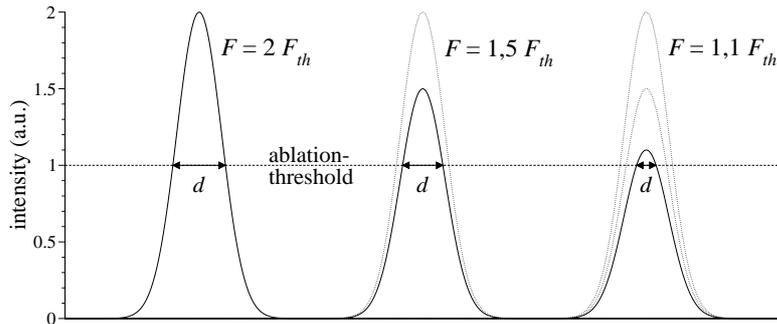
Figure 1. Schematic illustration of how one can overcome the diffraction limit by taking advantage of the well-defined ablation threshold

3. NANOSTRUCTURING OF METALS

In metals, nanostructures can be fabricated by direct ablation with tightly focused femtosecond pulses.[10] High-quality holes and structures in surfaces with a resolution (structure size) down to 100 nm are possible. One can think about applications like e.g. repairing lithographic masks, prototype fabrication (when lithography is too expensive) or structuring of non-plane surfaces.

Besides femtosecond laser ablation, metal nanostructures can be fabricated by using more complicated processes based on laser-induced dynamics in an ultra-small volume of a molten material. Due to the weak electron-phonon coupling in noble metals like Au or Ag, the energy transfer to the lattice is much slower than in transition metals like Cr, Mo, W or Fe. The molten phase exists much longer resulting in a drastical change of the ablation dynamics in these metals. Laser surface structuring without ablation is possible.

In a certain range of femtosecond laser parameters such a process can be used for the fabrication of nanojets on thin noble metal films. This technology is very reproducible (see left side of figure 2) and allows one to perform large-area nanostructuring.
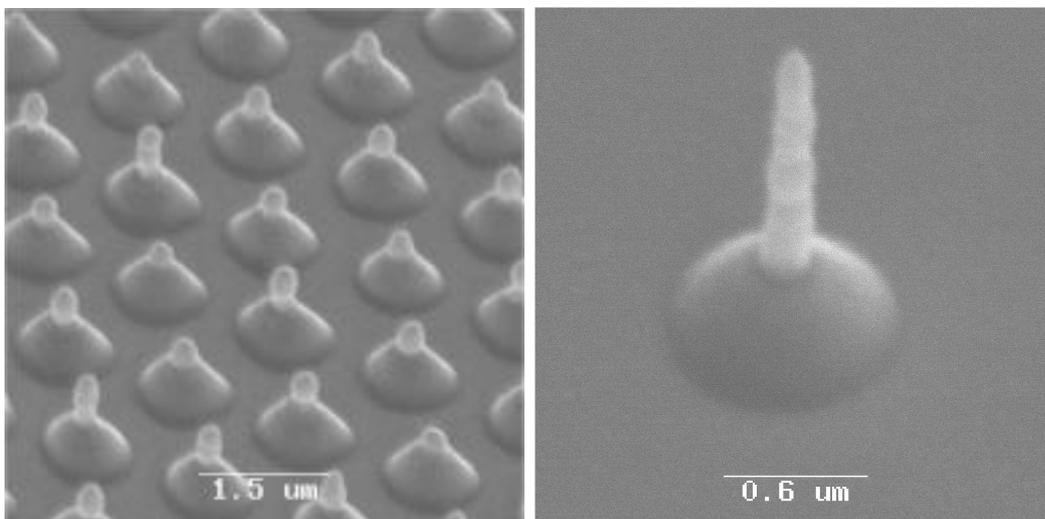

Figure 2. SEM images of an array of nanojets fabricated in a gold film with femtosecond laser pulses (*left*) and a single nanojet in detail (*right*)

Nanojets always appear on a bump-like structure. Both processes, the formation of a bump-like corrugated surface and nanojets, have well-defined thresholds. When the laser pulse energy is increased, first the bump-like structure appears on the target surface. Then the nanojets are formed. The microbumps are hollow inside, their

shell thickness is determined by the thickness of the molten layer. The length of the nanojets can exceed 1 μm (see right side of figure 2).

The dynamic picture of the processes induced by a femtosecond laser pulse in a molten gold layer is not yet fully understood. Qualitatively, the formation of microbumps and nanojets is analogous to that induced by a droplet fall into a glass filled with water. The surface waves initiated by a droplet falling, colliding at the center and forming a liquid jet, i.e. a splash. Everyone has seen this effect when observing drops falling onto the surface of water. It is possible that approximately the same happens in a molten metal film heated by a single femtosecond laser pulse. The waves initiated in melting collide at the center and produce, at first, a molten and then, a solid jet due to the fast solidification process.

Another explanation could be that not the molten but the solidification dynamics is responsible for the formation of microbumps and nanojets. Time-resolved investigations of this phenomena are in progress.

A possible application of this technology is e.g. the fabrication of metallic band-gap nanostructures utilizing surface plasmon polaritons as information carriers.

4. NANOSTRUCTURING OF TRANSPARENT MATERIALS

Due to the nonlinear nature of the interaction of femtosecond laser pulses with transparent materials, simultaneous absorption of several photons is required to initiate ablation. Multiphoton absorption produces initial free electrons that are further accelerated by the femtosecond laser electric field. These electrons induce avalanche ionization and optical breakdown, and generate a microplasma. The subsequent expansion of the microplasma results in the fabrication of a small structure at the target surface. The diameter of such a femtosecond laser drilled hole not only depends on the energy distribution in the laser-matter interaction area and the ablation threshold. There is also a dependence on the energy band gap of the material. To overcome a wider band gap more photons are needed. This results in a stronger limitation of the ionization process to the peak intensity region of the beam profile. The smaller absorbtion volume leads to a smaller hole diameter. This is, combined with the technique described in section 2, a further possibility to produce sub-diffraction limited structures.

The minimum structure size (for constant fluence ratio F/F_{th}) that can be produced by femtosecond laser pulses in materials with an energy band gap is determined by the equation

$$ d = \frac{k\,\lambda}{\sqrt{q}\,NA}\,, \tag{2} $$

where λ is the radiation wavelength, q is the number of photons required to overcome the energy band gap, NA is the numerical aperture of the focusing optics, and k is a proportionality constant ($k = 0.5\ldots1$). To illustrate this equation, figure 3 shows the effective beam profile and the ablation hole diameter for materials where one, two and four photons are needed for each ionization process.
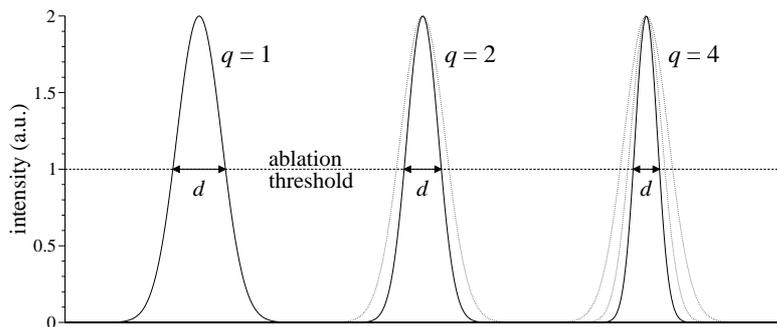

Figure 3. Effective beam profile and ablation hole diameter for materials where q =1, 2 and 4 photons are needed for each ionization process

To test this prediction, we investigated the dependence of the minimum structure size that can be fabricated in different transparent materials on their band gap energy. In these experiments, we used a commercial kilohertz femtosecond laser system delivering 1mJ, 30 fs laser pulses at a wavelength of 800 nm, and a $36\times$ Schwarzschild objective with $NA = 0.5$. In measurements of the structure size, an array of 10 holes fabricated with the same laser parameters was always used to obtain better statistics. Figure 6 shows the results for the fundamental wavelength of the laser system. Furthermore, it represents the theoretical curve from equation 2. Because of q is a natural number, the latter one is a step function. Figure 7 shows the same for a wavelength of 400 nm, the frequency doubled emission of the aforementioned laser system.

As can be seen, for transparent materials, the minimum structure size is in good agreement with the above equation. The wider spreadig of the experimental values for 400 nm wavelength is in part a result of the higher laser intensity fluctuations after the frequency conversion. But also material properties come into play. Whereas microstructuring with femtosecond laser pulses has an universal character, results of nanostructuring are material-dependent. With smaller structure sizes this dependence of shape and size on material properties becomes stronger. Figure 4 shows SEM images of typical holes in different materials. It visualizes the material dependence of sub-micrometer ablation results.
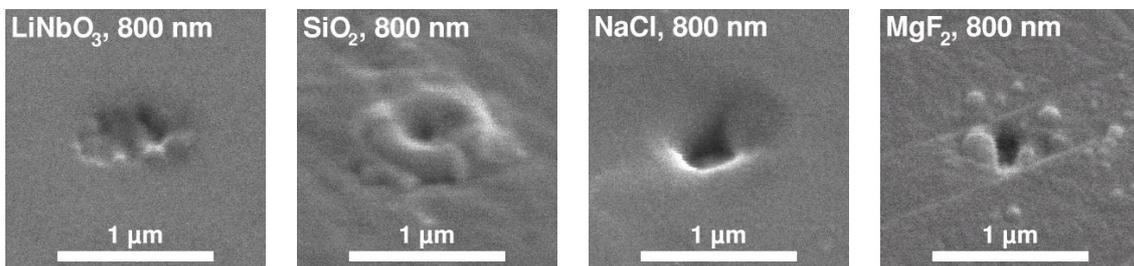

Figure 4. SEM images of sub-micrometer ablation results on different materials

In our experiments, we identified a class of materials that are suitable for nanostructuring with femtosecond laser pulses. An important example is a sapphire crystal, which can be nanostructured with sufficiently high quality. In figure 5, a first periodic nanostructure fabricated with femtosecond laser pulses in a sapphire crystal is shown. For each hole, ten laser pulses were used. The total processing time for 216 holes shown in figure 5 was 30 s (including the time required for sample positioning). This nanostructure can be considered as a two-dimensional photonic crystal with a defect cavity at the center. Nanostructures analogous to that shown in figure 5 are required for many applications in photonics.
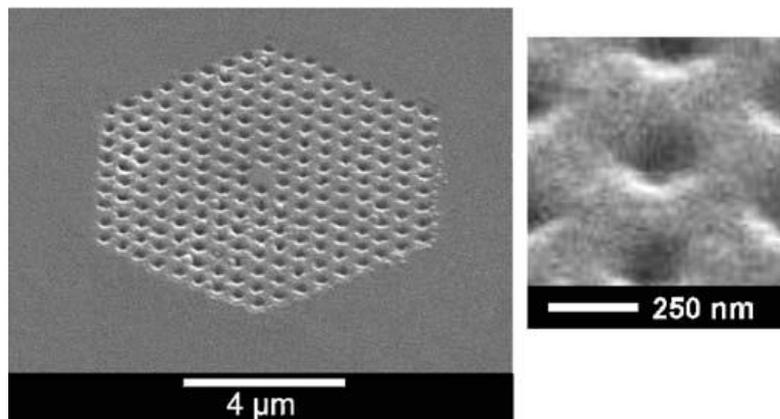

Figure 5. An example of a periodic nanostructure (with a defect cavity in the center) fabricated in a sapphire crystal with femtosecond laser pulses (*left*). On the *right side* an enlarged fragment of a single hole is shown.
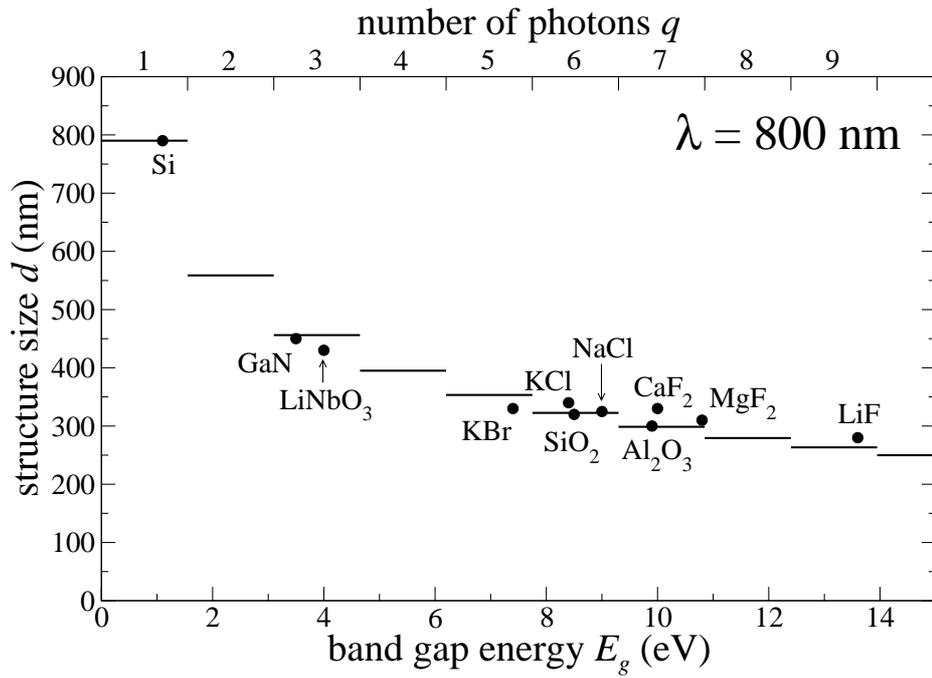
Figure 6. Structure sizes for a laser wavelength of 800 nm on materials with different band gap energies
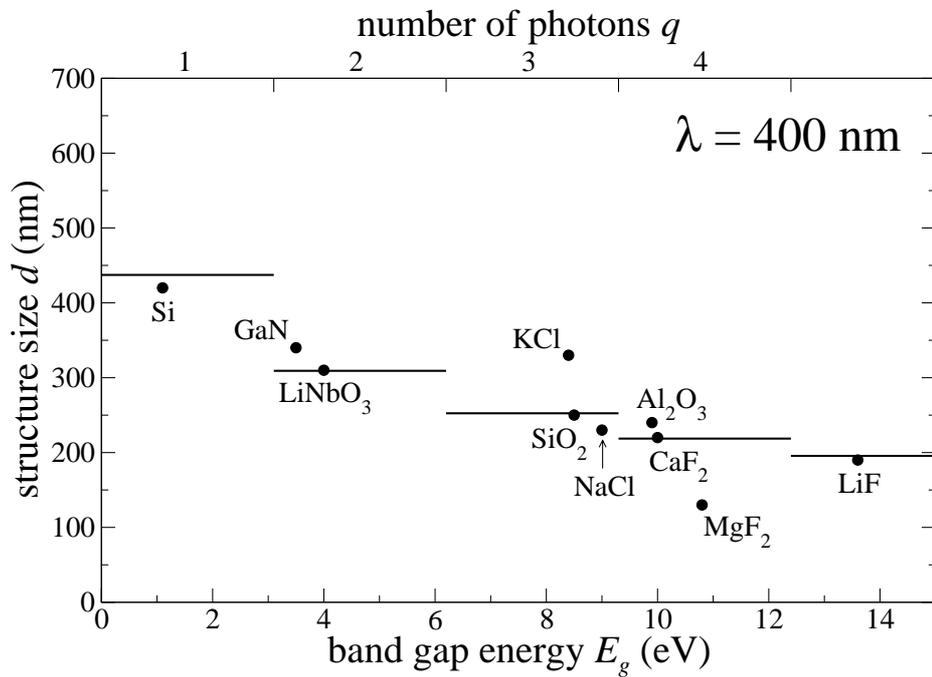

Figure 7. Structure sizes for a laser wavelength of 400 nm on materials with different band gap energies

5. CONCLUSION

Using femtosecond laser pulses tightly focused onto a target surface it is possible to fabricate nanostructures in metals and dielectrics with very high precision and reproducibility. The achievable structure size is not limited by diffraction but by the laser pulse stability. Furthermore, the ablation results show a growing influence of material properties with decreasing structure sizes.

In particular some transparent materials with wide energy band gaps are suitable for high resolution nano-structuring with femtosecond laser pulses. The fabrication of nanojets on noble metals is a promising technique for surface nanotexturing.

REFERENCES

1. P. P. Pronko, S. K. Dutta, J. Squier, J. V. Rudd, D. Du, and G. Mourou, "Machining of sub-micron holes using a femtosecond laser at 800 nm," *Opt. Commun.* **114**, p. 106, 1995.
2. C. Momma, B. N. Chichkov, S. Nolte, F. von Alvensleben, A. Tünnermann, and H. Welling *Opt. Commun.* **129**, p. 134, 1996.
3. B. N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, and A. Tünnermann, "Femtosecond, picosecond and nanosecond laser ablation of solids," *Appl. Phys. A* **63**, p. 109, 1996.
4. B. C. Stuart, M. D. Feit, S. Herman, A. M. Rubenchik, B. W. Shore, and M. D. Perry *J. Opt. Soc. Am. B* **13**, p. 459, 1996.
5. P. Simon and J. Ihlemann *Appl. Phys. A* **63**, p. 505, 1996.
6. W. Kautek, J. Krger, M. Lenzner, S. Sartania, C. Spielmann, and F. Krausz *Appl. Phys. Lett.* **69**, p. 3146, 1996.
7. S. Nolte, C. Momma, H. Jacobs, A. Tünnermann, B. N. Chichkov, B. Wellegehausen, and H. Welling *J. Opt. Soc. Am. B* **14**, p. 2716, 1997.
8. in *Laser Ablation*, J. S. Horwitz, H.-U. Krebs, K. Murakami, and M. Stuke, eds., *Proceedings of the 5th International Conference*, 1999.
9. S. Nolte, B. N. Chichkov, H. Welling, Y. Shani, K. Lieberman, and H. Terkel *Opt. Lett.* **24**, p. 914, 1999.
10. F. Korte, J. Serbin, J. Koch, A. Egbert, C. Fallnich, A. Ostendorf, and B. N. Cichkov, "Towards nanostructuring with femtosecond laser pulses," *Appl. Phys. A* **77**, p. 229, 2003.