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Direct Microstructure Deposition by Micromirror Direct Patterning and Laser Sintering of Nanoparticles

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Direct Microstructure Deposition by Micromirror Direct Patterning and Laser Sintering of Nanoparticles

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ABSTRACT

The emerging demand for low cost, medium volume production and flexible micro-fabrication techniques has been advanced by the development of MEMS and limitations of the existing technique. As a promising building block for future MEMS and IC industry, nanoparticles are attracting more and more attention due to their interesting electronic, catalytic and optical properties, which can be finely tuned by varying their size. A novel process for the manufacturing of functional microstructures by modulated laser direct patterning and curing of nanoparticles is presented.

The first part of the thesis aims to understand the possibility and process of using modulated laser to sinter and pattern the nanoparticles. A thin layer of nanoparticles is deposited on the glass or silicon substrate through controlled dip-coating technology. Laser modulated by a digital micro-mirror array and focused is employed as the principle patterning technique for selective sintering/melting of NPs. A method to monitor and optimize thin film thickness is developed and discussed. Scanning electron microscopy and parameters studies on the effect of the laser initiating time during evaporation on the topology are reported.

In the second part, this maskless laser patterning combined with coaxial nanoparticle aerosol deposition is demonstrated. The silver nanoparticles (30nm) aerosolized by the eletrospray process are collimated by a coaxial nozzle and deposited on substrate. Laser pattern is applied simultaneously during the deposition, enabling the selective sintering of the deposited nanoparticles. During a subsequent washing step in ethanol solution, nanoparticles at unexposed regions are removed, leaving behind the desired pattern. The results of fabrication of microstructures are presented.

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Manufacturing of Micro Structure by Micromirror Direct Patterning and Laser Curing of Nanoparticle

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Abstract

This paper presents a novel process for the manufacturing of functional microstructures such as electronic microresistors and microsensors. A thin layer of nanoparticle is deposited on the glass or silicon substrate through controlled dip-coating technology. Laser modulated by a digital micro-mirror array and focused is employed as the principle patterning technique for selective sintering/melting of NPs. Patterned laser irradiation is utilized to evaporate the solvent and sinter the nanoparticles to form a 2-D electrically conducting microstructure on the substrate. 3-D structure can be generated by the layer-by-layer deposition process. A method to monitor and optimize thin film thickness is developed and discussed. Scanning electron microscopy and parameters studies on the effect of the laser initiating time during evaporation on the topology are reported.

1. Introduction

Recently, the dimensions of electronic devices, such as sensors, actuators, batteries, etc. are continuously being shrunk to increase the packing density. Micro and

nanofabrication will have an important impact in a number of fields including biotechnology, optics and semiconductor device fabrication [1-2]. This requires not only miniaturization, but also enhancing the functionality and cost-effectiveness of the micro-devices components. In particular, the trend is toward the fabrication of micro-scale devices which can be incorporated into any type of platform. Traditional lithography-based micro-fabrication techniques require expensive facilities, long turnaround times and extreme process conditions. Recent advances in non-lithography, such as direct writing [3-5], micro-contact [6-7], offset liquid embossing [8-9] and e-beam lithography [10-11], allow for a more flexible 3-D micro-fabrication without the need for expensive tooling, dies, or lithographic masks. However, the speed of direct writing is slow, and it is only suitable for low volume production. The emerging demand for low cost, medium volume production and flexible micro-fabrication techniques has been advanced by the development of MEMS and limitations of the existing technique.

The practice of laser curing of nanoparticles to form an electrical conductive line has been demonstrated by Bieri [12-14]. This work introduces and investigates a novel LBL micro-fabrication method for producing electrically conductive micro structure by laser directly patterning of nanoparticles through micromirror arrays. The reason for using nanoparticles lies in the significant melting temperature depressing compared to their bulk counterpart [15]. A thin film of nanoparticles is deposited on silicon wafer through dip-coating technique. Compared with other nanoparticle delivery and assembly technique, such as ink-jet, dip-coating technique is more promising for the LBL fabrication method for producing 3-D structure. The deposited film is exposed to a 2-D laser pattern, which forms through micromirror arrays, to selectively sinter the

nanoparticles and produce a continuous thin layer of microsturcture. A laser is used to sinter the nanoparticles and only elevates the temperature locally and in a controlled manner, therefore protecting the thermally sensitive substrate and limiting the thermal effects. A 2-D pattern generated through micromirror arrays makes this technique flexible and effective. Unsintered nanoparticles are rinsed off and only the thin-film microstructure is left on the substrate. 3-D microstructure could be produced by using layer-by-layer fabrication technique.

In this work, silver nanoparticle with an average diameter size of 30nm suspended in ethanol solution was used for dip-coating. The silver structures produced are analyzed by different optical methods. A method to monitor and optimize thin film thickness is developed and discussed. Scanning electron microscopy and parameters studies on the effect of the laser initiating time during evaporation on the topology are reported.

2. **Experimental set-up**

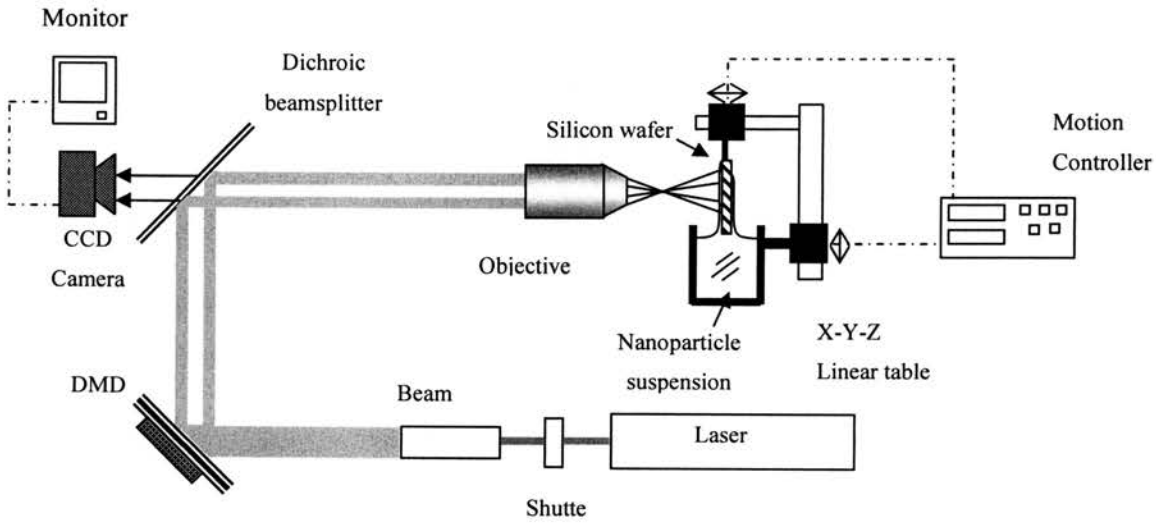


Fig.1. Experimental setup for dip-coating and laser patterning.

Nanoparticle ink used in this work for dip-coating consists of 0.5%wt, 2%wt, 4%wt silver nanoparticles (30nm, with organic coating for anti-agglomerate, Sumitomo Electric), suspended in the ethanol solution. This microfabrication system consists of three parts: dip-coating system, laser patterning system, and online monitoring system.

Various processes specifically aimed at formation of nanoparticle thin film have been developed and discussed, including Langmuir-Blodgett [16-17], spin-coating [18-19], and dip-coating methods [20-21]. Each of these processes has some advantages and disadvantages. However, the simple adsorption process of the dip-coating method offers many advantages especially for the layer-by-layer fabrication process. A self-limited monolayer of particles can be deposited because the adsorption process occurs by the interaction between the particle and substrate, and particles can be delivered onto planar, non-planar and patterned substrates [22]. A suspension container is placed on a z-axis fast precision positioning stage (Unidex IIIa, AEROTECH) and the substrate (10*10cm silicon wafer) is fixed on the x-axis stage. The surface vertical dip-coating is conducted by moving the nanoparticle suspension container vertically at controlled speed, which leads to the immersing in and withdrawing of the substrate from the suspension. The surface tension of the liquid leads to the adsorption of nanoparticles on the substrate.

The laser curing system consists of a continuous single mode argon ion laser (Stabelite 2017, Spectra Physics) with multiple wavelengths of 488-514nm, which are closed to the absorption peak of the silver nanoparticle [23]. The laser beam is expanded with a beam expander (Edmund, 10x magnification) before focusing in order to achieve spot sizes around 1cm on the micromirror device. A Digital Micromirror Device (DMD)

array (Texas instrument) is used to modulate the laser beam and obtain various 2-D laser patterns. The patterned reflective laser light is guided by the beamsplitter to the objective lens, which focuses the laser pattern generated through DMD to a micro pattern around 100 μm for curing. The distance between the substrate and the objective lens is adjusted with the x-translation stage to fit the focusing length of the objective lens.

In order to focus a laser pattern for curing and calibration of the process, an in-line optical system is built with an infinity-corrected long working distance objective lens (10x, Mitutoyo) and a CCD monochrome camera (Pulnix TM7CN). The laser endpoint evaporation and sintering process is magnified through the objective lens and visualized on the monitor. The whole experimental set-up, as shown in Figure 1, is isolated on a vibration isolation system (Micro-g, Technical Manufacturing Corporation) to ensure the homogeneity of thickness at each coating and curing process. All experiments are conducted in ambient environment and at room temperature.

3. Results and discussion

The influence of the concentration and pulling speed on the deposited nanoparticle layer is investigated first. Figure 2 presents plan-view scanning electron microscopy (Hitachi S-4700 field emission scanning electron microscopy) bright-field images of nanoparticles assemblies at nanoparticle concentrations of 0.5wt% and 4% wt with pulling speed at 5000μm/s, 2500μm/s, 500μm/s on the silicon substrate. Most of the particles deposited on the substrate are present as monomers or dimmers at the low concentration and the coverage increases with the increase of pulling rate. For the

0.5wt% suspension, as the pulling rate increase from 500μm/s, 2500μm/s, 5000μm/s, the area coverage of particles increases from 0.12, 0.25 to 0.31. This result is different from Tilley[21] and Diao's[24] observation in their research, which states that the particle coverage increases with the decrease of pulling rate. We believe the reason for this is the pulling speed used in our process is much higher than the normal dip-coating process. In this situation, the contribution of particles in the solution which clung to the substrate during pull-out is dominant compared to other absorption mechanisms. On the other hand, as the particle concentration is increased, the particles tend to assemble and multiple-layer aggregation of nanoparticles formed.

In order to produce a monolayer coverage of nanoparticles on the substrate with increasing coverage, single-adsorption with 2%wt concentration and multiple adsorption with 0.5%wt concentration with a pulling speed at 250μm/s to 50μm/s is conducted. Images of nanoparticle assemblies at a concentration of 2% with 250μm/s pulling rates are shown in Figure 3. Compared with low coverage of 0.5% suspension, the coverage of nanoparticle deposition from suspension with 2% concentration increased. Compared to deposition with high concentration suspension, a coverage of nanoparticles close to the monolayer is produced, although the aggregation of nanoparticles cannot be avoided.

Considering the random adsorption of particles, it is clear that producing monolayer coverage of particles by using a simple dipping process with particular suspension concentration is not an easy matter. In order to increase the coverage and decrease the aggregation of nanoparticles, a multiple-adsorption process is also used. The process of dipping and evaporating the solvent after withdrawing the substrate from suspension is repeated. The plane-view SEM images of nanoparticles deposition

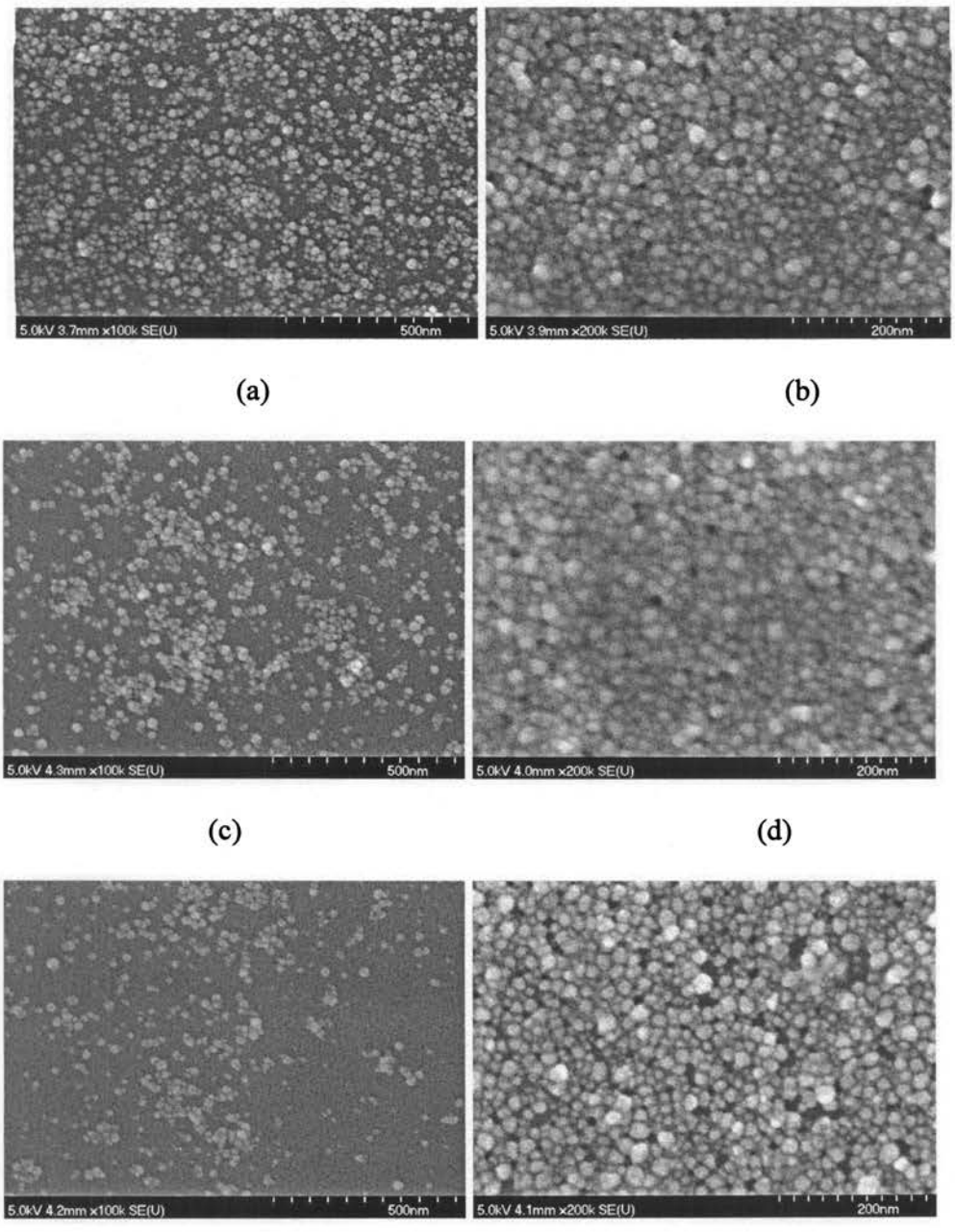


Fig.2. SEM images of deposition with various concentration and pulling rates. (a) pulling rate 5000, concentration 0.5%. (b) pulling rate 5000, concentration 4%. (c) pulling rate 2500, concentration 0.5%. (d) pulling rate 2500, concentration 4%. (e) pulling rate 500, concentration 0.5%. (f) pulling rate 500, concentration 4%.

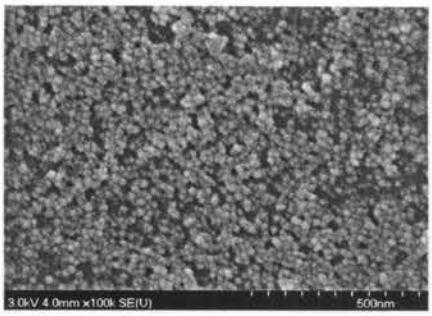


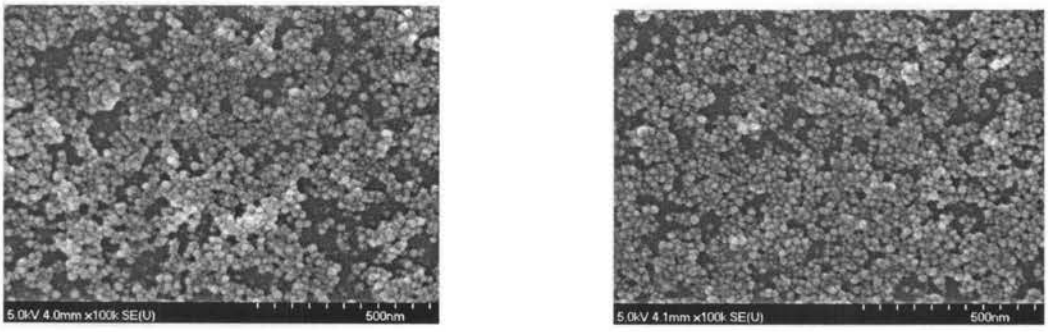
Fig.3. SEM images of deposition on Si substrate with 2% and 250μm/s pulling rates.

produced from 0.5%wt suspension with 10 dipping steps and two pulling speeds from 250μm/s to 50μm/s are shown in Figure 4. Compared with one step adsorption, after repeating the adsorption steps, particles cover nearly the whole surface with few aggregations. The decrease of pulling rate could improve the deposition quality through increasing the particle adsorption effect but minimize the particle clung effect.

The deposition and curing process are two dependent processes which are carried out sequentially. It is important to note that there exists an optimal time to initiate laser curing during the deposited solution evaporation process. To provide a better understanding on the thin film evaporation process after pullout, a inline optical system was used as a laser endpoint detector for monitoring the thin film evaporation process and measuring the film thickness [25].The basic principle of the laser endpoint detection is the generation of an interference pattern between reflections from the film surface and substrate surface. The two reflected waves will interfere constructively whenever they are in phase and destructively when they are out of phase. As the thickness of the film changes, as during the evaporation, the reflected signal intensity oscillates, passing through successive maxima and minima, until the evaporation completes and the incident laser is reflected from only one surface, resulting in a constant level. A series of images

illustrating the oscillation of light intensity due to interference are shown in Figure 5a. Figure 5b shows the measured evolution of evaporation represented by a series of maxima and minima. The level on the end of the curve depicts the end of evaporation. Knowing that the thin film thickness difference between neighboring maxima and minima is $\lambda/(4n)$, where λ is the probing laser wavelength (488nm) and n is the diffractive index in the measured material, the thickness of the pure ethanol thin film on the substrate before evaporation can be measured. The classical Landau-Levich equation [26] can be used to help understand the experimental observations. From the results shown in Figure 5c, we note that the film thickness increases with the withdrawing speed.

The measured thin film evaporation processes at different nanoparticle concentration and withdrawing speeds are shown in Figure 6. From these results, we found that the evaporation time of the thin films with either higher particle concentration or higher withdrawing speed is longer, which can be explained by the thickening effects induced by more nanoparticle additions and pullout speeds. With higher particle

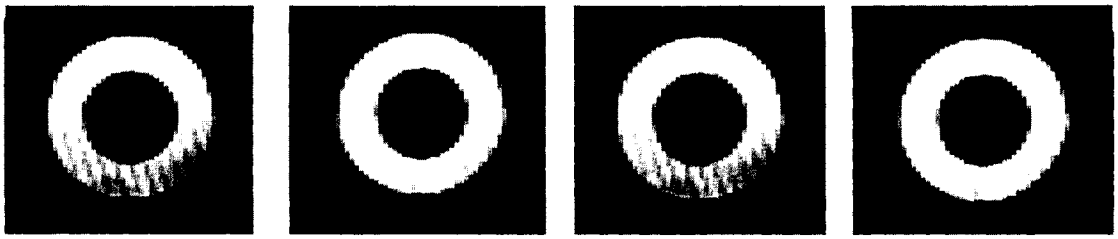


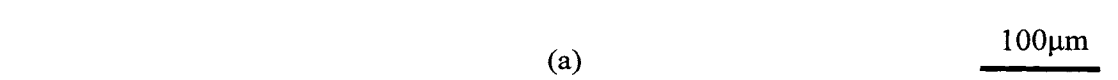
(a) (b)

Fig.4. SEM images of nanoparticle deposition with 0.5%wt and 10 dipping steps. a) pulling rate 250μm/s. b) pulling rate 50μm/s.

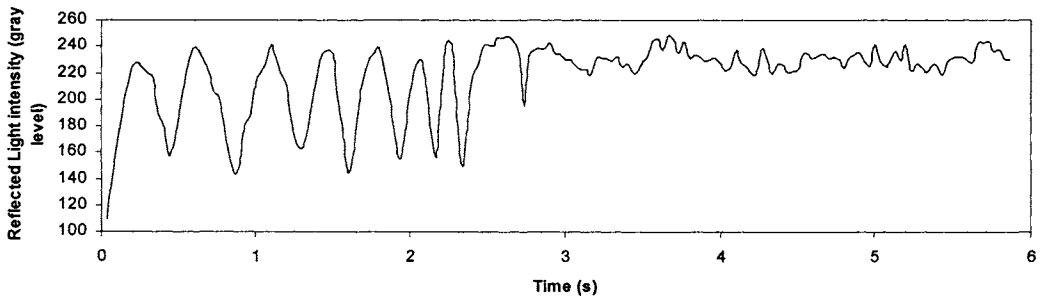
additions, the Marangoni-induced thickening of thin films will occur, where Marangoni stresses due to the varying distribution of particle additives between the continuous film region and the meniscus during pullout can generate an extra traction along the pulling direction towards the film and lead to the thickening of the film [27].

For the fabrication technology with nanoparticle suspension deposited on the substrate, the displacement of the nanoparticle due to surface tension gradient induced by the laser heating and evaporation of the carrier liquid during the curing process leads to the U-shaped concave in the center line of the pattern [13]. In our process, we try to minimize this Marangoni effect through the coordination of the deposited suspension evaporation time and laser curing initiating time. Figure 7 shows microscopic images of sintered micro-ring structures using 4%wt nanoparticle suspension after unsintered nanoparticles are washed away. The laser pattern power is ~60mW and the sintering time is 5 sec. The laser sintering starts at the beginning (a), the mid way (b) and the end (c) of the evaporation process after the substrate is pulled out of the suspension. It can be seen that as the time allowed for evaporation increases, the sintering switches from wet to dry process, the resulting structure becomes denser and better defined. This is due to the reduced volumetric boiling as the film thickness decreases. A Digital Instruments Nanoscope IIIa Atomic Force Microscope is employed to obtain the thickness of the deposition by measuring the surface profile at the edge of the rings. The variation of thickness against sinter starting time is shown in Figure 8a. A clear reduction of the thickness can be seen with a dry process. In order to obtain fully dense microstructure with better coverage and higher thickness, more layers are deposited. The thickness can be increased by multiple depositions, as shown in Figure 8b.

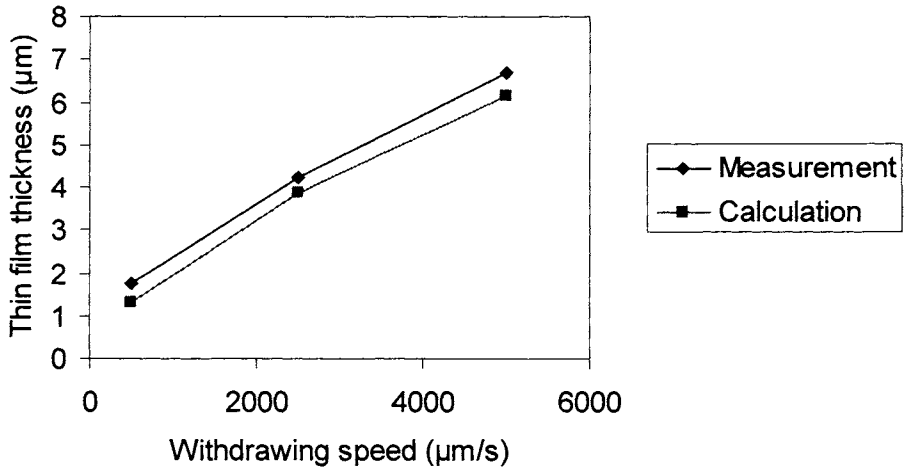




(a)



(b)



(c)

Fig.5. Laser endpoint detection. (a) Microscopic images of laser patterns reflected from wafer surface with intensity oscillations. (b) Monitoring at 488nm, the observed light intensity maxima and minima. (c) Measured and calculated ethanol thin film thickness at various withdrawing speeds.

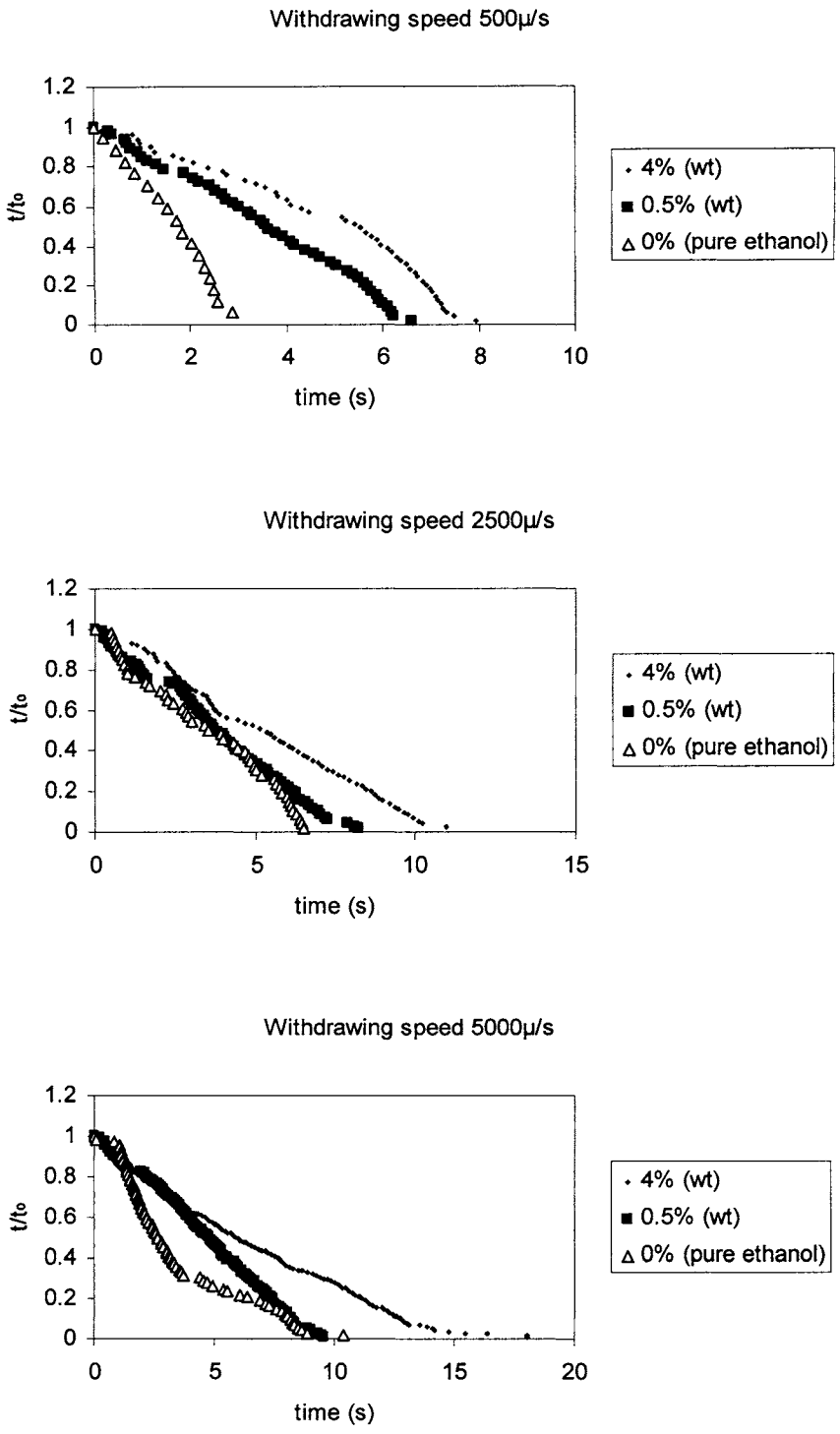
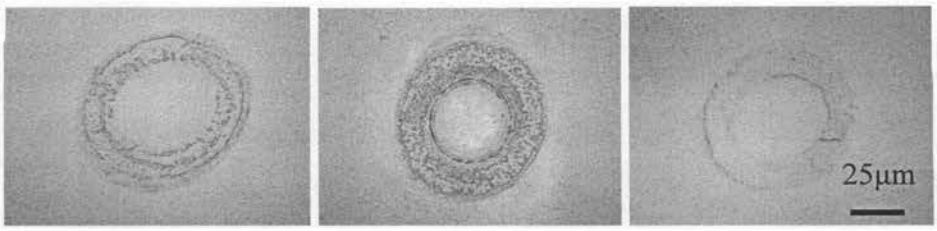
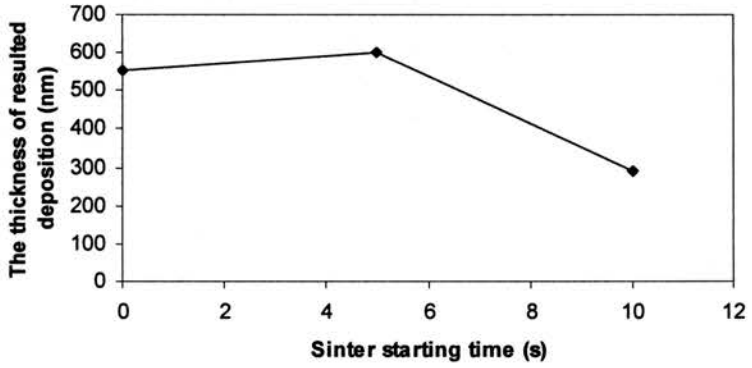


Fig.6. Evaporation processes in different suspensions with various pulling rates.

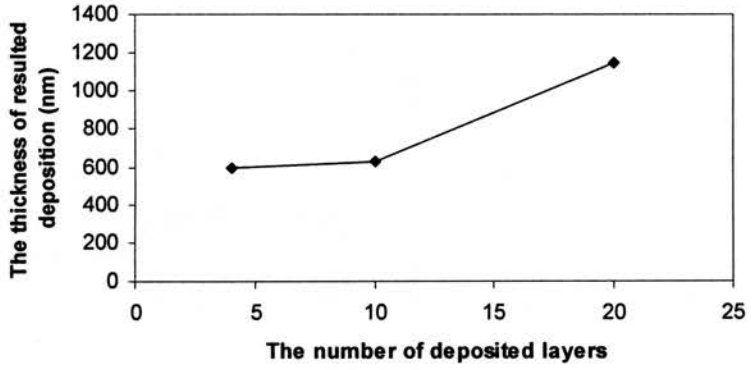


(a) (b) (c)

Fig.7. Microscopic images of deposited micro-rings. (a) Sintering started at 0s after pulling out, 4 layers. (b) Sintering started at 5s after pulling out, 4 layers. (c) Sintering started at 10s after pulling out, 4 layers.



(a)



(b)

Fig.8. The thickness variation with sinter starting time (a) and deposition layers (b).

To prove the possibility of applying our technique into functional electronic conductive devices fabrication, such as sensors, a more complex strain gauge pattern are deposited on the silicon substrate through our microfabrication process, as shown in Figure 9 The size of the strain gauge is about 100μm× 100μm and the line width of the strain gauge is about 10μm.

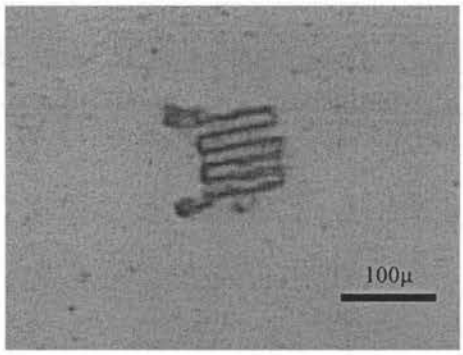


Fig.9. Microscopic images of deposited strain gauge.

Acknowledgements

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Direct Microstructure Deposition by Laser Patterning Coaxial-Fed Nanoparticles

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Abstract

We demonstrate a new direct addictive micro-fabrication method by combining maskless laser patterning with coaxial nanoparticle aerosol deposition. The silver nanoparticles (30nm) aerosolized by the eletro-spray process are collimated by a coaxial nozzle and deposited on a substrate. A laser pattern is applied simultaneously during the deposition, enabling the selective sintering of the deposited nanoparticles. During a subsequent washing step in ethanol solution, nanoparticles at unexposed regions are removed, leaving behind the desired pattern. The results of fabrication of microstructures are presented.

As a promising building block for future MEMS and IC industry, nanoparticles are attracting more and more attention due to their interesting electronic, catalytic and optical properties, which can be finely tuned by varying their size. To integrate nanoparticles in a rational manner to make a functional device or system has become a goal for researchers in this area. To achieve this goal, the understanding of nanoparticles and the appearance of new manufacturing techniques are required.

Various multi-step manufacturing processes have been extended to pattern nanoparticles monolayers for functional sensor/actuator fabrication, such as Cui *et al.* [1-

3], combinatorial approach [4,5], micro-contact [6,7], offset liquid embossing [8,9] and e-beam lithography [10-12]. However, these techniques require multiple steps, which are based on e-beam writing and photolithographic methods. Therefore very special, expensive and bulky equipment and facilities are required.

Recent developments in single-step deposition methods have been introduced by the emerging demand for low-cost, large area, and light weight microelectronics on flexible substrates. Direct writing (sequential) and patterning (parallel) are most common single-step deposition processes. Examples of direct writing/patterning of nanoparticles include: Ink-jet printing [13], Aerosol deposition [14], Aerosol deposition with mask [15-16], Laser guided direct write (LGDW) [18-19], Maskless mesoscale material deposition (M^3D)[20], E-beam induced deposition (EBID) [21], Laser curing of nanoparticle solutions [22-24], Nanoxerography [25] and Micro-fluidic method [26-27]. However, the speed of most of the sequential direct writing techniques is slow. To be useful for practical applications, parallel deposition is necessary to fulfill several requirements such as large area deposition, high deposition rate and low temperature processing. However, most parallel patterning of nanoparticles requires a mask or mold [14]. To reduce cost and accommodate flexible microfabrication, a maskless direct patterning of nanoparticles will be beneficial for rapid turnaround and/or pattern iteration or for modeling difficult circuits.

In this letter we show that subsonic nanoparticle deposition can be combined with a dynamic light modulation unit to realize maskless direct nanoparticle patterning. Nanoparticles are accelerated through a coaxial nozzle and deposited onto the substrate. Deposited nanoparticle thin film is sintered by a laser pattern simultaneously. A

microstructure can be obtained by washing off the unsintered nanoparticles. We demonstrate that, by exploiting the laser exposure timing and velocity of particles, it is possible to create structures with 10 μm resolution and controlled shape on silicon substrate at room temperature.

Figure 1 shows the constitution of the deposition apparatus. An electrospray aerosol generator is used to aerosolize the nanoparticle suspension. The electrospray pushes a charged nano-particle suspension through a capillary tube and exerts an electrical field on the liquid at the capillary tip. The electrical field pulls the suspension from the capillary, forming individual nanoparticles. Nitrogen is used as carrier gas. A coaxial nozzle is made to accelerate and collimate the nanoparticle beam. Velocities of particles are determined by carrier gas consumption, which is controlled by a gas regulator. During the collisions of the nanoparticles with substrate or the pre-deposited nanoparticles, a bonding between them is formed by conversion of the kinetic energy. The bonding is not enough to survive a following a rinsing process. Therefore a laser pattern is applied simultaneously during the deposition to selectively sinter the deposited nanoparticles. A Spectra-Physic 5W Argon-Ion laser is used to emit multiple wavelengths from 454 nm to 514 nm. The green line 514 nm is selected for this process. The laser pattern generated by micro-mirrors array (DMD) is focused by a long-working distance objective lens onto a silicon wafer substrate that is placed at 0.6mm past the focal point. The laser pattern is focused down to ~100 μm in width on the substrate. The power of the pattern after the lens is measured to be 80 mW using a power meter, which provides a local power density of $1\times10^{-5} W/\mu m^2$. A deposition chamber is used to enclose the deposition process to reduce nanoparticle contamination.

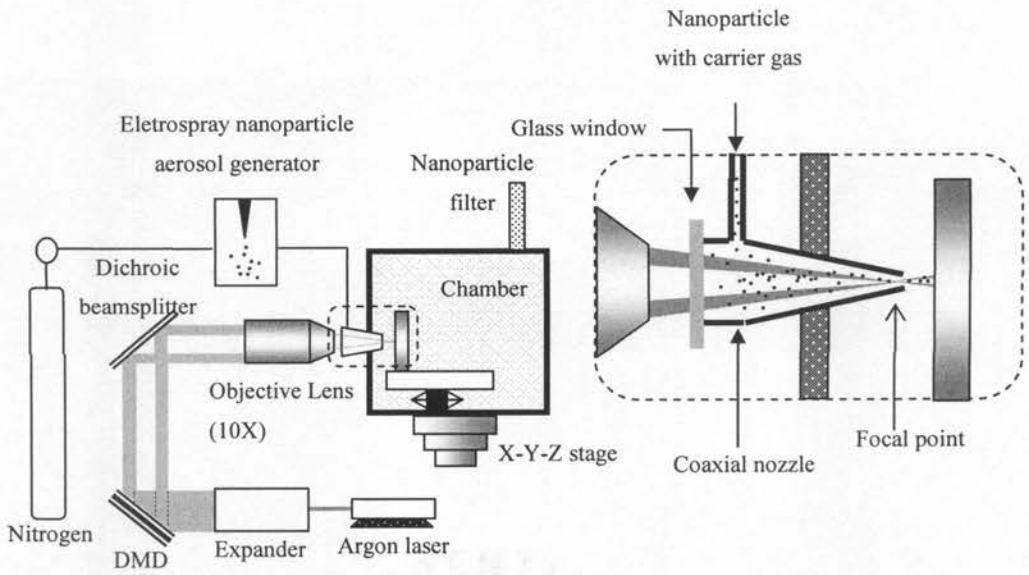


Fig.1. Experimental setup for coaxial feeding and laser patterning.

In the experiment, the starting nanoparticle suspension is obtained by adding the silver nanopowder (30nm diameter, with organic coating for anti-agglomerate, Sumitomo Electric) to ethanol solution. The nanoparticle suspension is diluted to obtain a 0.1%wt solution. The nanoparticle suspension is delivered at 3.5μl/min into the electrospray chamber through a capillary tube. Once the liquid is flowing from the capillary tip, the applied high voltage is adjusted to achieve cone-jet mode, as shown in Figure 2. This results in a stable generation of aerosol of nanoparticles. During the deposition, nanoparticles are supplied continuously while the laser pattern is triggered on and off intermittently with pre-determined timing. The typical timing is 1s for *on* and 10s for *off*. The deposition is considered complete after the amount of dispersed suspension reaches 500μl. In a final rinsing step, the substrate is submerged in ethanol solution for 1min, leaving the sintered microstructure anchored to the substrate.

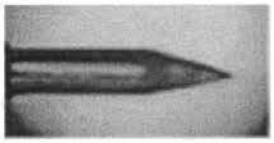
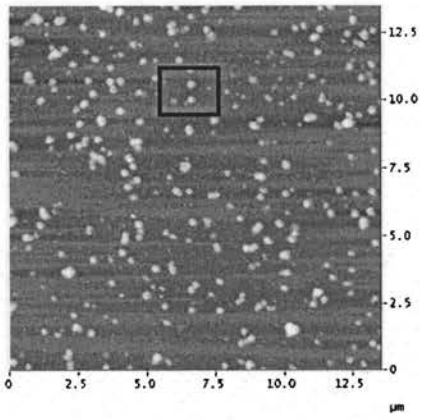
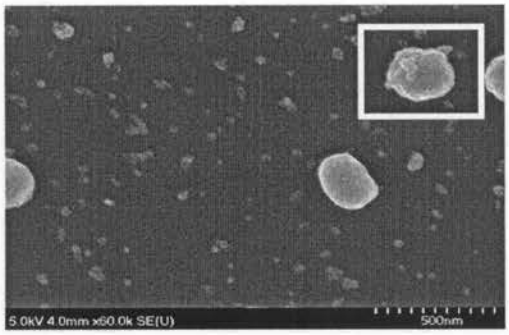


Fig.2. Cone-jet mode in the electrospray chamber.

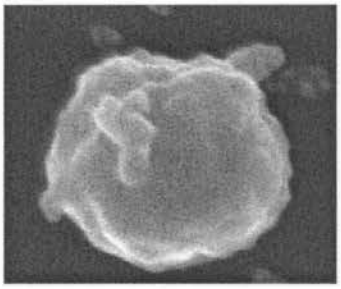
Figure 3a shows an AFM image of a layer of deposited nanoparticles in an unexposed area before the rinsing process. It can be seen that the particles are not closely packed yet. This is because in this preliminary research there is not an efficient nanoparticle collimation/focusing device used. Using an aerodynamic focusing nozzle, e.g. sheath gas focusing, is believed to enhance the coverage. The average particle size is around 100-200 nm. A high magnification SEM micrograph is presented in Figure 3b. It can be seen that besides the particles with a size of 100-200 nm, there are also smaller particles deposited with an average size of 30 nm which is actually the original size of the silver particles. The SEM image of one larger particle (Figure 3c) shows that the larger particle is agglomerate which contains many smaller particles. The question here is why there are two sizes of particles. According to [28], the diameter of the charged droplet as it first leaves the tip of the capillary, referred to as the primary droplet diameter D_d, can be calculated by $D_d = \frac{1}{C^{1/3}} D_p$, if D_p is the original particle diameter in the suspension and C is the volume concentration expressed as a decimal. The size of the droplets estimated using this expression is around 600 nm. One can see that the agglomerate size is somewhat smaller than D_d. This is because due to the evaporation of the solvent after the droplet breaks away from the tip, particles within the same droplet tend to form an agglomeration. However, at this stage, it is not clear how particles with a size of 30 nm are generated and deposited.



(a)



(b)



(c)

Fig.3. Deposited nanoparticles before rinsing.

Figure.4a shows an optical microscope image of a deposited strain gauge structure after washing off the unexposed regions. The brightness difference between exposed and unexposed regions indicates that more particles are left in an exposed area. Zoomed in AFM images of the exposed and unexposed regions after washing are shown in Figure 4b

and 4c respectively. By a direct comparison of Figure.4b with the sample imaged without laser patterning (Figure.3a), it can be seen that the laser exposure during patterning did not bring noticeable differences in average particle spacing and coverage. However, in the unexposed region, most of the particles with a size of 100-200 nm are removed after rinsing, as can be seen in Figure 4c. Presumably, the difference occurs through the sintering of nanoparticles with neighboring nanoparticles or substrate by laser in an exposed region. To prove this point, SEM images of particles in both exposed and unexposed regions are shown in Figure 5. It is clearly seen that sintering has occurred in exposed regions, as shown by the bridge between neighboring particles in Figure 5a. It is believed that it is because of the bonding enhancement that the particles can survive in the succeeding washing process. It should also be noted that nanoparticles with a size of 30 nm are not able to be removed by rinsing with ethanol in both exposed and unexposed areas, as shown in both Figure 5a and Figure 5b.

In Figure 6, we demonstrate the possibility of exploiting the laser exposure timing to obtain a different lateral resolution. The timing is 1s for *on* and 10s for *off* in Figure 6a and always on for Figure 6b. As the time for *on* increases, the ring width increases. This is due to both the increase of the area where the temperature is higher than the threshold value for the initiation of the sintering process and the enhanced lateral heat diffusion.

In summary, the preliminary experiments have demonstrated the feasibility of a simple technique to spatially arrange nanoparticles in a desired pattern. Nanoparticles with a size of 100-200 nm can be deposited on a silicon wafer by fine-tuning the coaxial nozzle design, stand-off distance and carrier-gas flow rate. The deposited nanoparticles with this size can be removed from the substrate by following a submersion rinsing.

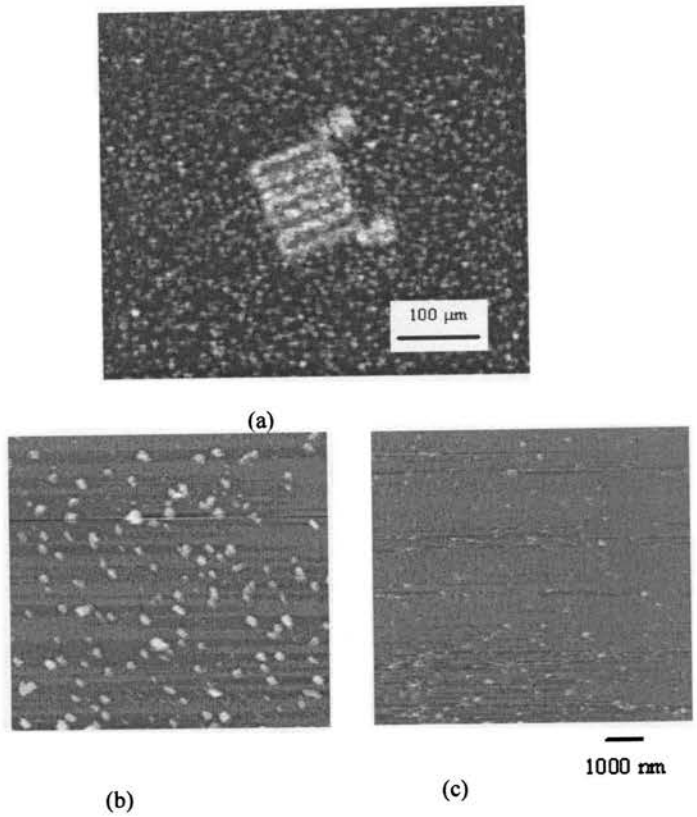


Fig.4. AFM images of exposed and unexposed area after rinsing. (a) Deposited strain gauge. (b) Nanoparticles at exposed region. (c) Unexposed region.

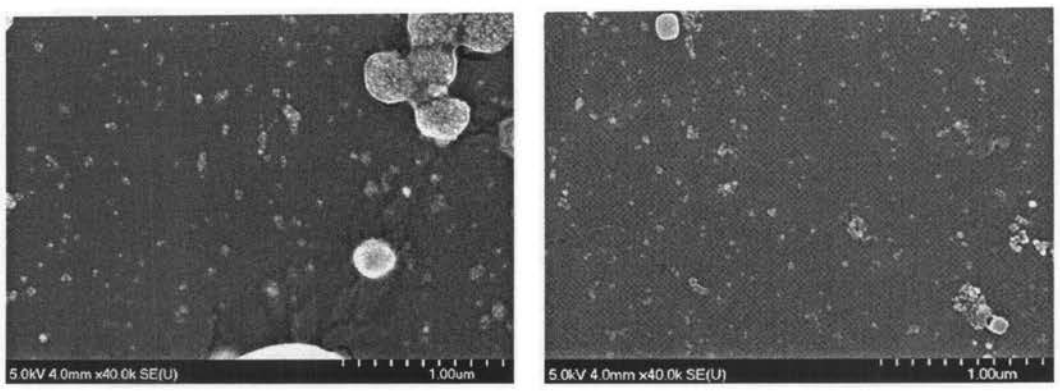
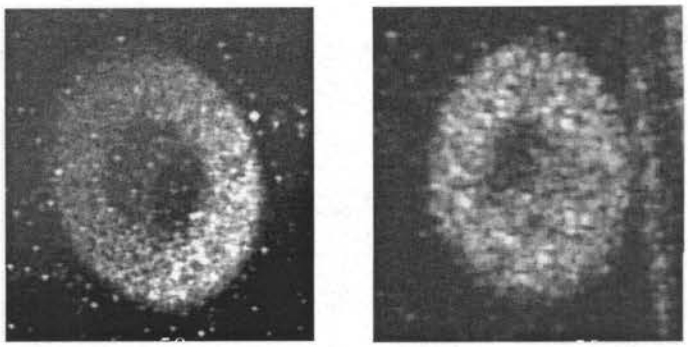


Fig.5. SEM images of exposed and unexposed area after rinsing. (a) After rinsing, larger nanoparticles sintered at exposed region are left, sintering is shown by the bridge between particles. (b) Only smaller nanoparticles are left, larger particles are washed off in unexposed region.



(a) (b)

Fig.6. Deposited ring structures with different sintering timing. (a) 1s for laser on and 10s for off; (b) laser is always on.

Sintered by a laser pattern with the remarkably low power of 80 mW, nanoparticles in selected regions will stick to the substrate or neighboring ones. Microstructure can be left after unexposed nanoparticles are washed off. The resolution of this process can be down to 10 μm. The inefficiency of the current process is its low nanoparticle coverage during the deposition. This can be substantially improved by introducing an aerosol focusing device. It has the potential to become a substitution process in a direct fabrication of sensor/actuator or circuit board on various substrates in medium production micro-fab industry with rapid turnaround.

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