SILVER CATALYSED NANOSCALE SILICON ETCHING IN WATER VAPOUR

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Abstract

N^+-doped silicon substrates were etched by water vapour under the silver nanoparticles acting as a catalyst. Thin silver layer was deposited on two silicon wafers, where one of them was thermally annealed in nitrogen to create silver nanoparticles. Subsequently, both samples were annealed in water vapour and afterwards analysed by Scanning Electron Microscope. The images have shown that the annealed silver nanoparticles burrowed into the silicon substrate in the case of both samples. This new method of silicon etching introduces an alternative way of manufacturing nanohole arrays in silicon substrates.

Key words:

silicon etching, water vapour, silver nanoparticles, thermal annealing

1. INTRODUCTION

Silicon etching is a powerful method of manufacturing various nanostructures [1]. Most procedures such as hydrofluoric acid silicon etching and preparation of black silicon require toxic chemicals or complicated and expensive instruments [1]. In this paper we report a new observation of a water vapour etching of silicon under silver nanoparticles acting as a catalyst. To our knowledge, this phenomenon has not been described in the known literature.

This effect could be used as a new method for preparation of silicon structures with arbitrarily arranged nanoholes. Such structures might have potential for applications in various fields of nanophysics or optics, especially in light trapping effects in thin silicon solar cells [2] or in other photonic structures. Here, we give a brief overview of the observation and its basic results.

2. EXPERIMENTAL

N^+-doped monocrystalline silicon wafers (13 Ω.cm) were used as substrates in this experiment. The advantage of using N^+-doped Si is an easier contacting for future Kelvin microscopy measurements [3, 4]. At first, the silicon substrates were rinsed in acetone to remove grease and etched in hydrofluoric acid to remove native SiO_2. Subsequently, the substrates were washed in distilled water and threated in an ultrasonic bath.

Thereafter, 13.5 nm thick silver layer was deposited by thermal evaporation on 2 of the cleaned substrates. First of the samples (sample No.1) was subsequently thermally preannealed at 450°C for 1 hour in nitrogen atmosphere to prepare Ag islands. This step was skipped for the second sample (sample No.2).

In the last step, both samples were heated to 450°C and exposed to water vapour at pressure 1 MPa for 1 hour. Full scheme of the experiment is shown in Fig. 1.

The samples were observed by an ultra-high resolution (1 nm at 15 kV beam energy) Scanning Electron Microscope (SEM) TESCAN MAIA 3 equipped with Schottky emitter, using 3 kV acceleration voltage.

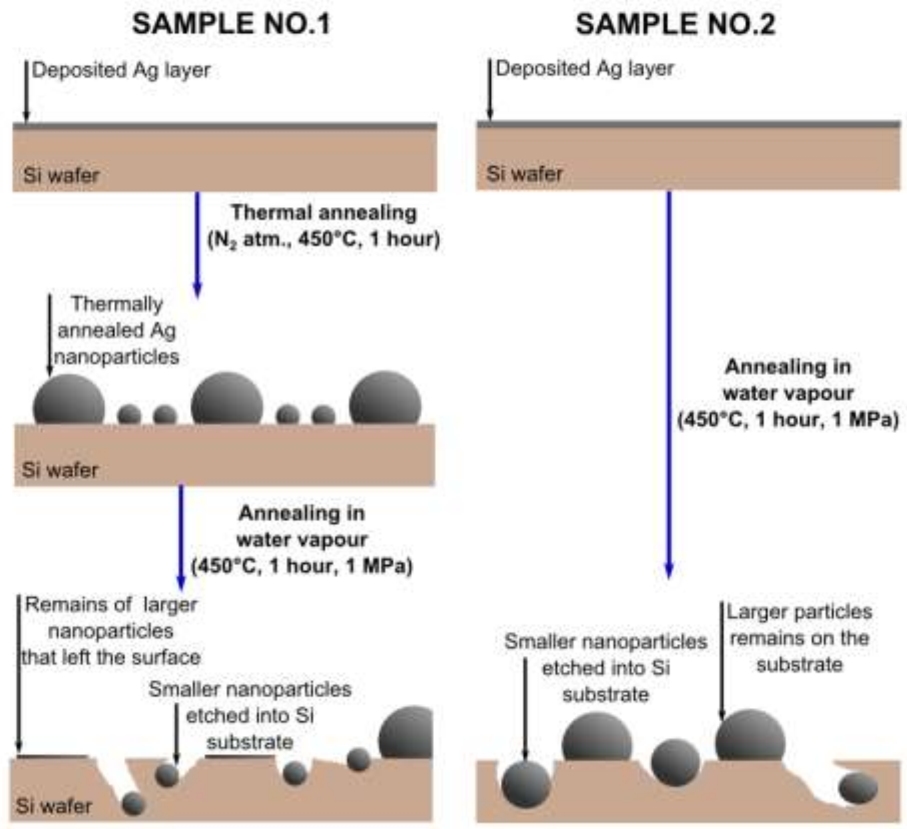

Fig. 1 Scheme of the experiment

3. RESULTS

The result of the thermal annealing in nitrogen of the sample No.1 is shown in Fig. 2. Larger (approx. 300 nm) and smaller (40 nm) silver nanoislands were created on the substrate during this process. The distribution of the nanoislands was homogeneous throughout the whole sample. Most of the nanoislands were spherical in shape.

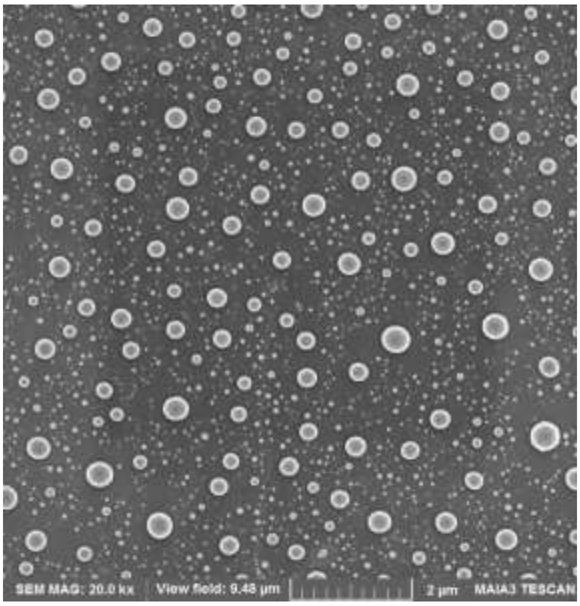

Fig. 2 SEM image of the preannealed sample No.1

The SEM images of both samples after exposure to water vapour are shown in Fig. 3. In the case of the preannealed sample No.1 larger nanoparticles were mostly removed from the surface. However, smaller particles burrowed into the substrate, see Fig. 3a. Thin white circles (highlighted by surrounding green circles) are residues of the larger nanoparticles and correspond to their initial positions. Some of the smaller nanoparticles were also removed from the surface, but most of them partly or completely burrowed into the substrate (highlighted by surrounding red circles). In the case of the sample No.2, we skipped the preannealing procedure. Nonetheless, nanoparticles were formed during the heating in water vapour too. SEM image of the sample No.1 after the water vapour treatment is shown in Fig. 3b. According to the image the annealed particles have lower dispersion in size. The smaller particles again burrowed into the substrate (red circles), but the larger particles (approx. 150 nm in diameter) stayed on the surface or travelled on it for short paths (blue circles).

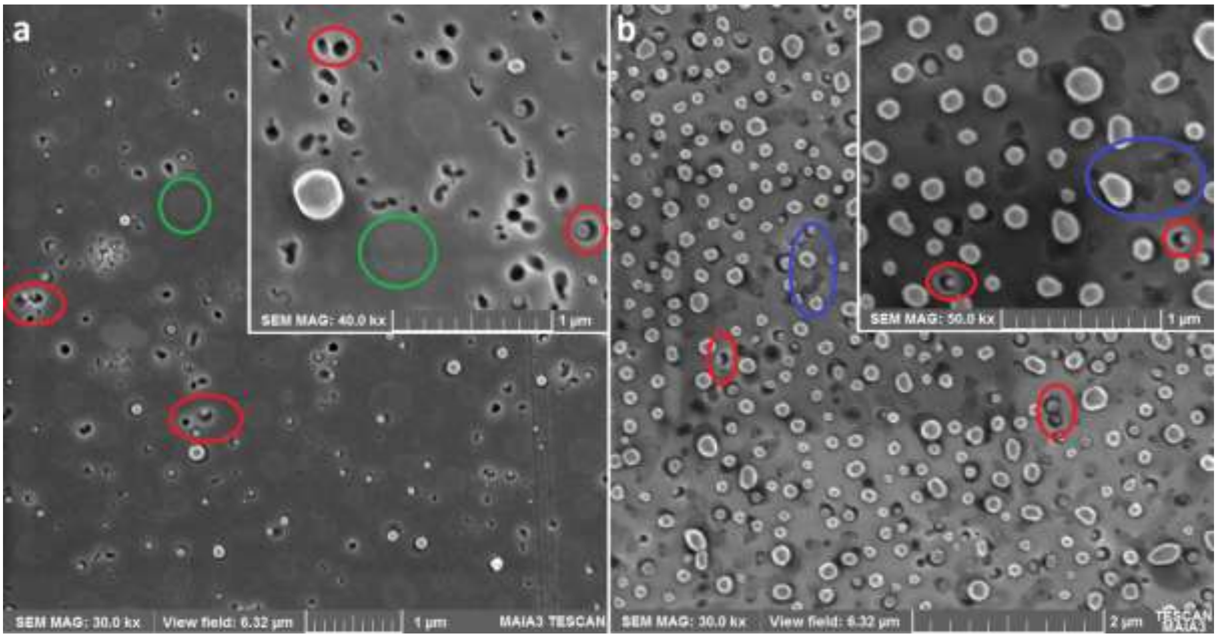

Fig. 2 SEM image of the preannealed sample No.1 (a) and sample No.2 (b) after the treatment in water vapour (red circles – nanoparticles burrowed into silicon, green circles – position of nanoparticles washed away, blue circles – travelling paths of larger nanoparticles)

4. DISCUSSION

In this experiment we observed silver nanoparticle etching in silicon substrates catalysed by water vapour. It seems that the process is strongly dependent on the size of the nanoparticles, or more precisely, on the thickness of the initial silver layer. We demonstrated that the smaller particles burrowed into the substrate, while larger particles were washed away from the surface. We have also observed pathways that indicated movements of the larger particles on the substrate.

Notable feature of the silicon etching in water vapour observed in this experiment is that there are no toxic or dangerous chemicals involved (unlike the common procedure based on hydrofluoric acid [5]). Also, it is very simple and does not require specialized instrumentation. That might be an advantage for specific applications. On the other hand, the disadvantages are relatively high temperature of the process or negative water vapour effects on instrumentation.

If we manage to achieve higher density of the nanoholes we might obtain an interesting baseline for light trapping in solar cells. This might be the case especially if we prove (e.g. by Kelvin microscopy) that the nanoparticles stay at the bottom of the etched holes and might act there as integrated plasmonic scatterers [6]. It should also be possible to use orderly arranged nanoparticle arrays to prepare predefined structures.

5. CONCLUSION

We have demonstrated a new, hitherto unobserved process of silicon etching by water vapour under the silver nanoparticles, analogous to the commonly used etching in hydrofluoric based solutions.

6. ACKNOWLEDGEMENT

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