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NANO-SCALE PATTERNING OF SILICON NANOPARTICLES ON SILICON SUBSTRATE BY DIP-PEN-NANOLITHOGRAPHY

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Dip-Pen Nanolithography technique has been used to write nano-scale patterns of silicon nanoparticles on Si/SiO_2 substrate using commercially available silicon nanoparticles suspension as ink (mean diameter 30 nm). Patterning experiments have been carried out under varying process conditions namely, temperature and humidity with varying writing speed. Line- width of 92 nm has been measured at writing speed of 0.1 μm/sec, which reduced to 54 nm at higher speed of 1.6 μm/sec. Obtained results would be useful for patterning nano-size features of other hard materials (semiconductors and metals) for applications in nanoelectronics and biotechnology.

Keywords: *DIP-PEN NANOLITHOGRAPHY, SELF-ASSEMBLED-MONOLAYERS, AFM, SILICON NANOPARTICLES, NANOPATTERNING, NANOELECTRONICS.*

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1. INTRODUCTION

Continued innovations in process technology, materials, device-structures have made possible to develop 32 nm microprocessor chips. Patterning capability of lithography process determines the component density on the chips. Various lithographic techniques namely, electron-beam lithography [1], micro-contact printing [2], focused ion beam [3], scanning probe [4] and nanoimprint [5] are capable of delineating sub-50 nm patterns. Dip-pen-nanolithography (DPN) [6] is a new lithography tool primarily for writing molecules onto substrates through self-assembled-monolayers (SAM). Creating nano-structures using DPN is a single step process and does not require resist. Basic schematic of the technique is shown in Fig. 1.

In this technique, atomic force microscope (AFM) tip is used to write nano-dimensional pattern on the substrate. The AFM tip is coated with the desired compatible molecular/other ink. The ink molecules are transported to the substrate via a water meniscus which is formed between tip and substrate when in close proximity of substrate. The writing process strongly depends upon environmental conditions, such as humidity, temperature, tip coating procedures, surface condition and substrate-ink interactions. In case of thiol-based inks, chemisorption of ink-molecules on the underlying substrate act as a driving force for moving the molecules from the tip to the unoccupied sites on substrate. Various ink-substrate combinations have been explored for writing nano-pattern using dip-pen-nanolithography (DPN) [6].

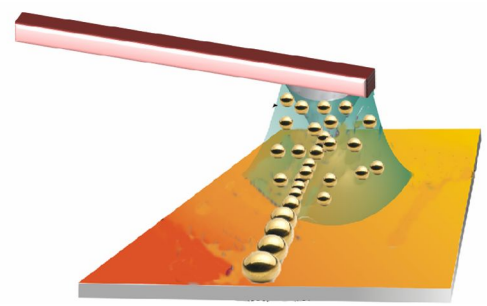


Fig. 1 *– Schematic representation of dip-pen-nanolithography (DPN) concept*

Recently, nano-patterning of metals, metal-oxides and semiconductors using dip-pen-nanolithography has been reported [9], [10]. In this work, the direct-writing capability of DPN has been explored in patterning of silicon nanoparticles on Si/SiO_2 substrate, using "suspension of silicon nanoparticles" as ink in place of generally used organic-molecule inks.

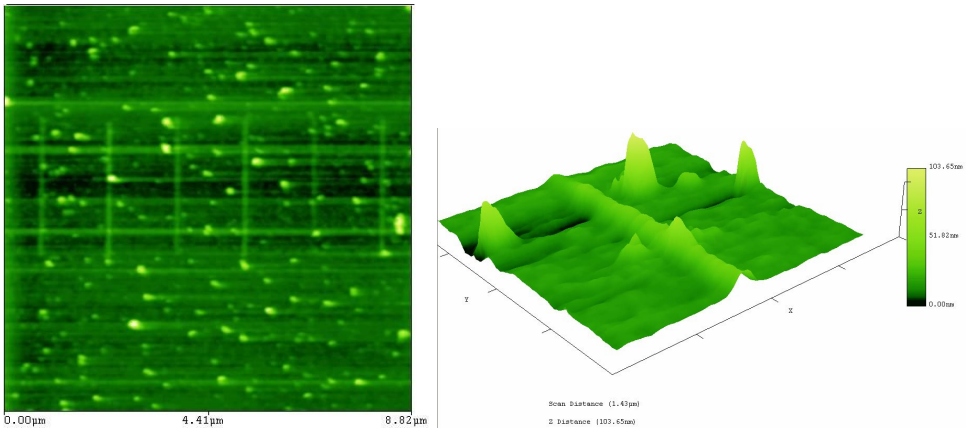
2. EXPERIMENTAL

Low-resistivity, n-type, ⟨100⟩, silicon wafers were used as substrate in the experiments. Thermal oxide (~ 50 nm) was grown after chemical cleaning. Silicon nanoparticles (polycrystalline) suspension in IPA, purchased from Meliorum Technologies, USA, was used as writing ink. The specified mean diameter of nanoparticles is 30 nm with 10 % monodispersity. There are particles with diameter in range 20 - 44 nm, while 40 % particles have diameter in range 28 - 34 nm. A very dilute (5 mM) solution was prepared from the received suspension. Triangular shape silicon nitride cantilever AFM tips were coated with silicon nanoparticles suspension using dipping method. Writing experiments were conducted on NSCRIPTOR system from Nanoink, USA. First, several ink-diffusion test experiments were conducted under different temperature and humidity conditions in the environment-control chamber, to reach the favorable writing conditions. The reported experiments were performed at temperature = 27 °C and RH = 38 % at different locations on the substrate. Lines were designed in supplied software, InkCAD, and writting was performed with tip movement speeds in the range 0.1 - 1.6 μm/sec. Imaging of written lines was done using same AFM tip in lateral force microscopy (LFM) mode at higher frequency. Achieved AFM images have been analyzed and results are presented in the next section.

3. RESULTS AND DISCUSSION

LFM images, of lines written with tip movement speed from 0.1, 0.2, 0.4, 0.8, 1.2 and 1.6 μm/sec respectively are shown in Fig. 2a, and an enlarged 3-D view of one such line is shown in Fig. 2b. These images have been analyzed in image processing software module "NanoRule". For more accurate analysis, images of two lines were enlarged and line analysis was performed across a horizontal line drawn on image. Screen shot of such analysis is shown in Fig. 3. Two markers were used to measure line-width from the line profile as shown in the figure. The measured line widths

varied from 92 nm to 54 nm by changing writing speed from 0.1 μm/sec to 1.6 μm/sec. The shown line widths are 65 nm and 54 nm for writing speeds of 1.2 μm/sec and 1.6 μm/sec respectively. Similarly, all six lines were processes and analyzed to estimate their width. The results are plotted in Fig. 4.



(a) (b)

Fig. 2 – LFM image lines of written using silicon nanoparticles ink with writing speeds of 0.1, 0.2, 0.4. 0.8, 1.2 *and* 1.6 *μm/sec respectively (a) and enlarged 3-D image of one such line (b)*

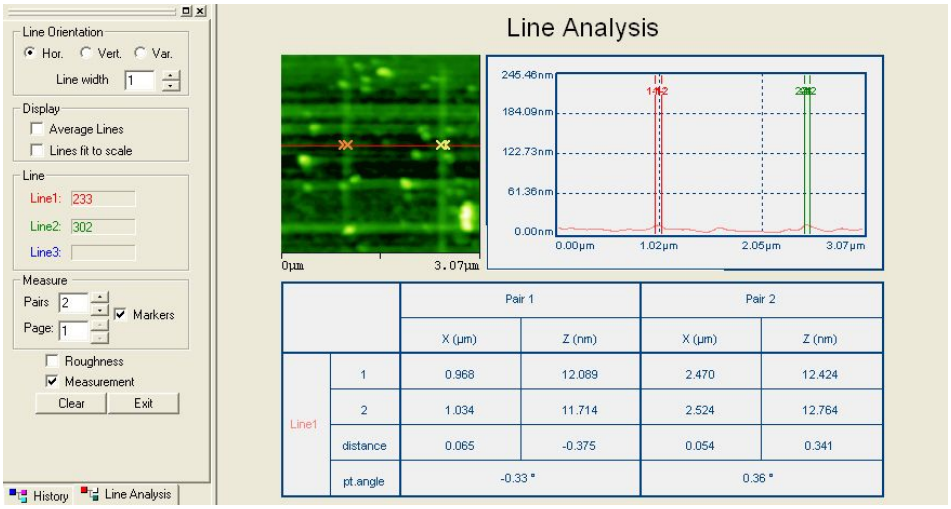


Fig. 3 *– Screen shot of image analysis of lines written with with speeds of* 1.2 *and* 1.6 *μm/sec, line profile across images and measured line widths are also shown*

Slow writing speed of 0.1 μm/sec resulted line of 92 nm width. Increasing speed to 0.2, 0.4, 0.8, 1.2 and finally 1.6 μm/sec, finer lines of width 80, 67, 67, 65 and 54 nm were achieved. Five sets of such experiments were performed on the same substrate and results were analyzed. Same trend of

decreasing line width with increasing writing speeds was observed. This may be explained as follows; at lower speed, the tip is at given point for longer time, more silicon-nanoparticles are transported to the substrate and adsorbed on surface forming a line. With increasing speed, lesser number of particles are transported and deposited making finer line. There is little variation in line-width at these locations for a given speed. These small variations may due to topography and other variation on the surface condition of the substrate. As mentioned above, the mean diameter of nanoparticles is 30 nm, and there are particles of lower as well as higher size in the suspension. The written lines with measured width may be considered to contain 2-3 particles of different diameter aligned horizontally. Using highly mono-disperse nanoparticles suspension, lines with better control over size can be patterned having one or two particles across width.

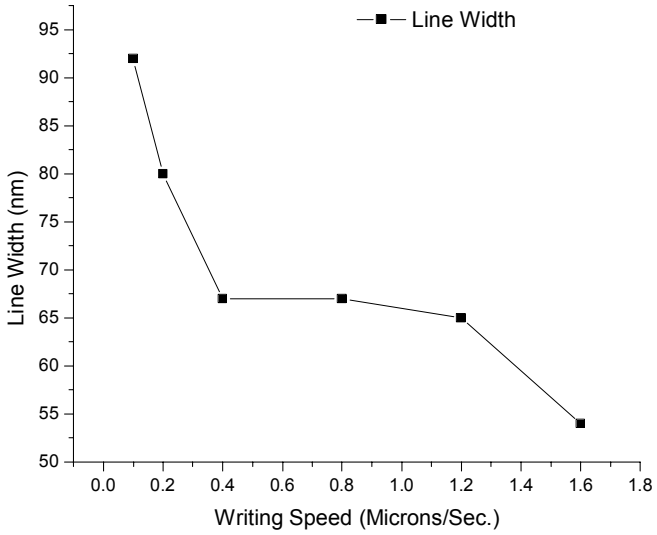


Fig. 4 *– Measured width of silicon nano-partilces lines with varying writing speeds from* 0.1 *to* 1.6 *μm/sec*

As the writing process is very sensitive to surface condition of local writing area, the lines have variation of ± 10% in their widths at different locations, with identical speeds. Few random bright spots are also visible in all the images. They appear to be nanometer size particles present on the substrate which might have been deposited during various fabrication processes of substrate. Great care is needed for substrate preparation and writing process. Surface contaminants and even roughness are detrimental to the controlled patterning. Storing the substrates after oxidation step in vacuum will improve the surface condition. Further, these bright spots may also be of some silicon nanoparticles diffused from the tip during movement and imaging. This problem may be controlled by reducing the amount of ink on the tip and imaging at higher speed. These lines may be considered as horizontal silicon nano-wires with silicon nanoparticles as beads, and find applications in nanoelectronic devices. These preliminary results demonstrate

the direct nano-scale deposition of silicon nano-particles on silicon substrate at desired locations. Further studies of structure and electronic and optical properties are required before applying in real device. Similar experiment may be performed to write nano-size dots for applications in quantum dot/molecular devices.

4. CONCLUSIONS

Direct writing of silicon nanoparticles on silicon substrate has been demonstrated using Dip-pen-nanolithography technique. AFM imaging and analysis has been employed to determine line width. Minimum line width of 54 nm has been achieved at writing speed of 1.6 μm/sec., may be considered having two nano-particles across its width. Mono-disperse suspension is expected to result in more controlled features. Further process optimization in substrate fabrication, environment conditions and writing process are needed for patterning single nanoparticle-lines. These initial efforts would be useful in the area of nanoelectronics and nano-biotechnology.

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