Nanoscale surface modification of glass using a 1064 nm pulsed laser

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We report a method to produce nanopatterns on borosilicate glass by a Nd:yttrium–aluminum–garnet laser (10 ns, 1064 nm), using silica nanospheres. Nonlinear absorption of the enhanced optical field between the spheres and glass sample is believed to be the primary reason for the creation of nanofeatures on the glass substrate. By shining the laser beam from the backside of the glass sample, the scattering effects are minimized and only the direct field enhancement due to the spheres is utilized for surface patterning. To confirm this, calculations based on the Mie scattering theory were performed, and the resulting intensity as a function of scattering angles are presented. The nanofeatures thus obtained by this method are 350 nm in diameter and the distance between them is around 640 nm, which is same as the size of spheres used. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1597425]

The enormous potential of borosilicate glasses has resulted in widespread applications in packaging and microtechnologies like micro-optics and biomedical devices.[1] In addition to their outstanding chemical, optical, and mechanical properties, borosilicate glasses also have the thermomechanical stability necessary for replication processes. This has led to many investigations on the processing characteristics of these dielectric materials. In general, due to their inert nature, they are very difficult to machine by most conventional machining techniques. Laser micromachining is an attractive approach for the machining of glass materials. However, the linear absorption for glasses is very low in the visible range and the absorption edge is near 310 nm.[2] Therefore, high power UV and CO_2 lasers have to be used for processing glass materials. The mechanism of bulk damage by nanosecond pulses involves heating of conduction band electrons by the incident radiation and transfer of this energy to the lattice.[3] Damage occurs via conventional heat deposition resulting in melting and boiling of the dielectric material. Also, the very low absorption cross section of these large band gap materials requires very high laser intensities in order to obtain sufficient energy absorption in the material to observe macroscopic material removal.[4] This high intensity leads to a large heat-affected zone and thermal stress build up which might even lead to cracking, eventually making this technique not suitable for microsystem technology.

A possible method to overcome this limitation is by employing ultrafast laser pulses for processing. Due to the short pulse duration, the heating time is less than the electron-phonon relaxation time, thereby improving the spatial resolution and reducing the heat-affected zone to a few micrometers.[5] Furthermore, it has been found that femtosecond infrared laser irradiation results in an increase in the refractive index at the focal point inside the glasses.[6] Other techniques such as laser-induced plasma-assisted ablation and laser induced backside etching[7] have been recently used for processing transparent glasses. But it is very difficult to produce nanofeatures on the glass substrate because of the ablation mechanism and the diffraction limit of the focusing laser beam.

To overcome the diffraction limit, near-field ablation induced by a laser beam can be used for fabrication. One approach involves illuminating the tip of a scanning tunneling microscope or an atomic force microscope with a pulsed laser. Structures well below $\lambda/2$ can be easily produced underneath the tip.[8] Another method is by depositing a monolayer of nanospheres on the surface of a substrate and utilizing the intensity enhancement to produce nanoscale holes on the substrate.[9] It is believed that the optical field enhancement is mainly due to the near-field effect and scattering by the spheres when the laser beam travels through the nanosphere and reaches the substrate.[10] In this letter, a pulsed Nd:yttrium–aluminum–garnet (YAG) laser beam (1064 nm, 10 ns) is used for processing borosilicate glass samples. By delivering the laser beam from the backside of the glass sample, we expect to minimize the scattering effect on surface modification. The field enhancement induced by silica (SiO_2) nanospheres on the surface is used for producing nanopatterns on the glass substrate.

The schematic of our experimental setup is shown in Fig. 1. The sample to be patterned is borosilicate glass of 500 μm in thickness. A colloidal suspension of monodispersed silica spheres of 640 nm diameter diluted with de-ionized water was applied on the glass sample and led dry. These spheres arrange to form a hexagonally closed-packed monolayer by means of a self-organizing process.[11] This was confirmed by observing the sample under a scanning electron microscope (SEM) as shown in Fig. 2. Since borosilicate glass is transparent to 1064 nm wavelength, the incident laser beam can pass through the glass substrate and illuminates the bottom surface of the spheres. As the size of spheres is smaller than the laser wavelength, the incident light intensity is enhanced and an optical near-field is produced around the spheres. The evanescent field is confined to a very small region around the spheres and decays exponentially in the radial direction.[12] After a single pulse of 3 J/cm^2, the spheres were ejected from the glass substrate and nanostructures were produced on the surface as shown in Fig. 3. The SEM

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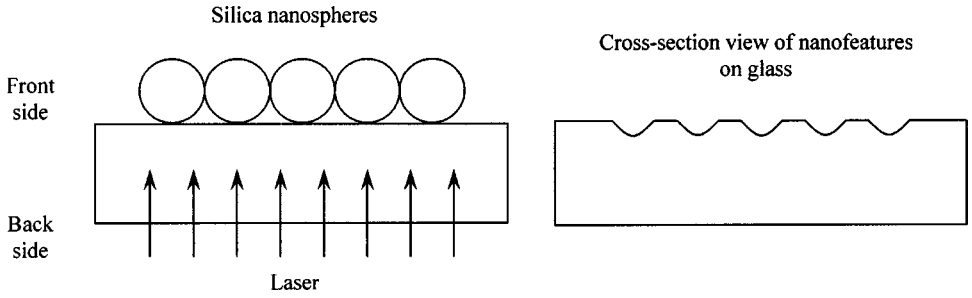

FIG. 1. Schematic of the irradiation of silica spheres on glass from the backside.

micrograph shows a periodic array of holes of 350 nm in diameter on the surface. The created features are arranged hexagonally and the distance between the centers of the features is about 640 nm, which is the same as the diameter of the spheres used. This confirms the formation of features underneath the location of spheres.

It has been shown that the enhanced optical near-field could be several orders of magnitude higher than the original incident intensity. Since the linear absorption coefficient of glass is very low at the experimental wavelength, we believe pattern formation is due to nonlinear absorption of the enhanced optical field by the glass material. Although the physical mechanisms responsible for infrared photosensitivity are still under investigation, the process is believed to be initiated by a multiphoton absorption process and therefore exhibits a highly nonlinear dependence on the intensity of the illuminating beam.[13] These intensity-dependent changes in the material's optical properties affect the propagation of the incident light. The refractive part of the nonlinearity gives rise to self-lensing, which can lead to optical damage. The absorptive part of the nonlinearity can decrease the transmittance at high intensity and provide a path for optical damage in the material at lower irradiances than conventional dielectric breakdown.[14] Also the presence of a surface breaks the inversion symmetry of the medium normal to the boundary and makes nonlinear interaction possible.[15]

The optical field enhancement could arise from several sources. Scattering and near-field effects are the obvious ones as demonstrated by previous work when the laser beam was incident on the top surface of the spheres.[16] Calculation of the field enhancement around the spheres illustrates that both focusing effects as well as near-field effects contribute to the size and shape of the features formed underneath the spheres. But when the sample is irradiated from the backside, the scattering effect is minimized. We calculated the intensity enhancement due to scattering by the dielectric spheres according to the Mie theory for a laser wavelength of 1064 and 640 nm silica spheres with a refractive index of 1.39. The intensity enhancement as a function of the scattering angle is plotted in Fig. 4. The calculations show that there is no significant intensity enhancement due to scattering for angles between 90° and 270°. This means that, at the interface between the sphere and the glass substrate, the field enhancement is not due to scattering.

The optical field enhancement could also come from the rear surface interference effect. Due to the interference of the incoming and reflected waves, the electric field strength is higher at the rear side of a weakly absorbing slab with $n > 1$, so that optical breakdown threshold is lower at the rear side. Rear surface ablation has been previously reported for fused silica and borosilicate glasses at 193 nm, which is very well absorbed by these glasses.[17] Despite this enhancement on the rear side, no damage was observed at the rear side in the experiments performed with 1064 nm laser in the absence of spheres at similar laser fluences. Whereas in the presence of spheres, even for a considerably low incident intensity, well defined features on the nanoscale depending on the size of the spheres were formed on the rear side.

In summary, a simple technique to produce nanopatterns on a borosilicate glass substrate by using a 1064 nm nanosecond Nd:YAG laser is presented in this letter. Due to the presence of an enhanced optical field around the spheres, nonlinear absorption is believed to be the phenomenon responsible for the nanofeature formation. The enhanced optical field is a result of the near-field effect. Scattering-induced

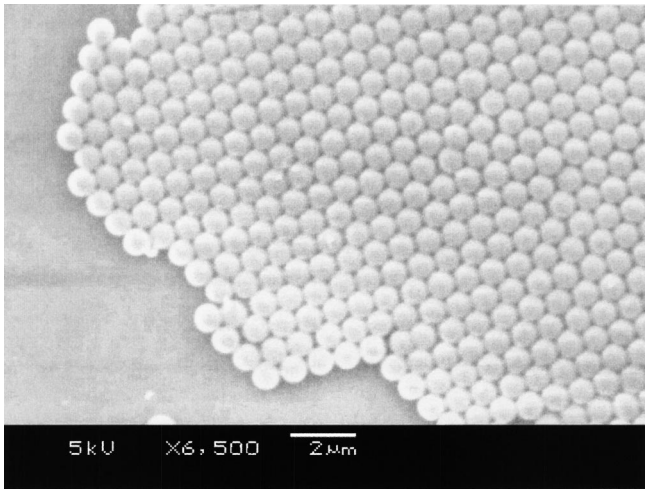

FIG. 2. SEM image of hexagonally close-packed monolayer of silica nanospheres of 640 nm in diameter on a glass substrate.

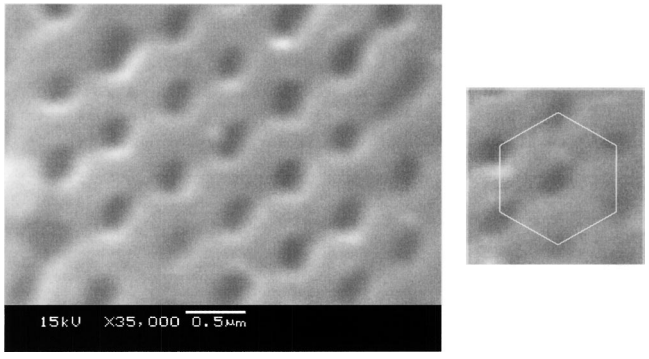

FIG. 3. SEM image of hexagonally arranged dent structures on borosilicate glass produced using silica nanospheres of 640 nm in diameter for a laser fluence of 3 J/cm^2.

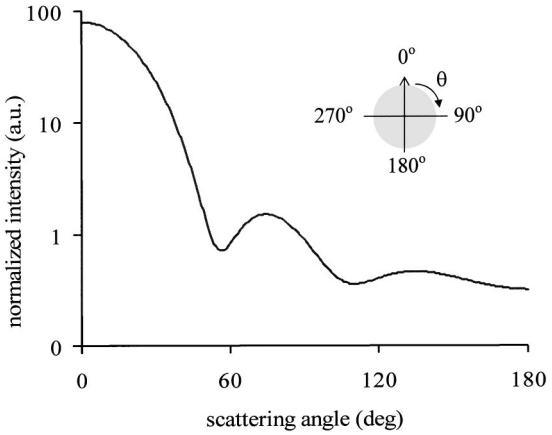

FIG. 4. Calculated laser intensity distribution around the nanosphere for 1064 nm incident laser beam on a 640 nm silica nanosphere.

focusing effect is eliminated in this work since the laser beam is incident from the backside of the sample.

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