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Optical Near Field Effects in Surface Nanostructuring and Laser Cleaning

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We present a method for directly imaging the undisturbed near field of a particle resting on a surface. A comparison with numerical computations shows good agreement with the results of our experiments. These results have important consequences for laser-assisted particle removal where field enhancement may cause local surface damage and is one of the physical key processes in this cleaning method. On the other hand, the application of near fields at particles allows structuring of surfaces with structure dimensions in the order of 100 nm and even below.

Keywords: near field, Mie scattering, imaging, nanostructuring, laser cleaning

1. Introduction

The current trend towards submicrometer structures requires new methods of surface structuring and has promoted intense research in recent years. As the traditional masking approach in optical lithography is limited to a minimal resolvable feature size of $\lambda/2$, a lot of alternative techniques have been developed. One approach in this respect consisted of the illumination of the tip of a scanning tunnelling microscope (STM) with a pulsed laser. Structures with lateral dimensions below 30 nm and therefore well below $\lambda/2$ could be produced underneath the tip [1,2]. It was proposed that the strong enhancement of the electromagnetic field in the vicinity of a tip, suggested e. g. by the calculations in [3], is responsible for this. Thus the setup seemed to be promising both for the study of field enhancement effects at sharp tips, a question of great interest in optics, and for surface structuring applications.

Further investigations showed that the structuring observed resulted from a thermal expansion of the tip and its subsequent mechanical contact with the surface rather than from field induced effects [4-6]. With regard to its application for structuring, the main disadvantage of the illumination of an STM tip is that the process is *serial*.

We changed to a method involving the illumination of micrometer and submicrometer sized spheres, which allows the study of field enhancement effects as well as its application for both a serial and *parallel* nanolithography process. Field enhancement underneath the spherical particles results in local ablation of the substrate wherever it is exposed to a sufficiently high energy density. Imaging of the ablation pattern, e.g. by an atomic force microscope (AFM), leads to a spatial mapping of the field in the surface plane. Consequently, this technique is not only of great interest as a new method for surface nanostructuring by local ablation. Since it allows the imaging of the field underneath a particle without disturbing the field distribution by a scanning probe tip, it might also be applied as a complementary approach in near field microscopy.

2. Experimental Setup

Sample preparation

As samples we used industrial silicon wafers with (100) orientation[1] and BK7 glass plates[2]. The samples were cleaned in an ultrasonic bath in water and subsequently in isopropyl alcohol (IPA). After this cleaning procedure a suspension of monodisperse polystyrene (PS) spheres with diameters of 320 nm and 800 nm was applied to the samples by a spin coating process. This technique has been described in detail in [7]. Alternatively, hexagonally close-packed colloidal monolayers were directly prepared onto the surface in a self-organizing process [8]. The surface of the samples prior and after laser treatment was characterised by a scanning electron microscope (SEM) and an AFM.

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Laser systems

To illuminate the samples, we used two different laser systems. In most of our experiments, a pulsed Ti:Sapphire-laser provided pulses of 100 fs duration with energies up to 10 mJ/pulse. They were generated by a mode locked Ti:Sa oscillator (Tsunami, Spectra Physics) and amplified by a Ti:Sa amplifier (TSA, Spectra Physics) with 10 Hz repetition rate. The wavelength was fixed to 800 nm and could be frequency doubled to 400 nm.

At the other system nanosecond pulses were generated by a frequency tripled Nd:YAG-laser (λ=355 nm) followed by an optical parametrical oscillator (OPO) which provides a wavelength range from 400 nm-2000 nm and a pulse duration of 8 ns. In the experiments described here a wavelength of 800 nm was used to enable a comparison of ablation induced by fs and ns pulses.

A spatially resolved mapping of the laser fluences in the irradiated region was obtained by combining imaging of the beam profile with a CCD-camera and detecting the total pulse energy for each pulse. The irradiated area of the sample was imaged using an optical microscope and could be correlated to the map of the laser fluences afterwards. All experiments were performed under ambient conditions.

3. Imaging of near fields

The scattered field of a spherical particle of arbitrary size in free space is described by the well-known Mie theory [9]. Therefore, we computed on the basis of this theory the field of polystyrene particles in the substrate plane by an algorithm taken from reference [10]. The patterns resulting from these calculations are shown in Fig. 1a for a 320 nm (bottom) and an 800 nm (top) particle illuminated by a plane wave with a wavelength of 800 nm. They exhibit a double-peak structure with a distance between the maxima of about 300 nm for both particle sizes, whereas the absolute value of the intensity enhancement differs by a factor of 4.5.

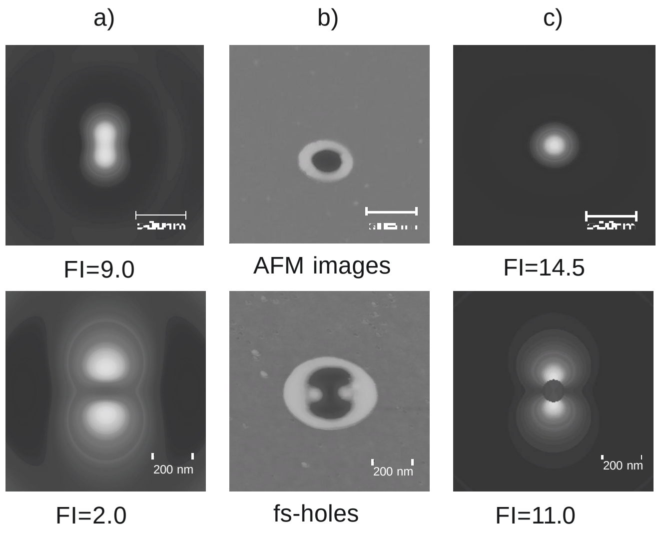

Fig. 1: Field intensity enhancement and ablation pattern underneath colloidal particles with diameters of 800 nm (top) and 320 nm (bottom) on a silicon substrate. The direction of the electrical field is orientated in the vertical direction.

a) Calculated field enhancement by neglecting the influence of the substrate. b) Ablation pattern resulting from

In a next step we compared these calculations to the experimental results shown in Fig. 1b. As previously shown [11], fs laser irradiation of particles on surfaces creates an ablation pattern underneath each illuminated particle. For constant laser fluences, all sites of ablation exhibit the same morphology. Underneath particles 320 nm in diameter, the ablation pattern shows a double hole structure, yet the distance between the maxima is obviously smaller than for the free space calculation. The pattern formed underneath an 800 nm particle does not show two peaks at all, but exhibits an elliptical shape.

Apparently, the Mie calculations differ substantially from the experimental findings. However, this theory holds only for an illuminated sphere in free space, thus neglecting the influence of the substrate. Consequently, these differences can be attributed to the influence of the silicon surface on the field distribution. In order to investigate this in more detail we performed semianalytical field calculations using the Multiple Multipole (MMP) technique [12]. Advantage was taken of the mirror symmetries of the problem and ring multipoles [13] were used to model the scattered fields both in the substrate and in vacuum. Optical constants were taken from reference [14]. The result of these calculations is shown in Fig.1c. The calculated field distributions fit the experimental findings well, if for the particles 800 nm in diameter we compare them to the results obtained in the substrate (10 nm below the surface) and for the smaller particles with those above (10 nm above the surface). The reason for this needs some further investigation. Besides the effect of ablation in the central part of the hole one observes the formation of a rim around the ablated area. In the development of this rim structure the dynamics of the melt influenced by viscosity and surface tension may play a role.

To investigate the influence of the duration of the laser pulse on the hole morphology we illuminated PS particles of various diameters also with ns pulses. In contrast to the rather sharp ablation holes that were generated using fs pulses, for ns pulses only shallow, broadened structures are observed (Fig. 2) as result of the lateral heat diffusion on the time scale of the laser pulse.

4. Surface nanostructuring

Besides the mapping of the field at particles, the creation of holes can be applied to a nanolithographic process. As colloidal particles can be deposited onto various materials including polymeric, biological, and semiconducting ones, this method seems to be feasible for nanostructuring of such technologically important substrates.

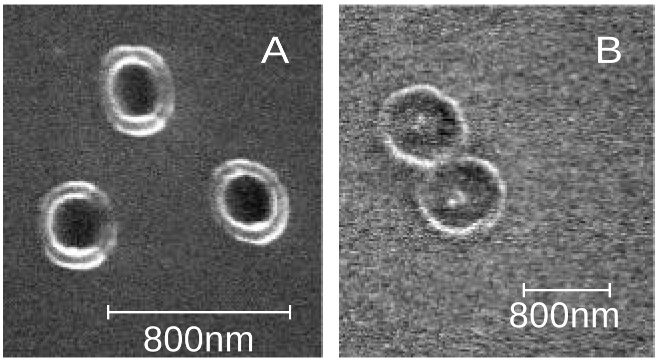

Fig. 2: Holes created by irradiation of 800 nm PS spheres with 100 fs (left) and 8 ns (right) laser pulses (λ=800 nm). Note the different length scales in A and B.

By controlled application of a colloidal suspension, deposition of isolated PS spheres at any desired concentration onto the substrate is possible. Such isolated spheres can be used to create single holes. An example is shown in Fig. 3. In order to decrease the hole's size, we chose an illumination wavelength of 400 nm and particles with 370 nm in diameter. Consequently, the size parameter is the same as in the experiments with 800 nm particles and a wavelength of 800 nm, mentioned before. Essentially, the shape of the hole in Fig. 3 appears to be similar to that in Fig. 1, but with a diameter of about 100 nm and thus half in size - as expected - compared to holes created by illumination at a wavelength of 800 nm.

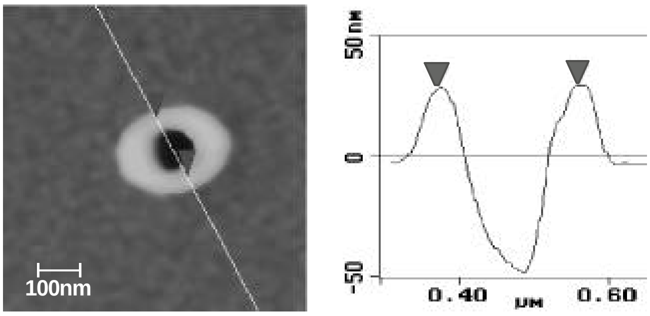

Fig. 3: AFM image of a singe hole created by irradiation of a 370 nm PS sphere with laser pulses from a frequency doubled Ti:Saphire-laser (λ=400 nm).

From a comparison with the shallow melting pools created by illumination with ns pulses (see Fig.2, FWHM=8ns) it is obvious that fs pulses are advantageous to create well-defined sharp edged structures, as the lateral heat diffusion is drastically reduced during the shorter pulses. This was also found when even longer (FWHM=23ns) pulses were used [15,16]. In this case rather washed out structures were obtained.

An exciting possibility besides the fabrication of single holes is the exploitation of self-organization processes, e. g. the utilization of 2-D colloidal monolayers, for the structuring process [8]. Illumination of an array of particles by an ultrashort laser pulse leads to an array of holes.

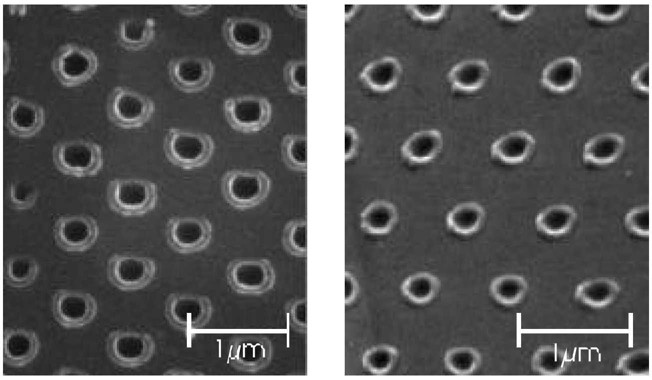

Fig: 4: Hole arrays formed after illumination of a hexagonal colloidal monolayer with fs laser pulses. Left: silicon substrate, right: germanium substrate.

This is shown in Fig. 4. Illumination of hexagonal monolayers of polystyrene spheres arranged e. g. on silicon or germanium surfaces results in a hexagonal pattern of holes at the semiconductor surface, reflecting the previous position of the colloid spheres. It is a parallel technique that allows the structuring of large substrate areas and can result in a million holes and more for a single shot, limited only by the size of the laser spot.

5. Field enhancement and laser cleaning

Besides its impact on nanostructuring and on the mapping of field distributions, the local substrate ablation induced by field enhancement is also important in the so-called "laser cleaning" process [17]. This process is currently discussed as an alternative technique for the removal of ultrasmall particle contaminants from surfaces of, e.g. silicon wafers, used by the semiconductor industry.

In this laser cleaning process, the surface to be cleaned is irradiated by a short laser pulse. It was observed that after the pulse and above a certain threshold fluence the particle contaminants were removed, as it is also the case for our experiments. This particle lift-off was attributed to the acceleration of the particles resulting from the thermal expansion of the substrate surface. The thermal expansion scenario was commonly accepted as removal mechanism for long. Only very recently it could be shown experimentally [18,19] that local ablation of the substrate can also play a dominating role in the cleaning process. This is further confirmed by the results discussed above. Especially for the case of fs pulses, particle removal always comes along with hole creation, i.e. local substrate ablation.

Besides accounting for another particle removal mechanism, field enhancement also drastically lowers the maximum laser fluence that can be applied to a contaminated surface. Taking into account the enhanced intensities underneath the particles the damage threshold of the system is given by the damage threshold of the substrate divided by the field enhancement factor.

From the above considerations it is clear that in order to accurately model the laser cleaning process a deeper understanding of field enhancement is an essential prerequisite. Therefore, further numerical computations as well as a crosscheck with the real field, experimentally observed as local ablation pattern, have to be done.

6. Conclusion

The results presented here are of relevance for the nano-structuring of surfaces, for the mapping of field distributions and for applications such as laser cleaning. From our investigations it is obvious that underneath the irradiated spheres one deals with light intensities far above the nominal applied ones. These enhanced field intensities can be used to pattern surfaces with holes of about 100 nm in diameter at a wavelength of 400 nm. Using 2D colloidal masks, it is even possible to create arrays with regularly arranged holes in a parallel process.

The shape of the field enhancement induced ablation pattern reflects the field distribution around a particle on a surface and can be computed numerically using the MMP technique. Imaging the ablation pattern with an AFM provides a possibility to map the near field of a particle resting on a surface without disturbing it by any probe tip. The results obtained from these investigations show that field enhancement and local ablation at particles on surfaces should be taken into account, whenever a pulsed laser illuminates such a particle-surface system. This is important in particular in the so called laser cleaning process, where local ablation induced by field enhancement results in particle removal and limits the maximum applicable laser fluence.

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