Nano-Holes in Silicon Wafers Using Laser-Induced Surface Plasmon Polaritons

Pal Molian1,*, Zhiqun Lin2, and Qingze Zou1

1Department of Mechanical Engineering and 2Department of Materials Science and Engineering, Laboratory for Lasers, MEMS and Nanotechnology, Iowa State University, Ames, IA 50011, USA

Surface Plasmon Polaritons (SPPs) have been explored for a multitude of applications including sub-wavelength lithography, data storage, microscopy and photonics. In this paper, we report the use of SPPs for nanomachining silicon in massively parallel fashion. A Q-switched Nd:YAG laser beam was impinged on gold-thin film deposited, porous alumina membrane (PAM) that contains periodic 2-D array of thousands of nano-holes. The silicon substrate was placed in close proximity with PAM. The formation of SPPs and their coherent interference at the exit of PAM holes created strong nanoscale electrical fields which in turn produced 50-70 nm diameter holes in silicon.

Keywords: Nano-Holes, Silicon Wafers, Plasmon.

Nanomachining is an indispensable process for the fabrication of nanodevices that include 3D binary data storage, photonics and medical devices (nano-hole drilling); waveguides (direct writing); glasses (nanofabrication); and microfluidics (nano-channels). A set of nanomanufacturing methods such as nanoimprint lithography (NIL), soft lithography (SL), nanotransfer patterning (nTP) and dip-pen nanolithography (DPN) are currently utilized to fabricate nanoscale features.1-5 NIL provides high-throughput and low cost, however, the challenging issues are poor tolerances due to resin heating, lack of conformability, requirement of 1X mold, and contamination from the tools which affect process repeatability, resolution, and shape. SL and nTP, based on self-assembled monolayers (SAM), use low-cost equipment, provide very high resolution and transfer 3D structures; however, the increased failure rate associated with the elastic properties of stamps, self-assembly defects, material compatibility with SAMs and surface strains due to the contact nature generate a number of problems. DPN is effective in producing massively parallel nanoscale features; however, the slow writing speed (throughput) and multiple probes giving rise to poor pattern uniformity and reliability are major concerns.

Laser nanomachining is an emerging technique but is severely limited by the diffraction limit and spherical aberration of the lens. Hence, a proximal probe-assisted type of laser nanomachining where the laser beam is transmitted through fiber probes in near-field scanning optical microscopy or focused in the near field of probe in scanning probe microscope is widely utilized.6-8 Despite many versions of near-field probes, these methods have not yet yielded repeatable results due to the difficulties in maintaining aperture/probe size and uniformity.

In this paper, we demonstrate a novel method of making nano-holes in silicon by generating surface plasmon polaritons (SPP) through the laser beam interaction with gold-thin film/alumina membrane containing nano-hole arrays (Fig. 1). It is well known that when monochromatic light is transmitted through a nano-hole array of metallic conductor/dielectric material combination (e.g., nanostructured gold on glass), SPPs are generated which propagate along the interface of the two materials.9,10 In the traditional sense, the nano-hole array will not transmit light. However, the formation of SPPs avoids this limitation.

Subsequent coherent interference of multiple scattered SPP waves was utilized to perform nanomachining by placing the silicon substrate in the near field statically (holes) or dynamically (channels) by moving it in a massively-parallel manner relative to the mask (porous aluminum membrane) under precision nanopositioning control. Since the technique is not diffraction limited, much finer structures can be produced with large laser wavelengths. SPPs have high field intensity and shorter wavelength compared to illumination light and their interference creates nanoscale field intensities sufficient enough to cause material removal.

The experimental work began with a two-step anodization of aluminum foil to produce porous aluminum membrane (PAM) which is composed of highly ordered hexagonal arrays of cylindrical nano-holes (Fig. 2). Pure
aluminum foil (99.999%; 0.13 mm thick) was degreased in a mixture of ethanol, chloroform, and acetone in the volumetric ratio of 1:2:1, followed by annealing at 500 °C in N₂ to remove mechanical stresses as well as cause recrystallization. Subsequently, it was electropolished in a mixture of sulfuric acid and phosphoric acid to produce a mirror-like finish. The foil was then first anodized in 0.3 M oxalic acid solution (0 °C in ice bath) at 42 V for 3 hr. The anodized alumina was then removed selectively by etching in the chromic acid (1.8 wt%) and phosphoric acid (6 wt%) mixture at 60 °C for 6 hrs. After cleaning with deionized water, second anodization of the sample was carried out with the same procedure as described above. Finally, the remaining aluminum and the barrier layer were removed with saturated copper chloride solution and 5 wt% phosphoric acid at 30 °C for 1 hr respectively. The resulting PAM, having dimensions 2 cm × 2 cm × 9 μm, consists of holes with a diameter of 60 nm and an inter-hole spacing of λ ~ 100 nm (Fig. 2). A layer of gold was sputtered on PAM to satisfy the necessary condition for SPP formation. Field emission scanning electron microscope examination of PAM revealed that the nano-holes in PAM were not blocked by gold deposition.

The PAM template was then used to generate the SPP effect by placing it in the laser beam path through the beam delivery unit. The laser used was a standard, commercially available Q-switched Nd:YAG with the following beam characteristics: 1064 nm wavelength, 100 ns pulse, 10 kHz repetition rate, 1 W average power and 1 mm diameter. A 50-mm diameter, 250-μm thick silicon substrate with (100) orientation was placed in close proximity of the PAM. The native oxide in silicon wafer was removed by an HF-dip for about 5 minutes of time, leaving the virgin surface for nanomachining. The distance between the PAM and silicon was 0.2 mm. The exact conformal contact is not necessary because the interference of SPP causes a highly directional, high intensity source that gives rise to a finite depth of field. Following laser nanomachining, the silicon samples were examined in the atomic force microscope under the tapping mode.

An important attribute of SPPs is their shorter wavelength compared to the excitation light, thus confining the plasmonic field to an area much smaller than those achieved by other near-field lithography methods and leading to higher resolution and stronger field intensity. The interaction of light and surface plasmons is governed by dispersion relation:

\[
k_{sp} = k_0 \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}
\]

(1)

where \(k_{sp}\) is the wave vector of surface plasmons, \(k_0\) is the wave vector of the illumination light, and \(\varepsilon_d\) and \(\varepsilon_m\) are dielectric constants of the metal and the surrounding dielectric material, respectively. In our work, the wavelength of the laser source is 1064 nm. The dielectric constant of alumina, \(\varepsilon_d\), is a real number with a value of 10. However, the dielectric behavior of gold is complex and has both real and complex components. For 1064 nm wavelength light, \(\varepsilon\) for Au = 50 + i5. Since the permittivity of metal and dielectric material must have opposite signs in order for SPPs to be created at the interface, the application of Eq. (1) yields the wavelength of SPPs as 300 nm.

One of the most striking features of SPPs is their ability to concentrate and tunnel the light through subwavelength structures such as nano-hole array. Ebbesen et al.¹¹ have done pioneering work in this area and demonstrated transmission efficiency in excess of 50% for subwavelength holes in metallic thick films. For example,
150-nm diameter holes with a periodicity of 600 nm in 2-μm thick silver (Ag)-films deposited on a dielectric material transmitted light with a maximum intensity at 1370 nm. Similarly, Chang et al.\textsuperscript{12} carried out finite-difference time-domain simulations of nano-hole arrays (200 nm diameter with a period of 600 nm) in thin gold films on a glass substrate with incident light from the glass side. Transmission efficiency of 60% at 950 nm wavelength was obtained. The higher transmission efficiency through sub-wavelength apertures, predicted by classical diffraction theory, is not only due to SPPs but also due to the periodic structures which act like an antenna.

The maximum transmission of plasmon wavelength through the nano-hole array is determined by the periodicity of the array. For a square, 2-D array of nanoholes with a period \( \Lambda \) that can act as a grating, the wavevector components are \( 2\pi n_x/\Lambda \) along \( x \) and \( 2\pi n_y/\Lambda \) along \( y \), with \( n_x \) and \( n_y \) integers. Hence the period, \( \Lambda \), that gives maximum transmission is given by:\textsuperscript{12}

\[
\lambda_{\text{plasmon}} = \Lambda \left( \frac{\varepsilon_m^{(0)} \varepsilon_d}{\varepsilon_m^{(0)} + \varepsilon_d} \right)^{1/2}
\]  

(2)

This is an implicit equation because the dielectric constant of a metal depends on wavelength and permittivity properties of the conductor and dielectric materials. Application of the above-equation in our work gives a period of approximately 100 nm for the nano-hole array.

Figures 3(a and b) display the AFM images of nano-holes that provide the following results and associated significance. The holes produced were about 50-70 nm diameter (Fig. 3(c)), indicating the proof of concept of SPP effect. Within the 5 μm by 5 μm area, numerous holes were fabricated, implying that the SPP effects were generated simultaneously through several nano-holes of the PAM. The average density of nanoholes (all through holes) compared to the pore density of alumina is about 30%. However there is no obvious relationship between the spatial arrangement of the pores in the alumina membrane and the nanoholes produced on the silicon surface. Two possible reasons are: (1) the silicon substrate was not close-enough to the PAM substrate; the SPP-generated plasmonics interfere in the far-field and hence the spatial pattern became much coarser; (2) the nanoscale spatial intensity distribution emitted from the hole array was quite complex as it is a function of a number of parameters including shape of hole, distance between holes, and wavelength. Clearly, there is a need to better understand the SPP-induced effects in obtaining the position and density of hole arrays between PAM and substrate.

**Fig. 3.** (a) AFM image of nano-holes in silicon; (b) Magnified view of one hole; (c) Profilometry of the single hole; (d) AFM image of single hole.

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However, these preliminary results suggest that this technique has potential for massively-parallel nanomanufacturing of silicon at low-cost.

The present contribution may be compared to a self-organized mask pattern transfer method for producing nano-holes in silicon and other substrates. In the pattern transfer nanolithography process, diblock copolymer-based gold nanoparticle arrays are self-assembled in the form of hexagonal patterns on the substrate; these nanoparticles serve as nanomasks for subsequent reactive ion etching (RIE) or ion milling, leading to the production of very-high density arrays of nanoholes or nanohills.¹³ Researchers have used this technique to prepare an array of diamond nanotips and silicon nanopillars.¹⁴ In another work, 14 ± 1 nm diameter nanoparticles with an average spacing of 90 nm were self-organized onto (001)-oriented crystalline and amorphous Si layers prepared by evaporation on a substrate.¹⁵ Anisotropic RIE process created the ordered arrays of cylindrical nanoholes with diameters >20 nm and aspect ratio of approximately 7. The benefits of our SPP process over this pattern transfer technique are higher aspect ratios and fewer processing steps.

In summary, the laser-induced SPPs show promise for a simple, high-resolution, high-density, mass production nanomachining method; upon further development this method can become an excellent alternative to the nanoimprint processes to achieve sub-50 nm lithography.

References and Notes


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