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Near-field nanopatterning

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P. Kühler, F. J. García de Abajo, J. Solis, M. Mosbacher, P. Leiderer, C.N. Afonso, and J. Siegel*

Control over the optical near field is a pillar stone of material processing,[1] microscopy,[2] and biosensing[3] at the submicrometer scale. The same applies to scanning probe techniques,[1,4] which produce an impressive spatial resolution, and to colloidal lithography[5] for casting large periodic nanostructure arrays. However, imaging near-field distributions with subwavelength detail[6] remains a challenge in this context. Here we demonstrate imaging of complex two-dimensional (2D) near-field patterns imprinted on photosensitive films, resulting from interference between laser light and light scattered by dielectric microspheres. We achieve control over the resulting patterns by varying the illumination conditions and the size and arrangement of the particles. Using chalcogenide films[7] to record the near field, the imprint produces optical,[8] electrical,[9] and topographical[10] contrast and allows for the writing of erasable features as small as 10 nm.[11] Our technique is directly applicable to any type of scattering particle (size, shape, and material), thus providing a simple way of imprinting its near field.

The optical near field in the vicinity of a micro- or nanoparticle illuminated by laser light has a spatial distribution that depends on the complex interplay between the properties of the scattering particle, the laser beam, and the substrate. Specifically, the local field enhancement induced by individual particles or sharp tips has been recently identified as a powerful means for nanopatterning applications,[12,13] opening the possibility to perform subwavelength surface carving of a variety of substrates.[1,14,15] In order to achieve controlled structuring, a detailed knowledge of the complex 2D near-field intensity distribution at the substrate plane is required. While different models have been proposed[12,15–17] to calculate this distribution, they all face the challenge to cope with non-symmetric complex structures.[18] Near-field ablation of the substrate accompanied by post-mortem atomic force microscopy (AFM) appears to be a powerful experimental method for studying the surface topography.[6] However, this method is hampered by the presence of non-linear interaction phenomena, the complexity of the ablation process, and the resulting debris. Alternatively, scanning near-field optical microscopy[19] (SNOM) has been shown to achieve spatial resolution of ≈30 nm, although this technique is compromised by the SNOM tip interaction with the near field, which is material- and topography-dependent and thus requires the use of modeling.

Here we report an experimental method to directly image with nanometer spatial resolution complex 2D near-field intensity distributions underneath the scattering particle by imprinting a corresponding 2D pattern in thin photosensitive films. The concept of our method is illustrated in Figure 1. A femtosecond laser is loosely focused onto a single particle or arrangement of particles sitting on a thin crystalline Ge$_2$Sb$_2$Te$_5$ film, exposing a region much larger than the particle(s).
Ge$_2$Sb$_2$Te$_5$ has been commercially used for decades in rewritable CDs and DVDs due to its ability to switch between a highly reflective, crystalline and a poorly reflective, amorphous phase upon exposure to pulsed laser radiation.[7] Using a single fs laser pulse of appropriate energy, the optical near field of the particle at the surface plane is imprinted by producing an amorphous 2D pattern within the crystalline matrix, which is directly linked to the near-field intensity distribution.

The beauty of this concept lies in its simplicity and applicability to any particle size, morphology, material, or arrangement. In contrast to near-field ablation,[6] we rely on linear absorption, melting, and rapid solidification, effectively “freezing” the melt into an amorphous pattern. The low optical bandgap of crystalline Ge$_2$Sb$_2$Te$_5$ (0.5 eV) allows us to do this over a wide range of wavelengths in the near-infrared region. Amorphization encompasses significant optical contrast (≈25% [20]), enormous changes in electrical resistivity,[9] (3 to 4 orders of magnitude), and a sizeable topographical contrast[10] (≈6% [21]). The latter two contrast types can be exploited using AFM,[11] ensuring nanometer spatial resolution, whereas optical contrast can be monitored with optical microscopy, yielding lower spatial resolution but allowing fast, in situ assessment and optimization of the resulting patterns. Previous studies using Ge$_2$Sb$_2$Te$_5$ films[14] did not show evidence of switching between the amorphous and crystalline phase, possibly related to the different initial phase of the films (amorphous) and the different laser used (ns excimer laser).

Figure 2a shows the darkening produced by a fs laser pulse incident on a Ge$_2$Sb$_2$Te$_5$ film at an angle of $\theta = 0^\circ$. The dark region corresponds to the amorphized material. The superimposed profiles of the measured laser intensity and film reflectivity distributions reveal their approximate opposite behavior. Figure 2b shows the result of a similar experiment, in the presence of a micrometer-sized silica particle, which is visible in the lower inset before irradiation, but is removed by interaction with the laser.[13] The pattern of concentric amorphous (dark) rings imprinted into the film, not present in Figure 2a, is a direct consequence of the interference of the incident light with the field scattered by the particle. The oscillation period far from the particle corresponds to the wavelength of the patterning laser ($\lambda_{\text{pat}} = 800$ nm), consistent with the expected far-field behavior. The exact position of the particle before irradiation is revealed by a central dark spot (film ablation originating from the lensing effect of the particle) and a surrounding bright ring (unmodified crystalline material).

We have modeled the experiment by rigorously solving Maxwell’s equations for a sphere supported on a layered planar substrate. The electromagnetic field produced in this system by an incident-light plane wave is self-consistently solved through expanding the scattered field of the sphere into spherical waves and the reflection of the substrate into evanescent and propagating plane waves. This leads to a set of multiple-scattering linear equations that we solve numerically. We have calculated the intensity distribution right underneath the surface (proportional to the local absorption). The relative intensity and position of the measured surface features in Figure 2b are correctly predicted by our calculation (upper inset). This agreement supports the validity of the model and

Figure 2. Near-field patterning with individual microspheres. Optical micrographs of crystalline GST films after exposure to fs laser irradiation (measured reflectivity in grayscale plots) are compared to near-field intensity calculations (color scale). a) Flat film exposed to a single fs pulse at normal incidence ($\theta = 0^\circ$), producing local amorphization (dark region). Superimposed are the normalized Gaussian laser intensity distribution $I/I_0$ (dashed curve) and the normalized film reflectivity $R/R_0$ (solid curve). b) Film supporting a SiO$_2$ microsphere (diameter $d = 4820$ nm). The microsphere, which was observed before normal-incidence irradiation (lower inset), is removed from the main image by the laser exposure. The calculated intensity $I/I_0$ is shown in the upper inset. c) Same film and particle as in (b), irradiated with s-polarized light incident from the left at an angle $\theta = 53^\circ$. The zoomed region has been measured by AFM and shows topography modulations with a period of 450 nm and a depth of 2 nm. d) Same as (c) for $d = 2340$ nm. e) Measured reflectivity pattern for $d = 2340$ nm: s-polarization (upper part) versus p-polarization (lower part). f) Calculated intensity pattern corresponding to the conditions of (e). The microsphere in (c) and (d) is not removed by the laser irradiation.
the suitability of the film material for these studies. The absence of non-linear absorption effects and exploitation of a simple amorphization mechanism enables a direct experiment–theory comparison by simply inverting the color scale used in the calculation (black = most intense). A more precise, quantitative comparison can easily be obtained by using the profiles for film reflectivity and laser fluence shown in Figure 2a as calibration curves, linking both quantities directly and unambiguously.

The richness of the information that can be directly accessed using this method becomes evident when changing basic experimental parameters. Figure 2c shows the pattern imprinted for oblique incidence ($\theta = 53^\circ$), which no longer has axial symmetry. The period $p$ of the observed fringes away from the particle can be estimated from the interference of the sphere far field $\sim \exp(ikr)/r$ and the incident plane wave. We find $p_{\text{fw}} = \lambda_{\text{pal}}(1 - \sin \theta) = 3973$ nm nm along the surface-projected forward direction, in good agreement with the optically observed value ($p_{\text{fw,exp}} \approx 4000$ nm), and $p_{\text{bw}} = \lambda_{\text{pal}}(1 + \sin \theta) = 445$ nm along the backward direction, which cannot be resolved in the micrograph (nominal optical resolution $> 300$ nm), but which is consistent with the value $p_{\text{bw,exp}} \approx 450$ nm measured by atomic force microscopy (see inset in Figure 2c). Actually, AFM is a suitable technique for resolving nanometer details of changes in topography$^{[10,11]}$ and electrical conductivity$^{[11]}$ produced upon local amorphization. These observations are again in excellent agreement with the calculated near-field intensity distribution (lower color inset in Figure 2c). Even the subtle angular discontinuities observed in the measured micrograph between the forward and backward directions are present in the calculated result. This agreement further supports the validity of our model in the transition from the near- to the far-field regime.

The influence of particle size is analyzed by comparing Figure 2d to Figure 2c, showing patterns imprinted by individual particles of diameters $d = 2340$ nm and $d = 4820$ nm, nm, respectively. While the period in the far field does not change, in agreement with the expected scaling $p_{\text{fw}} = \lambda_{\text{pal}}(1 - \sin \theta)$ (i.e., independent of particle size), the near-field pattern and the transition regime are very different in Figure 2d. Also here, the agreement between measured and calculated patterns is remarkable (see lower inset in Figure 2d).

The light polarization is found to have a strong influence on the imprinted pattern. Figure 2e shows a direct comparison of experimental results obtained upon irradiation with s-polarized (upper-half frame) and p-polarized (lower-half frame) light. A sizeable shift of the ring pattern for different polarizations is observed. This fringe shift is reproduced in the corresponding calculations (Figure 2f). Even subtle details, such as the reduced modulation depth in the upper-right corner of the s-polarization results and in the lower-left corner of the p-polarization results are correctly reproduced at the equivalent positions of the calculations.

The largest extension of a far-field pattern imprinted by the presence of an individual particle, defined as a radius $r_{\text{max}}$ measured from the particle center, is determined by the pulse duration, which affects the requirement of coherent interference between the scattered wave and the incident wave at a certain distance from the particle. Under the present conditions (120 fs pulse duration) the length of the wave packet is $L_{\text{pulse}} = 36$ µm, which directly yields the relation $r_{\text{max}} = L_{\text{pulse}}/(1 - \sin \theta)$. Close to normal incidence, the maximum extension of the far-field patterning is a few tens of micrometers, whereas at large angles of incidence $r_{\text{max}}$ increases dramatically, thus allowing us to control far-field patterns using single particles.

We have also explored the potential of this method for patterning complex structures using arrangements of spheres. Figure 3 shows two examples of patterns imprinted by simple arrangements at $\theta = 0^\circ$ (Figure 3a) and at $\theta = 53^\circ$ (Figure 3c). The coherent superposition of the individual electromagnetic far-field distributions gives rise to increasingly involved patterns, which are reasonably well described with our model (Figures 3b and d). In addition, any distortion of a coherent superposition, caused for instance by interaction between neighboring particles, can be directly visualized by imprinting the resulting optical near field. It turns out that this method is ideally suited for designing and imprinting complex patterns using controlled particle arrangements or self-assembled particles, and also for quantifying the effect of particle–particle interactions.

**Figure 3.** Near-field patterning with particle arrays. Optical micrographs of imprinted complex near-field patterns produced by irradiating arrangements of three silica particles on a GST film with fs laser pulses. a,c) Experimental patterns taken at $\theta = 0^\circ$ and $\theta = 53^\circ$ incidence, respectively. b,d) Calculated distributions corresponding to (a) and (c), respectively.
An exciting aspect of the phase-change material employed in this study lies in its ability to switch back and forth between amorphous and crystalline phases. This feature allows the erasing of imprinted amorphous patterns simply by heating the material above the crystallization temperature, which can be done either conventionally (through thermal heating) or by further exposure to laser or electrical pulses of longer duration (typically nanoseconds). In that way, complex patterns may be written, read (exploiting optical, electrical, or topographical contrast) and erased (thermally, optically, or electrically), thus paving the way towards applications in high-density information storage.

Our technique inherently allows for a down-scaling of the imprinted patterns, well into the nanometer regime (by using UV wavelengths). The photosensitive material used here, Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}, supports writing of stable erasable features smaller than 10 nm.\cite{11} Moreover, no evidence has yet been provided that this value should be an inherent limit of chalcogenide materials. Instead, novel deposition methods are being developed and alternative phase-change materials investigated\cite{22} in order to achieve even smaller structures. The method proposed here is directly benefiting from research efforts in that direction, triggered by interest in commercial exploitation and downscaling of electrical-phase-change storage in this type of material.\cite{23,24}

We anticipate our method to be capable of visualizing even more complex field distributions, such as those produced by non-spherical, asymmetric particles and complex particle arrays for which modeling would be too complex or time consuming. While the results shown here focus on the distributions produced by dielectrics particles, the extension to metal and semiconductor structures is straightforward. It is this flexibility that makes our method a most powerful technique for fundamental studies of the near field in involved scenarios and for a wide range of applications, including the casting of large periodic arrays of highly complex nanostructures.

**Experimental Section**

**Sample preparation:** The sputter-deposited samples consisted of 40-nm-thick, face-centered-cubic polycrystalline Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films on Si [001] wafers covered by a 10-nm-thick amorphous SiO\textsubscript{2} buffer layer, custom produced by Numonyx, Italy. The phase switching behavior of these films upon laser irradiation in the absence of microparticles and the optical properties of the different phases have been reported elsewhere.\cite{20} The specific optical properties at the laser wavelength used here (800 nm) are: amorphous SiO\textsubscript{2}; \(n = 1.453\), \(k = 0\); Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}; \(n = 3.825\), \(k = 5.567\); Si; \(n = 3.69\), \(k = 0.006\). Spherical silica particles (Bangs Laboratories, Inc.) with a polydispersity of \(<10\%\) in diameter, a measured refractive index of \(\approx 1.44\) at 589 nm, stored in isopropanol, were deposited on the substrate by means of spin coating. Using this technique makes it easy to control the particle density and particle isolation in the resulting distribution.

**Sample irradiation:** Laser irradiation was performed in air using a regeneratively amplified Ti:sapphire laser system (Tsunami–Spitfire, Spectra Physics) operating at 800 nm central wavelength with a pulse duration of 120 fs. The laser beam was focused onto the sample either at normal incidence to a circular spot size of 26.4 \(\mu\text{m}\) (1/e\textsuperscript{2} diameter) or at an angle of incidence of 5\(^\circ\) to an elliptical spot size of 87.3 \(\times\) 51.4 \(\mu\text{m}\) (1/e\textsuperscript{2} diameter). In both cases, a single pulse was selected from a 100 Hz pulse train by means of an electromechanical shutter to irradiate the targeted area. The sample was mounted on a movable table and observed in situ with a home-built microscope based on a microscope objective (20\(\times\), NA = 0.42) and a tube lens, equipped with a 12 bit charge-coupled device (CCD) camera. Illumination was provided by a white-light source. For irradiation at normal incidence, the laser beam was sent through the microscope objective after having passed a concave lens to induce divergence, effectively enlarging the size of the irradiated area.

**Characterization of the imprinted microstructures:** Bright-field images of the laser-exposed regions have been recorded ex situ with a commercial microscope (PLu, Sensofar) using an illumination wavelength of 460 nm and a high-magnification objective lens (100\(\times\), NA = 0.80). Topography images of the imprinted patterns have been recorded with a commercial AFM (EasyScan 2, Nanosurf) in tapping mode.

**Modeling of the intensity distribution:** The electric field in the illuminated structure is found by rigorous solution of Maxwell’s equations for a sphere sitting on a layered planar substrate, using methods similar to those of Reference \cite{25}. The incident-light plane wave is first reflected on the substrate. The resulting field is expanded into spherical waves around the sphere, and Mie scattering theory \cite{26} is used to determine the resulting outgoing waves. The latter are expressed as plane waves (both propagating and evanescent) moving towards the substrate, and reflected there using Fresnel’s coefficients. The reflected plane waves are in turn scattered by the sphere, so that a self-consistent set of equations is written to describe the infinite series of alternating multiple scattering events at the sphere and the substrate. The system is further reduced by integrating over parallel wavevector components of the plane-wave part of the field, leading to a set of linear equations involving only spherical-wave coefficients, which we solve for all multipoles up to an orbital angular number \(l = 24\) for full convergence. Arrangements of spheres (Figure 3) have been simulated by coherently adding the fields calculated for each individual supported particle. Finally, the electric-field intensity is calculated right underneath the surface, thus giving the fraction of light that penetrates into the film and is absorbed by it.

**Keywords:**

- chalcogenides
- data storage
- nanoparticles
- nanopatterning

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