From Transparent Particle Light Enhancement to Laser Nanoimprinting

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Laser beam, electron beam & focused ion beam are attracting much research interests in functional nanostructure fabrication. Laser irradiation under near field is one of the effective ways to break light diffraction limit and push patterning feature size down to dozens of nanometers. In this paper, nano-hole array patterning by a parallel particle mask is described. Transparent nanoparticles were self-assembled on phase change GST thin film surfaces. Following with the pulsed laser irradiation, nano-hole arrays were formed uniformly on the surfaces. Laser fluence effect and angle dependence of the nanostructures are investigated. Physics behind this laser nanostructuring shows that these transparent nanoparticles serve as "nano-lenses" to induce light intensity enhancement under the transparent particles. Theoretical simulations indicates that light intensity enhancement is related to particle size and light wavelength. To extend this technique application, the feasibility of laser nanoimprinting for next generation nanodevice fabrication is also studied.

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1. Introduction

Laser is becoming one of mature and reliable manufacturing tools in industries. It has been extensively applied in microelectronics, data storage, defense and bio-medicine for printed circuit board (PCB) via hole drilling, surface cleaning, wafer singulation and pulsed laser deposition. [1-2] To cater for the ever-increasing demand from the industries to fabricate smaller, faster and more functional micro/nanodevices, nanoengineering technology is evitable to push the device feature size down to 100 nm. Compared to electron beam and focused ion beam processing, laser nanoengineering has the advantages of low cost, high-speed process in air, vacuum or chemical environment and most importantly it has the capability to fulfill the flexible integration control.

How to break through the optical diffraction limit to get smaller feature sizes is attracting much research interests in the world. As the light wavelength reduces, current wafer process is achieving 0.13 micron (by KrF Excimer laser) and 0.1 micron (by ArF Excimer laser) photolithography. Liquid immersion lithography is at the current stage ready for 65 nm wafer production with the aid of a thin water layer (a few hundred microns thick) added between the lens and wafer substrate. [3-4] One of the driving forces for the industries to get smaller device feature sizes is to develop shorter wavelength light sources. EUV 13 nm laser source is in the initial stage of the technical development and targeted for the wafer production in the next 10 years. However, this top-down approach is facing high technical challenges to find stable & high power light sources, to apply high NA optics and suitable photoresist etc.

Ultra-fast laser irradiation has been applied to make nanostructures based on the mechanism of multi-photon absorption. [5-6] Laser irradiation under a near field is another effective way to obtain processed feature sizes down to dozens of nanometers. Recently, we have successfully demonstrated the combination of a second harmonic femtosecond laser (400 nm, 100 fs) with a near field scanning optical microscope (NSOM) to fabricate 20 nm line features on the photoresist surface. [7] In our research, it is also shown that pulsed 532 nm Nd:YAG laser irradiation on an AFM tip in a near field can also make 10 nm line width on the photoresist and metal thin films. [8] These methods have the highly potential applications to fabricate patterned media for ultra-high density data storage, memory device nano-cells (MRAM or CRAM), nano-templates for biosensor, nanoscale imaging and optical diagnostics.

Though these methods can achieve very small processing resolution, the nature of scanning microscopes makes the processing at a very slow speed (dozens of microns per second). It limits these techniques' applications in the microelectronics industries. To be capable for the large area and high speed mass production becomes a key issue for new nanoengineering techniques. One of our recent researches shows that pulsed laser irradiation of transparent nanoparticles can make nano-holes on the substrate surface. [9-10] Self-assembly of the transparent nanoparticles on the surfaces can meet the high speed & large area parallel fabrication. In this paper, combination of pulsed laser irradiation with transparent nanoparticles mask is carried out to create nano-hole arrays on Al and DVD phase change $Ge_2Sb_2Te_5$ (GST) thin film surfaces, which has much lower melting temperature of *616* °C than other materials. Angle dependence of the laser irradiation on the array nanostructure is studied and compared with Mie theory simulation. To extend this technology's application to nanodevice fabrication, feasibility study of the laser nanoimprinting is proposed. Advantages of this approach over current contact, heat embossing and UV nanoimprinting techniques are highlighted. [11-12] Engineering issues and challenges for the successful applications of this technique is discussed.

2. Experimental

Mono-disperse silica (SiO_2) or polystyrene (PS) spheres with the diameters from 140 to 1000 nm were used to form a particle mask (size: 2 mm × 2mm) by the self-assembly approach before the surface nanopatterning. These particles are transparent to most laser sources from UV to IR light spectra. These particles were first dissolved into a liquid and their suspension was then disposed onto the sample surface. The sample was slightly titled at an angle of 5^o and kept in a refrigerator at ~10 ^oC for the surface drying. The sample was finally baked in a vacuum oven at ~80 ^oC for 10 minutes to remove the water molecules on the surface. Figure 1 shows a hexagonally closed-packed colloidal monolayer of 1 μm PS particles (refractive index n=1.6, 2% size deviation in suspension form) deposited on a 100-nm $Ge_2Sb_2Te_5$ (GST)/Al thin film surface.

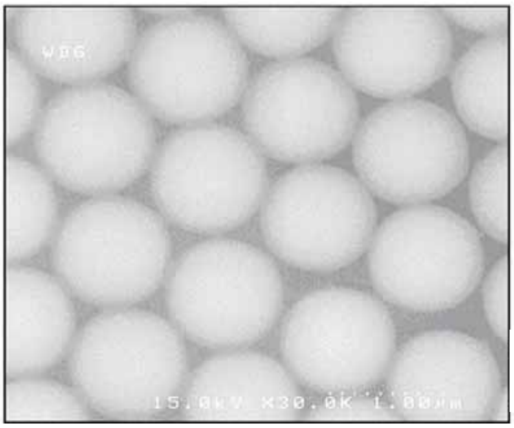


Fig. 1 Optical image of 2D PS particle mask prepared by self-assembly on a 100-nm GST/Al thin film surface.

A KrF 248-nm excimer laser (Lambda Physik LPX100) with a pulse duration of 23 ns (FWHM) was applied to irradiate the sample surfaces. Laser fluence was adjusted by the laser controller to change laser fluence. A beam homogenizer was applied to get a uniform light distribution over a rectangular spot size of 25 mm × 5 mm.

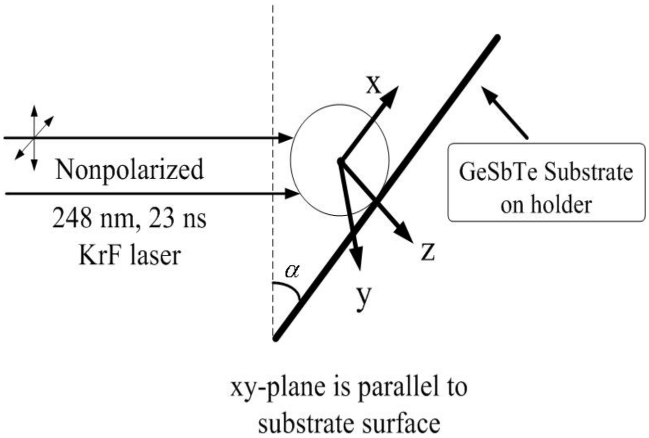


Fig. 2 Schematic drawing of experiment setup for GST thin film surface nanopatterning.

Each sample was irradiated with one laser pulse. Substrate surfaces before and after laser treatment were observed under a high-resolution optical microscope and scanning electron microscope (SEM). A substrate holder was applied in the experiment to change laser irradiation angle on the substrate surface to study the angle dependence of the nano-hole array structures at a fixed laser fluence (laser pulse energy tuned due to the variation of laser spot size on the substrate surface at different incident angles).

3. Results and discussion

3.1 Nano-hole array formation by light enhancement

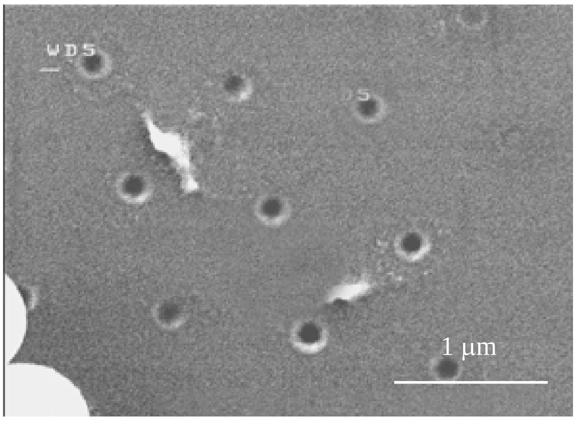


Fig. 3 SEM image of nano-hole arrays formed on GST thin film surface after one pulse of KrF excimer laser irradiation at a laser fluence of 5.8 mJ/cm^2 and an incident angle of 0^o.

Figure 3 shows a SEM image of nano-hole arrays formed on the GST thin film surface after one pulse of KrF excimer laser irradiation at a laser fluence of 5.8 mJ/cm^2 and an incident angle of 0^o. It can be observed that the bowl-shape nano-holes have a uniform diameter around 120 nm. It is fabricated due to light intensity enhancement near the contact area between the transparent particles and substrate. Figure 4 shows the laser light intensity distribution calculated based on Mie theory. Since the distance

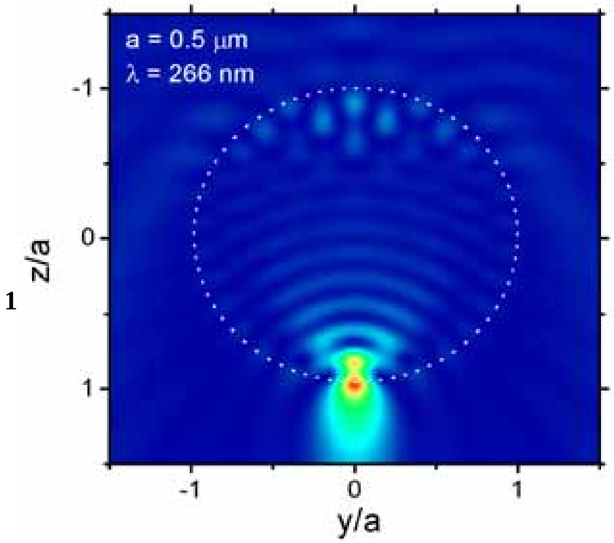
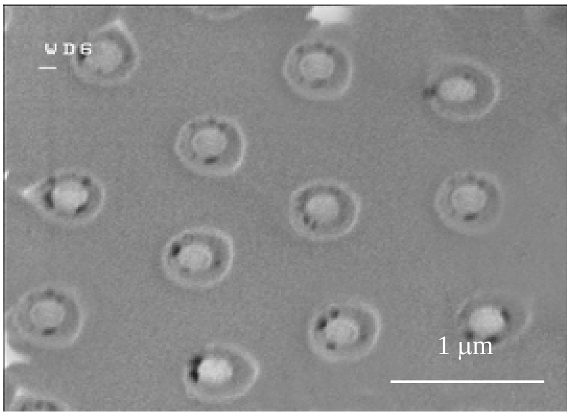


Fig. 4 Laser light intensity $|E|^2$distribution inside & outside a 1.0 μm PS particle illuminated by a laser pulse at λ =266 nm.

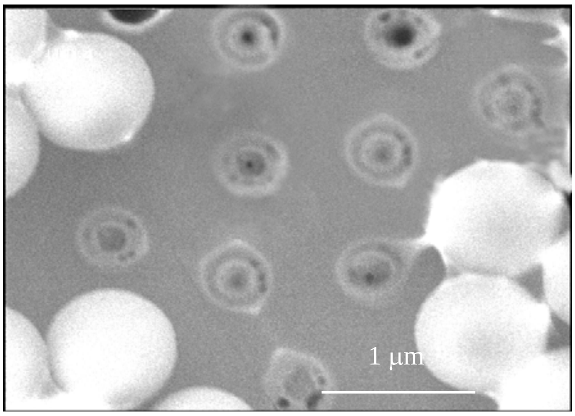
between the particle and substrate is much smaller than light wavelength and the particle size is smaller or in the order of light wavelength, laser irradiation of the particles on the substrate is different from the situation as a sphere lens focusing in the far field. There is an optical resonance effect in the near field. Theoretical calculation with Mie theory shows that light energy is concentrated in a small area less than 100 nm (red color region under the bottom of the particle) under the particle. The light enhancement is closely related to the ratio of the particle size to the laser wavelength. For the 248 nm excimer laser irradiation on a 1 μm PS transparent particle, the laser light can be enhanced upto 60 times just under the particle surface. It is also shown that light enhancement increases as the particle diameter increases and the light wavelength decreases. [13] However, to increase particle size will result in a larger light enhancement area and the nano-hole fabricated becomes bigger. It is not a good option for the surface nanostructuring. Meanwhile, due to the nature of transparent particle materials, there is not a big room to select a shorter wavelength laser. As an example, 157 nm F_2 excimer laser is the shorter wavelength light source next to 248 nm excimer laser. But this laser light is strongly absorbed by most of optical materials and even air. Therefore, in order to get smaller light enhancement region, small particle size needs to be selected with the sacrificing of the light enhancement effect. The 2nd, 3rd or 4th harmonics femtosecond laser can be one of the excellent light sources to get much smaller nano-hole sizes with the combination of light enhancement and multi-photon absorption effects.

3.2 Control of laser fluence for nanostructuring

Laser fluence is one of the important parameters in the surface nanostructuring. At a low laser fluence, there are no nano-holes formed on the thin film surface since the laser dose is not high enough to induce the materials removal. Though a higher laser fluence can result in a higher laser intensity under the particles. Excess heat generated will make the nanostructuring process complicated and worsen the nanostructure qualities. In the experiment, it was found that the shape of the nano-hole arrays on the GST thin film surfaces did not change too much for the laser fluence less than 7.2 mJ/cm^2. However, sombrero-shape bumps with an outer rim were formed at a laser fluence of 8.5 mJ/cm^2, as shown in Fig. 5a. When laser fluence increases further to 10.5 mJ/cm^2, halo-shape dents with an outer ring were formed as shown in Fig. 5b. The mechanism for the formation of these different nanostructures is related to the fact that surface melting could result in the excitation of convective fluxes within the liquid layer. Thermocapillary and chemicapillary forces are two main origins that lead to the changes in the surface tension. [14] Since the optical field enhancement has a Gaussian-like distribution, the temperature decreases from the center of the molten zone to its edge. For a uniform distributed material concentration, the temperature gradient causes an outward flow of the molten materials to the edge. It causes the formation of the outer rim and the bowl-shape nano-dent. When laser fluence is high enough to trigger the concentration change of the materials, convective flow could reverse its direction and sombrero-shape can be observed. When laser fluence becomes even higher, strong evaporation takes place in the central region that generates recoil pressure on the molten materials, leading to a halo structure in the center. At the tail region, Marangoni convection remains and an outer ring still exists.



(a)



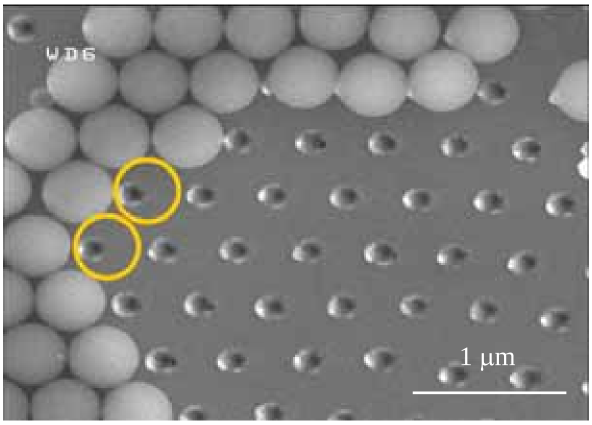
(b)

Fig. 5 SEM images of nano-hole arrays formed on GST thin film surface after one pulse of KrF excimer laser irradiation at laser fluences of (a) 8.5 mJ/cm^2 & 10.5 mJ/cm^2 (incident angle: 0^o).

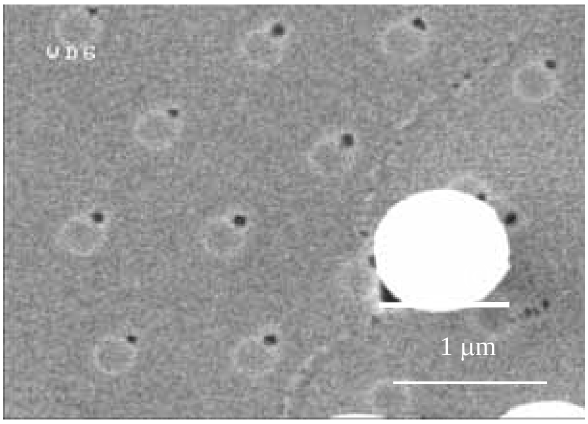
The surface materials redistribution makes the bigger and rougher nanostructures. Therefore, in order to obtain the high quality nano-hole arrays, laser fluence for the surface nanostructuring needs to be set as a value just above the threshold fluence for the nano-hole formation.

3.3 Angle dependence of nano-hole arrays

Figure 6 shows the SEM images of nano-hole arrays formed on the GST thin film surface after one pulse of KrF excimer laser irradiation at a laser fluence of 8.5 J/cm^2 and incident angles of 30^o and 60^o, respectively. At the normal incidence as shown in Fig. 5 (a), it can be found that the formation of sombrero-shape bumps with an outer rim under the removed spheres. Surface profile analysis by an AFM shows that the height of the outer rim and the center bump are around 35 nm. When the incidence angle increases to 30^o, it can be seen that the sombrero-shape structures disappeared and a clean bowl-shape nano-hole arrays were obtained, as shown in Fig. 6 (a). It was discussed in the previous section that the nano-holes change their shapes at difference laser fluences at the normal incidence for the GST thin film surfaces: bowl-shape nano-holes at a low laser fluence and sombrero-shape nano-dents at a high laser fluence. The formation of the bowl-shape nano-holes at the incident angle of 30^o implies that the laser light intensity distribution under the transparent particles is lower than that at the normal incidence (incident angle as 0^o). The depth of the bowl-shape nano-holes is around 50 nm. Meanwhile, it can also be observed that the center locations of these nano-holes are shifted from the particle contacting point to a position around 250 nm away, as indicated by the circle marked in Fig. 6 (a). As the incident angle increases further to 60^o, the depth of the nano-holes decreases to around 20 nm and the centers are shifted from the contacting point to a further position around 800 nm away.



(a)



(b)

Fig. 6 SEM images of nano-hole arrays formed on GST thin film surface after one pulse of KrF excimer laser irradiation at a laser fluence of 8.5 J/cm^2 and incident angles of 30^o and 60^o.

From the above discussion, it is clear that the laser incident angle changes the shapes of the nano-hole arrays and shifts the positions of the nano-hole centers greatly. In order to obtain the high quality nano-hole arrays in a fine control nanoengineering process, the normal laser light irradiation on the transparent particle mask is an optimal option for the surface parallel nanopatterning.

3.4 Development of laser nanoimprinting technique

Laser light intensity enhancement through a transparent particle mask can be used to achieve large area and fast speed parallel surface nanostructuring. The laser fluence applied is low (only a few J/cm^2 for a low melting temperature GST thin film surfaces) and one pulse of the laser irradiation can fabricate the nano-hole arrays on the thin films. It can be applied as one of novel laser nanofabrication techniques [15]. However, it is a technical challenge how to make a large area (upto a few cm scale) monolayer particle mask due to the nature of particle self-assembly. Meanwhile, the deposited nanoparticles are removed away from the substrate surfaces after one pulse of the pulsed laser irradiation. It is impossible to use this mask again to make a deeper nano-hole array by high pulse number of the laser irradiation. The removed nanoparticles will redeposit on the nearby surface as the surface contaminants, which are very difficult to be cleaned away from the surface. Furthermore, it is also difficult to form a complete shape of the nanoparticle mask for a device structure by the self-assembly technique. As shown in Fig. 7, there are big spacing gaps among the nearby particles gathered together inside a pre-patterned structure. It will not transfer this complete pre-patterned structure after the laser irradiation. The laser light intensity in the region among the particle gaps is almost as low as zero, since most of the laser energy is concentrated under the particles. What are fabricated would be the nano-hole arrays with the outer contour defined by the pre-patterned device shape, instead of the whole pre-patterned structure. All these issues limit this laser nanopatterning approach to be applied in the industries as a next generation nanoengineering method.

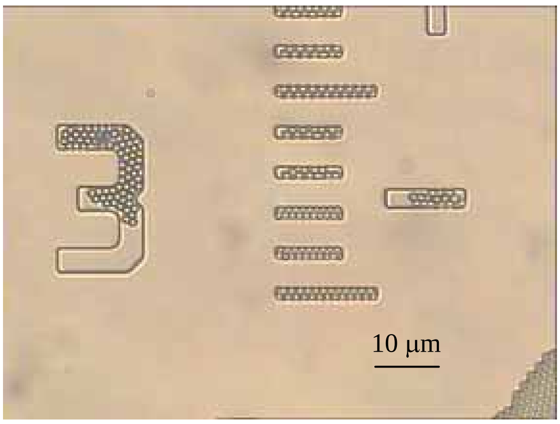


Fig. 7 Optical images of transparent nanoparticles deposited inside pre-patterned structures by the self-assembly method.

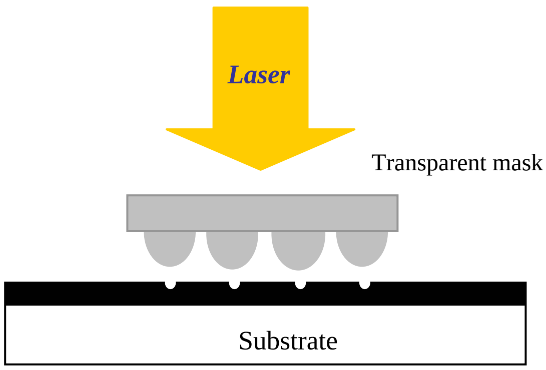


Fig. 8 Schematic drawing of laser nanoimprinting.

Transparent mask fabricated on a quartz substrate could be a feasible way to solve the above problems faced to the self-assembly particle mask. The bottom surface of the quartz is fabricated into half ball shapes, as shown in Fig. 8, by photolithography, RIE and chemical etching processes. As the laser light goes through the mask, the half ball transparent structures induce the light enhancement and transfer the mask design to the substrate surface. One of the key advantages of this method is that there is a fixed transparent mask available and it can be used for more laser pulse irradiation to fabricate deeper nanostructures.

Besides the transparent mask fabrication, how to control the distance between the transparent mask and substrate surface is another technical issue. Figure 9 depicts the laser light intensity distribution along the laser irradiation direction during KrF excimer laser normal irradiation of 1 μm PS particle. It can be found that the light intensity is enhanced upto 60 times just under the particle (z/a=1.0) and then decays very fast to zero at z/a=2.0 (the distance 500 nm away the particle contacting point). To ensure the light enhancement of 25 times, the distance between the mask and substrate would be set as 125 nm (at z/a=1.25 in Fig. 9). To create this near field environment for the light enhancement, a nano-stage is required to control and tune the mask-to-substrate distance.

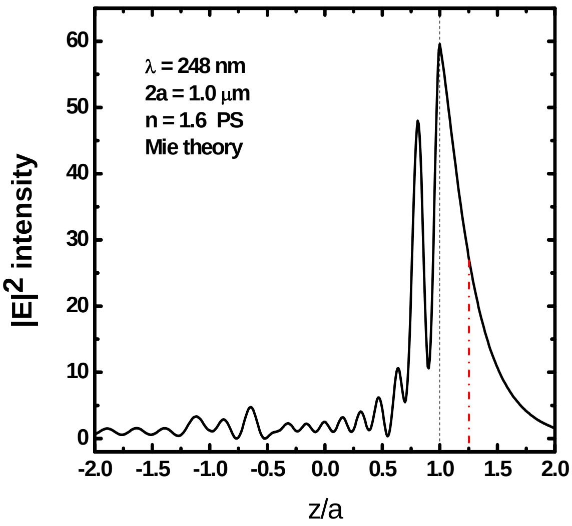


Fig. 9 Laser light intensity along laser irradiation direction (*z*-axis, *z* = 1.0 is the particle contacting point to the substrate.) during the KrF excimer laser irradiation of 1.0 μm PS particle.

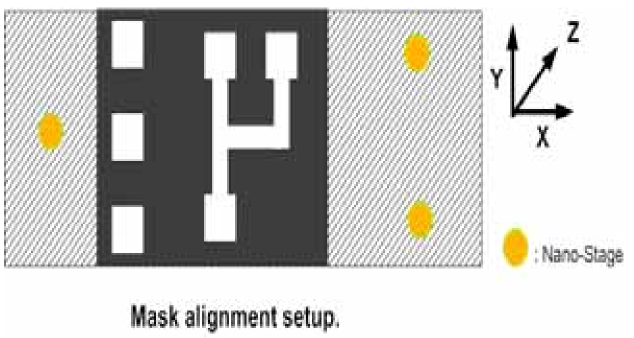


Fig. 10 Mask alignment and three sets of ellipsometers (yellow circle points) to ensure the mask parallel to the substrate with a same distance in dozens of nanometers for the light enhancement.

For the uniform surface nanoimprinting, the transparent mask must be parallel to the substrate to ensure a same gap distance (dozens of nanometers) away for the substrate surface. Mask alignment and three sets of ellipsometers, as shown in Fig. 10, will be included in the laser nanoimprinting system. Compared to current heat embossing, pressure contact and UV curing step & flash nanoimprinting techniques, the laser nanoimprinting approach has the advantages of non-contact and room temperature process. There are no pressures applied and no liquid etc. involved. The mask feature can be scaled down on the substrate surface due to the light enhancement effect.

4. Conclusions

Laser light enhancement effect during the pulsed laser irradiation through a transparent particle mask is investigated. It is found that nano-hole arrays can be fabricated on the thin film surfaces with the self-assembly of the transparent 1 μm PS particles with only one pulse of laser irradiation at a laser fluence of a few mJ/cm^2. For 248 nm laser irradiation, the light enhancement can be upto 60 times under the particles. The shape of the nanostructures fabricated is closely related to the laser fluence and laser incident angle. To obtain high quality nano-hole arrays, the laser fluence needs to be set at a value just above threshold fluence for the nanostructure formation and the normal incidence of laser beam is the optimal way for the surface nanostructuring. To solve the engineering problems for the nanoparticle mask applications, the laser nanoimprinting approach was proposed. Technical issues on the transparent mask fabrication, distance between the mask and substrate surface and mask alignment & tuning for a near field light enhancement environment is discussed.

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