Laser Sub-Micron Patterning of Rough Surfaces by Micro-Particle Lens Arrays

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ABSTRACT

Laser surface patterning by Contact Particles Lens Arrays (CPLA) has been widely utilized for patterning of smooth surfaces but there is no technique developed by which CPLA can be deposited on a rough surface. For deposition of CPLA, conventional techniques require the surface to be flat, smooth and hydrophilic. In this study, a new method for the deposition of CPLA on a rough surface is proposed and utilized for patterning. In this method, a hexagonal closed pack monolayer of SiO_2 spheres was first formed by self-assembly on a flat glass surface. The formed monolayer of particles was picked up by a flexible sticky surface and then placed on the rough surface to be patterned. A Nd:YVO_4 laser was used to irradiate the substrate with the laser passing through the sticky plastic and the particles. Experimental investigations have been carried out to determine the properties of the patterns.

Keywords: *Contact Particle Lens Array (CPLA), CPLA Deposition, Laser Nanopatterning, Near-Field Enhancement, Rough Surfaces*

INTRODUCTION

Within the last two decades research in novel manufacturing techniques on sub-micron, nano and even atomic scales has been accelerated by the increasing demand for miniaturized devices. Ever smaller devices can only be realized with modern precision manufacturing techniques which are also economical. With the reducing size of these devices surface patterning is also gaining more importance. Lasers have been extensively used for surface patterning at micron scale (Bäuerle, 2000; Hon et al., 2008; Pena et al., 2009). Laser is a tool which is widely utilized for manufacturing because of the advantages of being a non contact process, capable of generating complicated structures without the need of photomask and able to work in air, vacuum or water. These advantages have earned lasers a reputable position in the manufacturing industry. Moreover the laser can easily be focused down

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to a micrometer scale which makes it a tool of choice in the micro device fabrication.

Laser assisted Lithography is one of the commonly used industrial technique for submicron and nano production. However, lithography is also reaching its limit. Although smaller features can be generated by using F_2 157 nm and Extreme Ultra Violet lithography (EUV) but high resolution comes with the drawback of high cost, low output and unstable light intensity. Also these lasers need to carry the process in vacuum or high purity dry nitrogen because of the high absorption of the laser in air. Moreover there is a need of special reflective mirrors, and need very high power to achieve intensities suitable for lithography (Bjorkholm et al., 1990; Ito et al., 2000; Chong et al., 2009). These limitations have thus restricted the use of EUV for industrial production. Lithography techniques and their limitation have been summarized by Ito et al. (Ito et al., 2000). The direct use of laser in sub-micron patterning is limited because of the fact that light cannot be confined to a lateral dimension smaller than half its wavelength called the diffraction limit of light (Abbe, 1873). However, this limitation can be overcome by utilizing near-field enhancement. Laser processing in the near-field has been successfully utilized to generate features with sizes smaller than 100 nm (Chong et al., 2009). Several techniques for utilizing the advantages of near-field have been developed including Near-field Scanning Optical Microscope (NSOM) patterning (Betzig et al., 1992; Chong et al., 2009), Plasmonic Lithography (Srituravanich et al., 2004; Liu et al., 2005; Chong et al., 2009) and Laser in combination with Scanning Probe Microscopy (SPM) for tip patterning (Chimmalgi et al., 2003; Chong et al., 2009; Miyashita et al., 2009), Microlens array (MLA) nanolithography.

In laser assisted NSOM method an optical fibre cone with a nano scaled output aperture diameter is used to transmit laser for surface processing in the near field region. The tip surface is coated with metal thin film for improved transmission of the fibre. The fibre tip can have output aperture diameter of about 50 nm. The process was utilized by Korte et al. (1999) to generate 200 nm wide and 100 nm deep groves on a Cr thin film by using a frequency tripled Femtosecond laser ($\lambda \sim 260$ nm) with an aperture size of 100 nm (Korte et al., 1999). The technique was used by Lieberman et al. to remove the manufacturing defects from a Cr thin film mask (Lieberman et al., 1999). Laser in combination with Scanning Probe Microscopy (SPM) is a modification of Scanning probe microscopy. In SPM a fine tip is scanned over the sample to be characterized and the morphology of the surface is recorded by the movement of the tip. In this method a laser is focused on a SPM tip. During laser irradiation the SPM tip acts as a source of near field enhancement. The high electric field in the near field region causes the material removal and generates nano features on the substrate surface. Grigoropoulos et al. use the technique with a femto-second laser to achieve spatial resolution down to 10 nm (Chimmalgi et al., 2003). The technique has the advantage/capability to fabricate complicated designs. Alphabets "DSI" abbreviation for Data Storage Institute were written by this technique in a space of 400 nm x 400 nm (Hong et al., 2003).

Micro Lens Array (MLA) patterning is a near field patterning technique which could be used to generate patterns over large area efficiently. The technique consists of micro lenses with same size and focal length fixed on a substrate. The lenses are arranged in a square or hexagonally packed structure. These micro lens arrays focus the laser into a series of parallel light spots. Each of the spots generates features on the substrate in the near field. The technique was used by Kato et al. (2005) using a Femtosecond laser to generate arrays of 1600 "N" microletters with a thickness of 300 nm. By proper control of parameters and stage movement in 3D they also generated a self standing micro spring. However, these techniques share some common disadvantages. These techniques need to accurately control distances between the sample and the components in the range of zero to several hundred nanometres and thus require expensive and sophisticated equipment.

In addition, they have a very low throughput because of their serial nature. Moreover, they require a smooth polished surface to start with. Thus, there is a need for a simple, high speed and economical patterning method to satisfy the industrial demands.

Laser assisted CPLA is a near-field technique which was introduced recently. The technique could generate features over large areas at a very high speed. The greatest advantage of the CPLA technique is that microns sized particles could be used to generate sub-micron and nano features. In this technique, a monolayer is formed on the surface of the substrate by drying an aqueous solution of the particles. During drying the particles arrange themselves into a hexagonal closed pack monolayer array under the self assembly (Denkov et al., 1992). The substrate with the monolayer CPLA is then scanned by a laser beam of a suitable wavelength. During laser irradiation laser interacts with the particles and generates high intensity evanescent waves in the near-field. The laser is thus effectively split into hundreds of high intensity spots with sub-micron or even nano-sized diameters, each generating a feature on the surface of the substrate. Several million similar patterns can be generated in a few seconds by this method (Guo et al., 2007).

Laser assisted CPLA patterning has got immense advantages but its applications are limited because the process can only be applied to ideal surfaces (i.e. flat, smooth and hydrophilic) (Burmeister et al., 1997, 1998). For patterning of a surface by micro particles, the surface needs to be perfectly polished so that the particles could form a monolayer array on it. To the best of authors' knowledge, there is no known method by which a monolayer array can be deposited on a rough surface. Polishing itself is an expensive and tedious job. In this work, the possibility of a rough surface for patterning with CPLA is demonstrated.

This paper reports a technique for generating a monolayer on a smooth surface and then transporting it to a rough surface by using a flexible, transparent sticky surface (referred to as the 'Ribbon'). Although attempts have been made nearly a decade earlier by Burmiester et al. (1997, 1998) to transport CPLA monolayer but the process required sophisticated equipment, was applicable only to polystyrene particles and patterning was not demonstrated. Recently a method for transporting monolayer was demonstrated and used for patterning but the process was only applicable to smooth and flat surface (O'Connell et al., 2010). In our earlier work, the proposed method was used to pattern curved surface (Khan et al., 2010).

For accurate modelling in the near field Particle on Surface (POS) model is used instead of Mie theory. Mie theory is the exact solution for the Maxwell equation for the excitation of arbitrary sphere under plane wave. Mie theory was developed independently by German Physicist Gustav Mie and Danish Physicist Ludwig Valetine Lorenz. However, the Mie theory is limited because it deals with the interaction of only single particle and does not take into account the electromagnetic interactions of the substrate with the particle. The POS theory was developed to describe the propagation of dipole interaction along a flat surface (Bobbert et al., 1986). The field distribution by the POS is quiet different because of the reflection and secondary scattering of the reflected radiations from the substrate. Simply put the substrate acts as a mirror which is coupled with and spherical resonator which results in an increase in the optical enhancement and decrease in the area of the field.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Materials and Equipment

A high purity titanium substrate was used as the rough surface (Ra~ 0.23 μm) to be patterned. Pure titanium has a melting point of ~1870 ^{o}C (Park et al., 2009) which is 480^{o}C greater than one of the commonly used Stainless steel (Melting point of 316L ~1387 °C) (Wang et al., 2007).

The surface of titanium was too rough for the particles to form a monolayer array of particles by self-assembly. Silica Spheres (Bangs

Laboratories, diameter 2a = 4.74 μm, refractive index η = 1.51) are used for patterning. A Glass slide (Agar Scientific, soda lime microscope glass slide) was used as the smooth surface for the preparation of a monolayer array of particles.

A Diode pumped Nd:YVO_4 (Laserline - Laserval Violino, wavelength λ =532 nm, pulse duration τ =7 ns and repetition rate from 1 to 30 kHz, S-polarized) laser was used as the irradiation source.

The ribbon used for the transportation of particles array monolayer is a carefully chosen flexible thin, transparent (to the laser at 532 nm) plastic (Biaxial oriented polypropylene, thickness 45 μm) with an adhesive resin (polyolefin) for firmly securing the particles monolayer array. The ribbon material was chosen to have maximum transmission at the laser wavelength and flexibility to conform to rough surface. The transmission spectrum of light for the transparent plastic was measured by a Spectrophotometer (Analytik Jena - Specord 250, 200-1100 nm).

A Scanning Electron Microscope (Hitachi High Technologies - S-3400N) was used for imaging the surface of the sample. A 3D optical Microscope (Alicona Infinite Focus) was used for measuring the depth of the patterns.

Glass Cleaning and Monolayer Preparation

The glass slides were first cleaned by soapy water and then sonicated in warm acetone and methanol for 10 minutes each, respectively. The samples were rinsed and treated by 30% Nitric Acid solution for 24 hours for making them hydrophilic. A solution of the particles diluted to an appropriate concentration was applied to the cleaned glass slide. The samples were finally rinsed with DI water and dried by flow of N_2 gas (Wang et al., 2008). A hexagonal closed pack monolayer of silica spheres was formed on the cleaned surface of a glass slide by self-assembly under room conditions. The glass slides were dried overnight which formed a perfect monolayer array of the particles.

Monolayer Transportation

The complete monolayer was picked up by the ribbon. The ribbon was placed perpendicularly from the top over the monolayer to secure the particles firmly at its positions and was then peeled off. Although the monolayer adhered strongly to the glass (Guo et al., 2008), the adhesion of the resin was sufficient to peel off the particles as a monolayer array. The flexible surface along with the particles was then carefully placed on the titanium rough surface to be patterned. Since the ribbon was flexible, it followed the contours of the rough surface and the whole surface was covered by particles array. Schematic representation of the procedures developed for transfer of the particles from the smooth to rough surface is shown in Figure 1. The sample was then irradiated by the laser such that the laser passed through the flexible surface and was then focused by the particles monolayer array. The transmission spectrum of light for the ribbon, as measured by the Spectrophotometer, is shown in Figure 2.

RESULTS AND DISCUSSION

Particle on surface model (Extended Mie Theory) was used to calculate the optical near-field around the particle (Bobbert et al., 1986). FDTD (Finite Difference Time Domain) simulation was used to simulate the electromagnetic modes and evanescent modes; shown in Figure 3. A detailed explanation of the theoretical formulation can be found in work done earlier (Wang et al., 2004). It can be seen that the maximum field intensity is just outside the particle and decays rapidly along the incident path.

The roughness of the unprocessed surface of titanium is clearly visible in the SEM images shown in Figure 4a and 4b. At laser fluence higher than 0.379 J/cm^2 the ribbon was ablated by the laser and the melted plastic was depos-

Figure 1. Schematic representation of the transfer of the particles (a) Monolayer on the surface of the glass (b) monolayer secured by the ribbon (c) monolayer is lifted by the ribbon (d) particles transferred to the rough surface

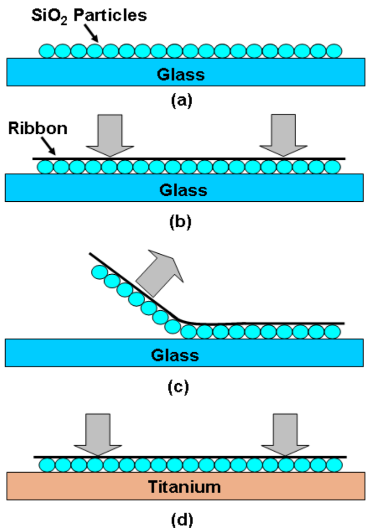


Figure 2. Transmission spectrum of light for the ribbon

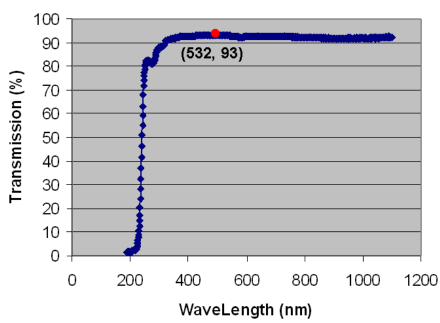


Figure 3. Calculated Poynting intensity distribution Sz for λ = 532 nm radiation under a SiO_2 sphere (n = 1.51) on a Ti substrate. The maximum field enhancement is about 68 times

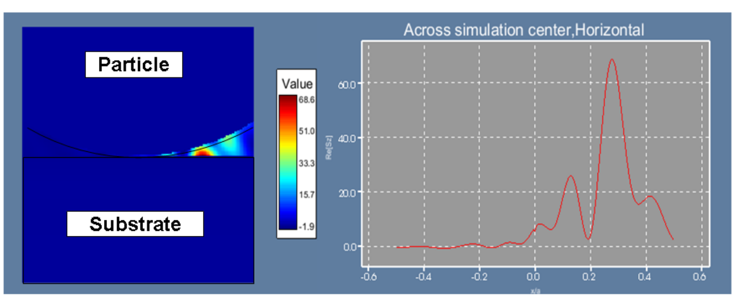


Figure 4. SEM Images of Surface of Titanium before patterning

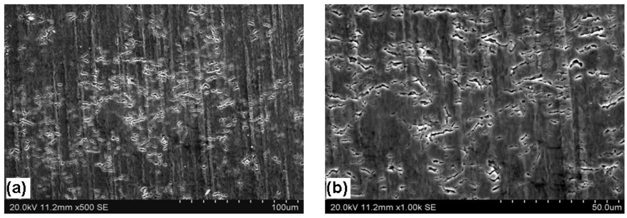


Figure 5. (a) SEM Images of debris from the ribbon on the surface of titanium. (b-f) SEM Images of patterns generated on the surface of Titanium

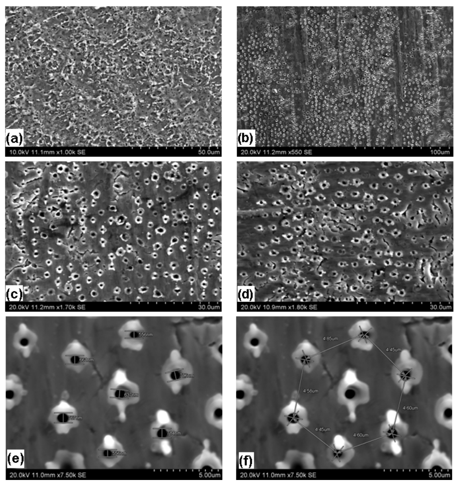
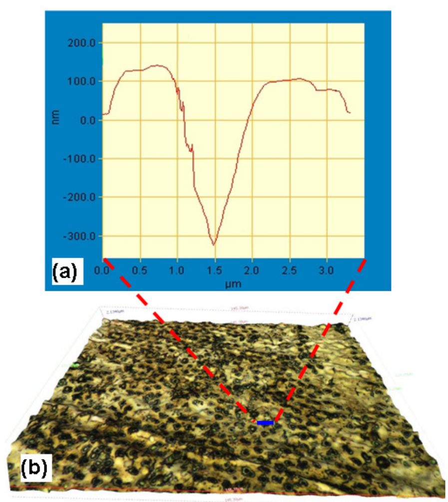


Figure 6. (a) Depth of the generated feature (b) Patterned surface



ited on the surface of titanium as shown in Figure 5a. However, at fluence below 0.379 J/cm^2 an optimum processing window was investigated. Under the reduced laser fluence, the ribbon was not damaged. The laser passed through the ribbon and was focused by the Contact particles. The intensity enhancement by the particles was found to be sufficient to pattern the titanium surface. Figure 5b to 5f shows the patterns generated on the rough surface of titanium by laser incident at 15 Degrees. An area of 1 cm^2 was scanned by the laser and good quality patterns were generated on the scanned area. Figure 5f shows the diameter of the features to be between 500 to 700 nm. Since a material with very high melting point has been patterned, the technique can be expected to work for materials with a wide range of melting points.

The depth of generated patterns was measured by a 3D optical imaging Microscope. In addition, to the depth, the true colour and the roughness of the sample are also visible in Figure 6. The depth of the features generated was in the range of 300 nm to 400 nm.

CONCLUSION

A technique for patterning of rough surfaces using particles lens array has been demonstrated which was previously not possible. It is shown that selection of a suitable flexible plastic and optimized fluence range can lead to the successful patterning of rough surfaces. Features with high spatial density were generated over large areas on a rough surface of titanium. The high melting point of titanium suggests that the technique could be applied to materials with a wide range of melting points.

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