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# Characterization of Diamond Replicas Microfabricated Using Silicon Molds

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**Abstract.** Diamond replicas, concerning to the fidelity, were quantitatively evaluated in this work. We analyzed the dimensions and morphology of the silicon molds and diamond replicas by atomic force microscopy. The micrometric and nanometric characterization were performed for different substrate pretreatments.

## Introduction

The microelectromechanical systems (MEMS), up to now, have been mostly based on silicon. This is due to the technological know-how developed on the manipulation, machining and manufacturing of silicon. However, the silicon properties are poor, when compared with some materials, especially diamond, concerning to the wear resistance, chemical inertness, thermal conductivity, etc. Therefore, fabrication of diamond microstructures is a promising field for MEMS [1 - 7].

In this work we evaluated quantitatively the fidelity of the diamond replicas, concerning to the dimensions and morphology of the silicon molds. The basic technique used to obtain the replicas can be summarized as: in the first step, the silicon mold is fabricated using well established process technology [8], in the second step a diamond film is grown on it [9] and, finally, the silicon substrate is etched out. In this way we obtain a diamond replica of a silicon mold, as the final device [10 - 14]. In what follows, the diamond surface formed in contact with the silicon substrates will be named "back" of the film and the upward side of the diamond film will be called "top" of the film.

## Material and Methods

The silicon mode preparation was made using a conventional microfabrication method (see the sequence in fig. 1). Initially the silicon wafer was cleaned and an aluminum thin film was deposited on it (fig. 1a). A photoresist layer was then deposited on the aluminum film (fig. 1b) and, using a desired mask, the wafer was exposed to ultraviolet light. The photoresist was then developed (fig. 1c) and, using wet etching, we removed selectively part of the aluminum film (fig. 1d). Following, a plasma etching was used to remove selectively part of the silicon wafer (fig. 1e). The aluminum film and the photoresist were then completely wet etched (fig. 1f). At that time we have already the microstructure on the silicon wafer. Note that, the aluminum film was used to avoid the silicon etching in the masked region, since the photoresist is also etched by the plasma etching.

In the next step, diamond microparticles were seeded on silicon to improve the diamond nucleation. We used two different grain sizes of diamond microparticles. In both cases the mold was immersed in an ultrasonic bath containing water, alcohol and diamond powder. Then it was dried in an oven. In the first case we have used diamond powder 1 μm and the time for ultrasonic bath was 18 minutes; this case, that in what follows, will be referred as "treatment 1 μm". In the second case we have used diamond powder ¼ µm and the ultrasonic bath during 10 minutes. This case, in what follows, will be referred as "treatment ¼ µm".

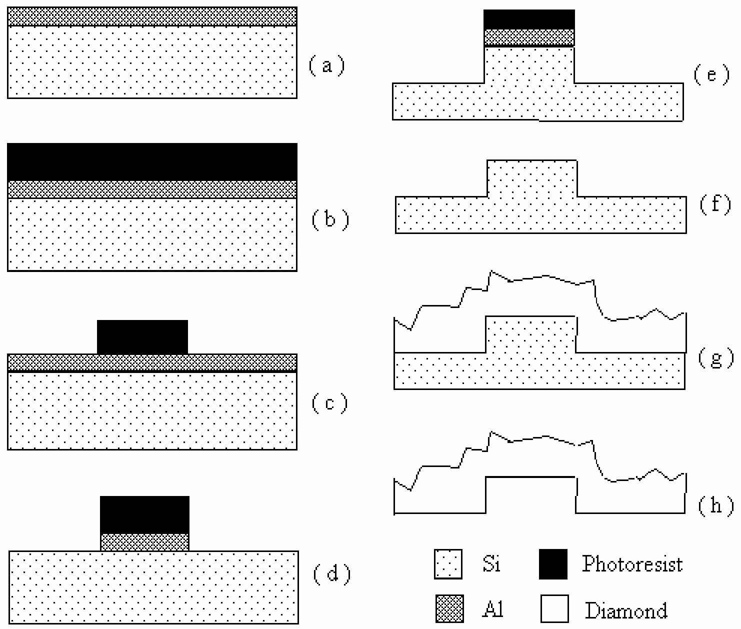


Figure 1: Sequence used in the microfabrication on the silicon surface.

In the next step, a diamond film was deposited using a microwave plasma assisted chemical vapor deposition (CVD) system (fig. 1g). The CVD equipment is described elsewhere [9, 15]. The growth parameters were fixed: 300 sccm hydrogen flow rate, 3 sccm methane flow rate (1-vol% methane in hydrogen), 80 torr chamber pressure, 820$^{o}$ C substrate temperature, with a nominal 850 W microwave power and the growth time was 24 h.

Finally, the silicon substrate, used as a mold, was wet etched, with a solution composed of a mixture of hydrofluoric acid, nitric acid, and acetic acid at 23°C. The $HF:HNO_3:HC_2H_3O_2$ volume ratio was 2:1:1. The acetic acid was added to prevent violent reaction that can fracture the diamond film during the substrate etching (fig. 1h).

In this way, a diamond replica was obtained, reproducing the microstructure of the silicon surface.

An Atomic Force Microscope, the NANOSCOPE IIIA, from Digital Instruments, performed the micrometric and nanometric characterization of the diamond replicas and the substrates. A silicon nitride tip was used, with a highest measurable angle of about 65°. The radius of the tip used for the AFM measurements was about 50 nm, what mean that approximately 20 nm of the tip was in contact with the sample. Considering that the highest magnification used was (32 x 32) µm, the smallest pixel used for the images was 63 nm, then it is not necessary to take into account the convolution effect of the tip shape and surface profile.

We have imaged different regions of the silicon molds with scan size between 32 µm and 64µm and, after the replica preparation, we have imaged exactly the same regions on the back of the diamond replicas. Then, the corresponding images mold/replica was compared quantitatively.

**Results and Discussions**

An important parameter to determine the fidelity of the replicas [16] is the surface roughness ω, defined by Eq. 1

$$\omega = \sqrt{\frac{\sum_i (Z_i - Z_{ave})^2}{N}}, \qquad (1)$$

where $Z_{ave}$ is the average height and N is the number of points considered in the sample surface (number of pixels). It is the standard deviation (rms) of the heights ($Z_i$) for N points on the surface. That is, the roughness ω gives the uncertainty of the measured heights on a given surface.

We measured, by AFM, the roughness of the silicon molds surface and the roughness of the diamond replicas, on its back. These values are given in Table 1. Note that, etched or not etched regions, for the diamond replicas, are related to the regions that were in contact with the silicon mold etched or not etched.

Table 1: Roughness rms for the silicon molds and diamond replicas.

| | Silicon Molds [nm] | Back of Diamond Replicas [nm] | |
|---|---|---|---|
| | | Treatment 1 μm | Treatment ¼ μm |
| Etched region | 0.7 | 10 | 2.8 |
| No etched region | 0.3 | 10 | 3.1 |

With these results, we can conclude that, for the deposition parameters used here, we do not expect to reproduce the silicon mold with precision better than 10 nm for the samples with "treatment 1 μm" and 3 nm for the samples with "treatment ¼ μm".

Fig. 2a shows an AFM image of the silicon substrate and Fig. 2b an image of the corresponding region on the back of the diamond replica, with "treatment 1 μm". The area for both images is (32 x 32) $\mu m^2$ and the z range is 500 nm.

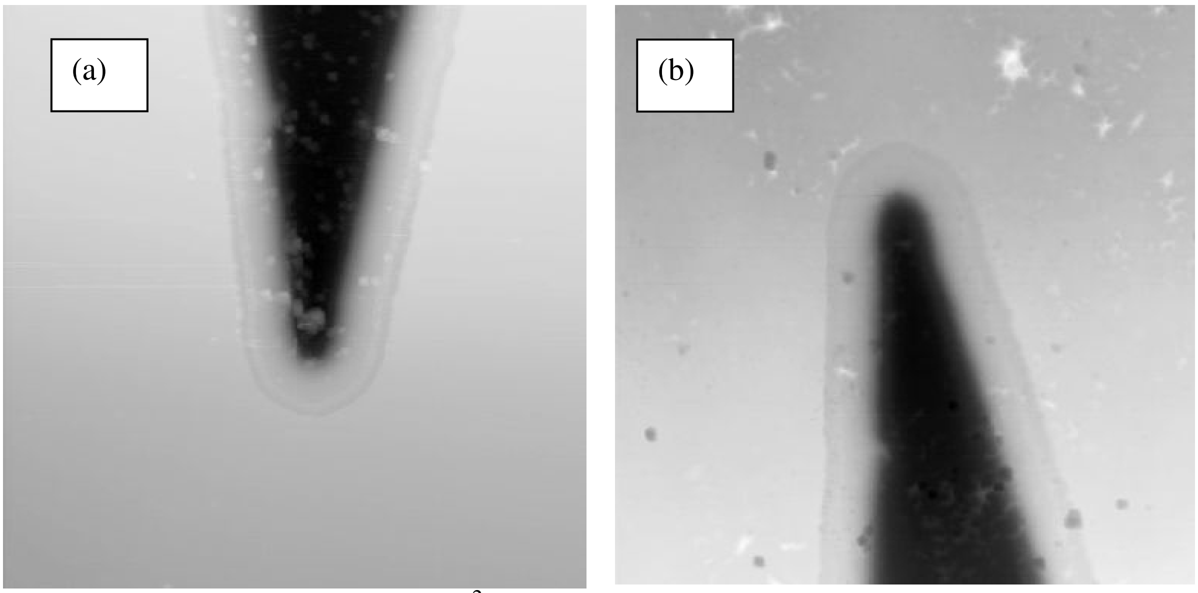


Figure 2: AFM images (32 x 32) $\mu m^2$ and a z range of 500 nm of (a) silicon substrate and of (b) the corresponding region on the back of the diamond replica with "treatment 1 μm".

Fig. 3a shows another AFM image of the silicon substrate and Fig. 3b an image of the corresponding region on the back of the diamond replica, with “treatment ¼ μm”. The area for both images, in this case, is (32 x 32) $\mu m^2$ and the z range is 500 nm for the mold and 700 nm for the replica.

Note that, in Fig. 2b and Fig. 3b, the diamond replica images were inverted (z → -z), so, in this way, it is easier to compare them. It is important to observe that the replica images, in Fig. 2b and Fig. 3b, present the surface that was in contact with the silicon surface shown in Fig. 2a and Fig. 3a, respectively.

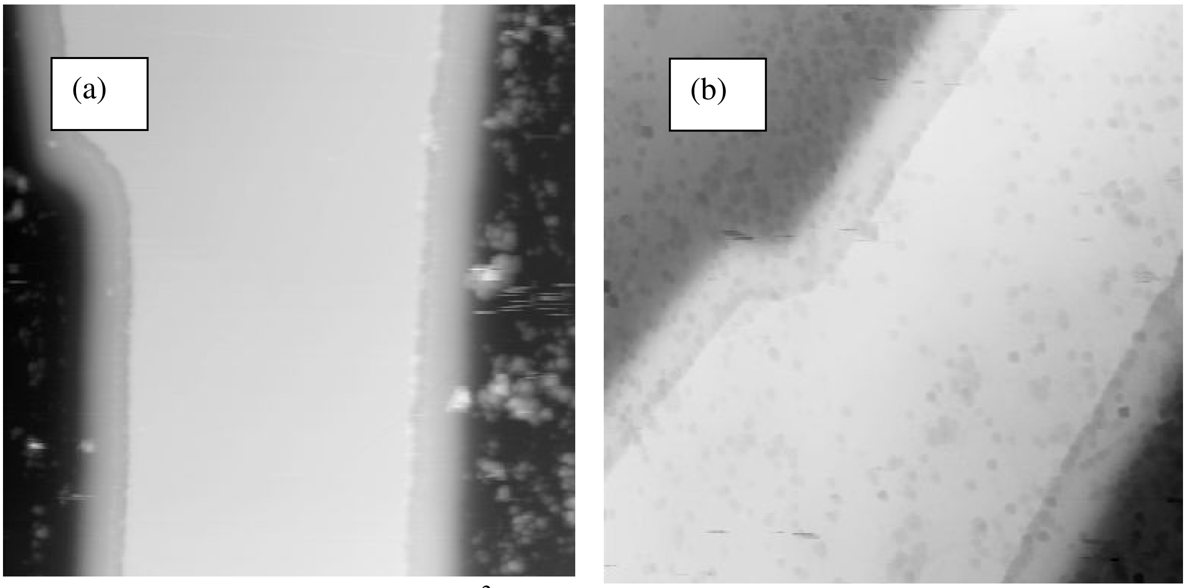


Figure 3: AFM images (32 x 32) $\mu m^2$ of (a) silicon substrate with a z range of 500 nm and of (b) the corresponding region on the back of the diamond replica with a z range of 700 nm, with “treatment ¼ μm”.

In the AFM images of the silicon molds, the step was between about 200 and 400 nm. In Fig.2a and Fig. 3a it is possible to observe, on the edges of the no etched regions, a small step ~ 2 μm width and height between 20 and 60 nm.

So, in this work we measured two steps in different scales range: the larger step, in a scale of hundred of nm, and the smaller step, giving information about the replica reproduction for a reduced scale.

We measured steps of the silicon molds and the corresponding regions of the diamond replicas, on its back, for both substrate treatments. We have analyzed a total of 18 regions, measuring 10 steps in each scale and each region. The deviations between the mold and replica measurements were calculated and the averages are presented in Table 2. Note that, when we say “corresponding region”, it means that we have measured in the diamond replica exactly the same place measured in the silicon mold.

Table 2: Average deviations between the mold and replica measurements.

| | Average deviations between the mold and replica measurements | |
|---|---|---|
| | Treatment 1 μm | Treatment ¼ μm |
| Larger Scale (200 - 400nm) | 11 % | 5.7 % |
| Smaller Scale (20 – 60nm) | 18 % | 17 % |

In the case of the samples with "treatment 1 µm", for the larger scale, the average shift of the reproduction was 11%. And for the smaller scale, the average shift was 18%.

As expected, for the scale between 20 and 60 nm (the smaller one), the shift was larger due to replica roughness, around rms = 10 nm. But for the scale between 200 and 400 nm, the shift was also high, which cannot be justified by the roughness of the back of the diamond replica.

In the case of samples with "treatment ¼ µm", for the larger scale, the average shift of reproduction was 5.7%. And for the smaller scale, the average shift was 17%.

Comparing the results for samples with "treatment 1 µm" and with "treatment ¼ µm", we see that the reproducibility is better in the second case, where the reduced diamond grain size played an important role in the diamond nucleation, covering better the mold surface.

Considering now the results of the larger scale and the smaller scale for the samples with "treatment ¼ µm", the shift was larger for the smaller scale, also due to the replica roughness, around rms = 3 nm. For the scale between 200 and 400 nm (larger scale) the shift was a factor of 2 smaller that the case of "treatment 1 µm", that is already explained above by the reduced grain size used in "treatment ¼ µm".

A possible explanation for the observed high shift, between the height of the silicon mold and the diamond replica in the case of the larger scale, is the stress of the diamond film. Probably, when the silicon substrate is etched out, the relaxation of the diamond film deforms, changing the original local profile of the replica.

## Summary and Conclusions

We have analyzed the micro and nanostructure reproducibility of silicon in diamond replicas using the AFM technique. In order to perform this analysis we have measured the roughness and vertical distances on the silicon mold and on the back of the diamond replica. We have seeded the substrate with two different diamond powders before the diamond deposition: the first one was 1 µm and the second one was ¼ µm.

The results showed that the reproducibility is better for the sample with "treatment ¼ µm", where the reduced diamond grain size covered more precisely the mold surface, allowing better diamond nucleation.

The analyses were performed in two different scales: one between 20 and 60 nm and the other one between 200 and 400 nm. In both cases, "treatment 1 µm" and "¼ µm", the shift was larger for the smaller scale (20 – 60 nm), which can be justified by the replica roughness, that was 10 nm for "treatment 1 µm" and about 3 nm for "treatment ¼ µm".

The high shift observed in the larger scale (200 – 400 nm), that was 18% for "treatment 1 µm" and 17% for "treatment ¼ µm", could not be justified by the replica roughness. In this paper, we suggest that the stress of the diamond film can also affect the fidelity of the diamond replica.

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