

Enhancing Oxide Growth Rate in Rolling Nanoelectrode Lithography (RNEL) Process

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We demonstrated that surface manipulation of silicon substrate with ethyl alcohol can increase the oxide growth rate during the rolling nanoelectrode lithography (RNEL) process. Here, we performed the oxidation process with the modified silicon substrate which shows an enhanced oxidation growth rate by almost an order of magnitude that of in unmodified silicon substrate. The parametric effects on oxide growth were performed, where the rolling speed and the applied bias voltage were identified as the primary control parameters for oxide growth. Experimental studies show the linear dependence of the oxide height as a function of the applied voltage, whereas the oxide height is increased with decreasing the rolling speed. The present results show that the rolling nanoelectrode lithography can be a suitable large-area fabrication approach to fabricate nanostructures with high throughput.

1. Introduction

Although photolithography has been driving the massive success of the semiconductor industry for more than a few decades, it has approached its ultimate limits. Extensive efforts have been devoted to alternative lithography techniques such as Extreme Ultraviolet Lithography (EUVL), Electron Beam Lithography (EBL), Nanoimprint Lithography (NIL), and Directed Self-assembly (DSA). They have demonstrated excellent potential as promising candidates for future industrial nanofabrication. However, all these technologies are in their development phases and still need further work to overcome some challenges. The EUVL infrastructure still requires significant improvement in source reliability, line edge roughness (LER), and defectivity [1]. EBL is a very slow process and requires high capital and operational costs. In addition, overlay, defectivity, tool design, and placement accuracy remain the main concerns for NIL and DSA technologies [1, 2 - 4].

On the other hand, local oxidation-based techniques have shown promising capability to fabricate nanostructures and devices [5 - 10]. It has been strengthened in recent years as one of the most promising methods due to its high reproducibility, simplicity, resistless process, low cost, and versatility. However, this method based on AFM/SPM exhibits a drawback of limited throughput due to its serial nature and small practical patternable area (generally tens of microns). To scale up this process, a nanoelectrode lithography (NEL) technique has been proposed where the AFM tip is replaced by the protrusions of a conductive flat stamp [11 - 14]. However, the NEL process with a flat

stamp is not suitable for large-area nanopatterning as non-uniformity becomes an issue when they use large stamps. Firstly, it is difficult to achieve uniform contact between the stamp and the specimen on a large scale due to the disuse of the resist materials. Again, another critical challenge in the NEL process is to maintain uniform pressure over the whole contact area during oxidation. These challenges severely limit the application of NEL for large-area nanopatterning. These limits have been addressed by using a roller in place of the flat stamp (rolling nanoelectrode lithography, RNEL), which could significantly improve the pattern transfer uniformity [15]. Although the RNEL process can be advantageous as it enables continuous patterning and easy demolding in large-area nanofabrication, low throughput remains still an issue.

Throughput can be increased by accelerating the oxidation process. Previous studies suggested that a higher growth rate can be obtained by using an atmosphere saturated with organic solvents such as ethyl alcohol, hexadecane, 2-propanol, 1-octane, and octane [16 - 19]. Ricardo Garcia's group showed that the growth rate of local oxides can be increased by almost an order of magnitude by using oxyanions from ethyl alcohol molecules [16]. The experiments were carried out in a closed chamber filled with ethanol vapour. They fabricated the low-dimensional structures of SiC_x on Si substrates [20].

In this work, we study the possibility of using ethanol drops to manipulate the Si surface that can be a way to enhance the oxidation rate. The ethanol molecule initially interacts with the Si surface through the barrierless formation of a dative bond; from this physisorbed state, the O-H bond cleavage process is the kinetically favored dissociation

reaction [21, 22]. We have performed a comparative study of the oxide growth rate using Si substrate and manipulated Si substrate. We have also investigated the influence of experimental parameters such as applied voltage, rolling speed and relative humidity on the oxidation process.

2. Experimental Details

The experiments were carried out using our developed RNEL system where the roller stamp rolls over the sample while voltage is applied between the stamp and the sample. The roller maintains uniform pressure over the whole surface area that ensures a uniform oxidation process over a large area of the samples. In order to prepare the stamp, a cylindrical roller (13 mm diameter and 100 mm long) machined from brass materials was first wrapped with a 2 mm thick and 10 mm wide layer of synthetic rubber (polyisobutylene and 2 mol% isoprene), which increases the elasticity of the stamp as well as the contact area. After that, a polycarbonate strip (peeled from a DVD-R) adhered to the rubber surface. The polycarbonate strip was composed of spiral guide grooves with a periodicity of 1.8 μm , an 850 nm linewidth at half height, and a 40 nm depth. The strip was covered with a reflective metal layer of aluminum, which makes the stamp electrically conductive. The overall diameter and width of the nanostructured area of the roller became 17.2 mm and 10 mm, respectively.

In the next step, an air bushing (13.02 mm inner diameter) with the roller stamp was mounted on the Z-axis of a three-axis translational motion control system. The sample was placed on a metal base that can move along the X and Y axes. The motions of these three axes were controlled by a computer, which allowed the correct positioning of the sample relative to the roller stamp. The roller descended to make gentle contact with the sample. When the sample moved along the X-axis, the roller also rotated due to adhesive force at the contact between them. Thus, the roller rolled over the sample and fabricated the whole sample surface. A hygrometer and a weighing scale were used to measure the relative humidity and the force applied on the roller, respectively. The system was placed into a closed chamber with an inlet and outlet for dry nitrogen and water vapors. Figure 1 shows an overview of the implemented R-NEL system.

The sample was p-type silicon (100) with resistivity $\rho = 10 - 15 \Omega\text{-cm}$ that was cleaned with ultrasound in an $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (1:1:5) solution for 10 min. The cleaning process was repeated thrice to achieve optimal cleaning with a low density of particles on the surface. An atomic force microscope (DI Dimension 3100) was used to inspect the nanostructures on the specimen surfaces. The numerical data presented in Figures 3 - 6 are the average of three samples under the same conditions (the standard deviation is approximately 10% of the average value).

3. Results and Discussions

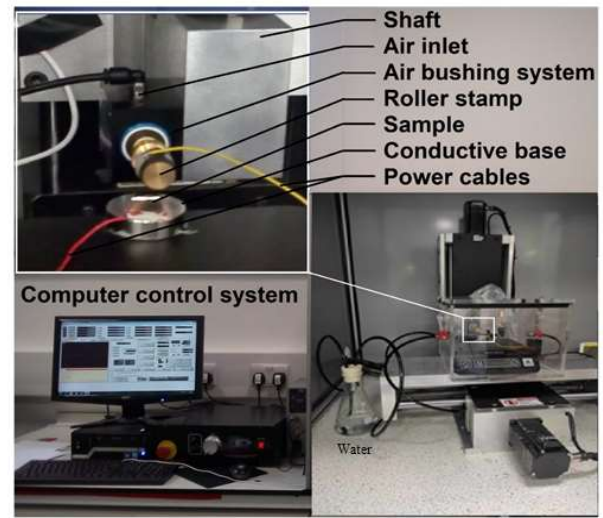


Fig. 1 Experimental set-up for RNEL system

3.1 Patterning by RNEL

In this experiment, an ethanol drop was deposited on the silicon surface using a dropper. Pure ethanol drops spread and formed a thin film in a short time onto the Si surface. Then the ethanol was started to evaporate and adsorb onto the Si surface. Figure 2 shows the result of the oxidation after applying a 1.8 N force and a voltage of 28 V at a rolling speed of 6 mm/min. The nanostructures (L/S) have been successfully fabricated with a mean height of 30 nm (The heights were

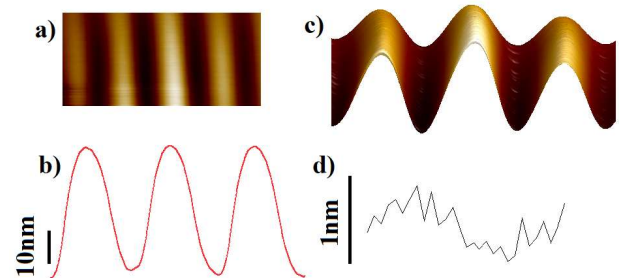


Fig. 2 AFM image of the oxide lines. (a) Overall aspect. (b) Three-dimensional section of the lines shown in (a). (c) Profile of the oxide lines. (d) Surface topography on the top of a line.

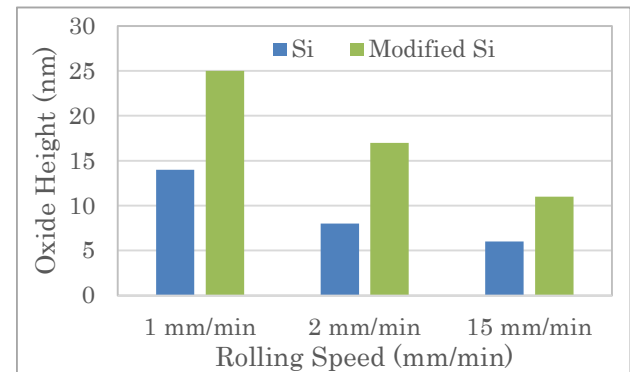


Fig. 3 Comparative results at 28 V and 50% RH

measured with respect to the bare silicon substrate) and full width at half maximum (FWHM) of 945 nm on an area of about $5 \times 5 \text{ mm}^2$. The periodicity of the fabricated oxide lines was $1.8 \mu\text{m}$ which matched the nanoelectrode patterns. The result indicates a dramatic increase in the growth rate and consequently in the height (1.5 - 2 times higher) compared to the results obtained under identical conditions using an unmodified Si substrate (shown in Figure 3).

To characterize the surface morphology, we calculated the roughness of the surface by using the characterization methodology proposed in [23]. The root mean square (RMS) roughness for the oxide lines was found to be 245 pm, while the skewness and the kurtosis were estimated as -0.3787 and 2.9. These results indicate a similar uniform pattern compared to the other results obtained with the RNEL in a humid environment [15].

3.2 Parametric effects on oxide growth

The rolling speed, the applied voltage and the relative humidity are the major parameters that can be altered to optimize the RNEL process. To investigate the influences of rolling speed on oxide growth, the rolling speed was varied from 0.33 to 4 mm/min at 28V. As shown in Fig. 3, there is an inverse relationship between the oxide height and the rolling speed. The height increases with the decrease in the rolling speed. The kinetics is characterized by a rapid initial growth rate that slows down. It can be explained by the fact that, as the rolling speed decreases, the exposure time for the contact area increases. In our experiments, the contact area is 1.1 mm which is measured using the method described in reference 15. Hence, a rolling speed of 1 mm/min ensures an exposure time of ~ 1 minute. The previous study also showed that the height of the oxides increases with the oxidation time in a humid environment [11].

The reason for the slowness of the oxide growth is explained in several ways. Dagata et al. described the reason as the accumulation of ionic charges of the oxides after its creation that affects the charge diffusion in the water bridge [24]. Avouris et al. have proposed that large stresses are developed due to the density mismatch between silicon and SiO_2 [25]. The increase in the stress eventually increases the activation energy for oxidation, which in turn acts as a barrier to the oxide growth. Moreover, some researchers also revealed that the electric field within the oxide film decreases with the increase of the oxide thickness [26, 27]. The adsorbed oxygen and the initial oxidized silicon at the silicon-oxide interface generate an electric potential (Mott potential), which effectively reduces the energy barriers for ionic diffusion through the oxide.

In order to investigate the effect of applied voltage, the oxidation was performed with a bias voltage ranging from 5 to 36 V at a rolling speed of 0.50 mm/min. Figure 5 shows that the oxide height also increases linearly with the applied voltage. A similar linear relationship was also observed for the parameter of relative humidity. Figure 6 shows the oxide height obtained for the relative humidity ranging from 38% to 72% RH at a rolling speed of 2 mm/min. These parametric influences follow similar qualitative trends found in other RNEL experiments in a humid environment [15].

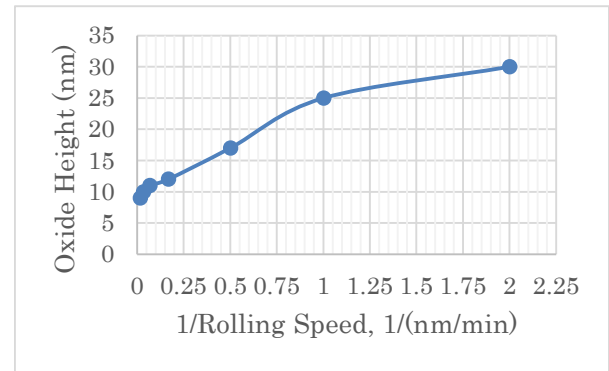


Fig. 4 Relationship between the rolling speed and oxide height

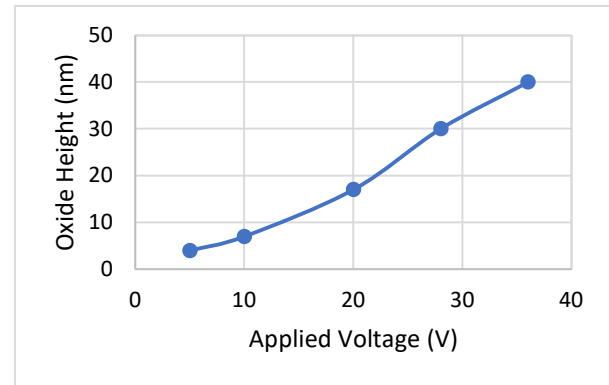


Fig. 5 Relationship between the bias voltage and oxide height

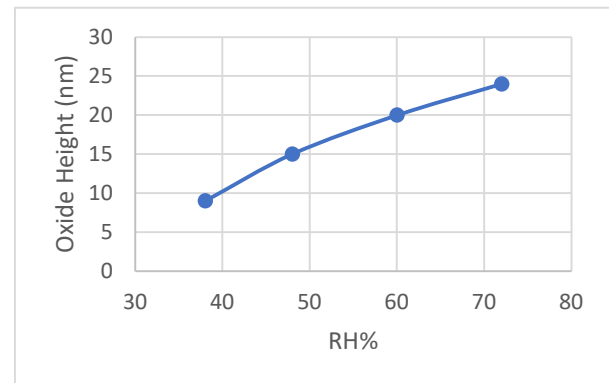


Fig. 6 Relationship between the relative humidity and oxide height

4. Conclusions

This paper presented an RNEL process by which oxidation growth can be enhanced by 1.5 - 2 times by using ethanol. Thus, the local oxidation rate can be accelerated by using an organic solvent like ethanol that eventually increases the throughput. Moreover, Experimental studies show the linear dependence of the oxide height as a function of the applied voltage. The higher electric field can make the surface more oxidized. A similar characteristic is also observed for the RH values. The oxidation growth is also found inversely proportional to the rolling speed. These results show that the RNEL system allows the control of the parameters involved in the oxidation process, and can be a promising alternative for the nanomanufacturing

industries.

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