Silicon Nanostructures Formation by V_2O_5 and HF Stain Etching

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Abstract

In this work we report the fabrication of silicon pillar array by a simple chemical etching of silicon in vanadium oxide/fluorhydric acid solution. Different etching parameters including the solution concentration, temperature and orientation of Si substrates and thin metal catalyst film deposition (Pd) on the Si surface were studied. The etched surfaces characterized by Scanning Electron Microscopy are shown below. It has been found that the morphology depends on both etching time and the presence of the catalyst. The attack, on the surfaces with a Palladium deposit, begins by creating circular pores on silicon in which we distinguish the formation of nanopillars of silicon. After several minutes of etching, silicon pillars appear, but the morphology seems strongly conditioned by drying, like in metal assisted etched SiNWs and highly porous silicon. Finally, taking into account the obtained results, a mechamism of the chemical etching is proposed.

Keywords:silicon nanopillars; metal catalyst;chemical etching

1. Introduction

In recent years, much effort has been made for the manufacture of one dimensional nanostructured materials for use in nanodevices. Silicon is a basic material in microelectronics, especially nanowires and silicon nanopillars. Both of these nanostructures have attracted much attention for their application as nanoscale biosensors. Silicon pillars can be formed by means of chemically enhanced laser ablation using either nanosecond or femtosecond [3,4,5,6] laser ablation combined with wet etching to vary the inter pillar spacing. The group of J.L.Gole [7] has outlined a simple and inexpensive method to generate pillared and uniformly spaced nano-needle arrays formed by electrochemical modification of nano-walled pore structure.

Recently, a promising way to fabricate such structure is to cover a crystalline silicon substrate with mono disperse nanosized objects, which subsequently are used as a mask for silicon etching. The next interesting step of progress was made when silicon pillars were synthesized in a form of highly ordered

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two-dimensional arrays using the advances of nanosphere lithography [1,2]. Such organized structure of silicon pillars are of potential interest for different applications in the gas sensing.

In this work we propose a comparative study about the formation of nanopillars of silicon using a solution of vanadium oxide/fluorhydric acid and/or with thin metal catalyst film deposition (Pd) on the Si surfaces at different etching parameters. silicon where the etching process is accelerated and the morphology of the surface is different.

2. Experimental

The samples used were from p-type Silicon (1 0 0) single crystal, Boron doped with 1-10 Ωcm resistivity and 250-300 µm thickness. The etching solution was composed by vanadium oxide (V_2O_5) added to aqueous HF (39%).
Before the etching process, the samples were cleaned and deoxidized using a diluted HF solution (1:10) for 30 sec. For our comparative study we had deposited 20 nm of Palladium (Pd) by evaporation technique on some samples. Deposition of significantly thinner Pd film can result in uniform etching of the entire surface during the fabrication process. The formation of the silicon nanostructures consists of etching the Si and Pd/Si in a mixture of X ml of HF (Aldrich, 39%) and Y mg of V_2O_5 (Aldrich) for different period (30, 60, 90 and 120 min) at room temperature. The etching solution was stirred sufficiently enough to exclude the effect of mass transfer on the liquid-solid reaction. The etched surfaces were analyzed using SEM (scanning electron microscope) FEI Inspect F SEM (at INRIM) and JEOL JSM 6360 LV(at CDTA), FTIR (Fourier Transform Infrared spectroscopy) Thermo Nicolet, EDS (Energy Dispersive X-ray Spectroscopy) and Spectrophotometry.

3. Results

The effect of the etching time on the etch rate was determined by measuring the etch depth as a function of etching time . The etch depth was calculated by dividing the etch amount of silicon by surface area exposed to the etching solution ($\rho = 2{,}33\ 10^3 kg/m^3$). The etch rate was deduced by dividing the etch depth by the reaction time. The etch rate increases linearly to attain the limit at 60 min(fig 1) and decreases after 30min.

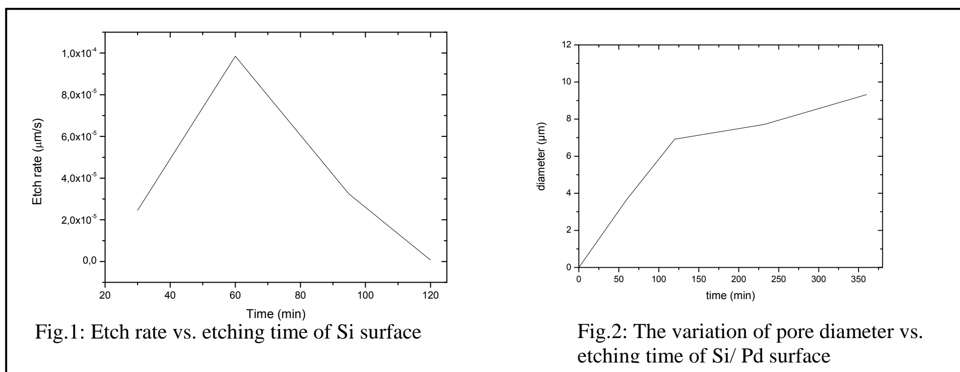

Fig.1: Etch rate vs. etching time of Si surface

Fig.2: The variation of pore diameter vs. etching time of Si/ Pd surface

The average diameter of the pores increases with time to reach the maximum value then it stabilize which corresponds to the disappearance of Palladium and then leads to the slowing down of the etching process(fig 2).

The SEM results of the surfaces etched with and without Palladium deposit show a different morphology in each case. For the samples with Palladium deposit (a) and (b) we observe an uniform circular pores in which we can distinguish the formation of nanostructures inner of the macropores. The diameter of the macropores increases with etching time. In the second part, we present the cross section of the silicon surfaces stain etched (c) and (d) where we observe that a cracked surface with the formation of porous pyramidal structures.

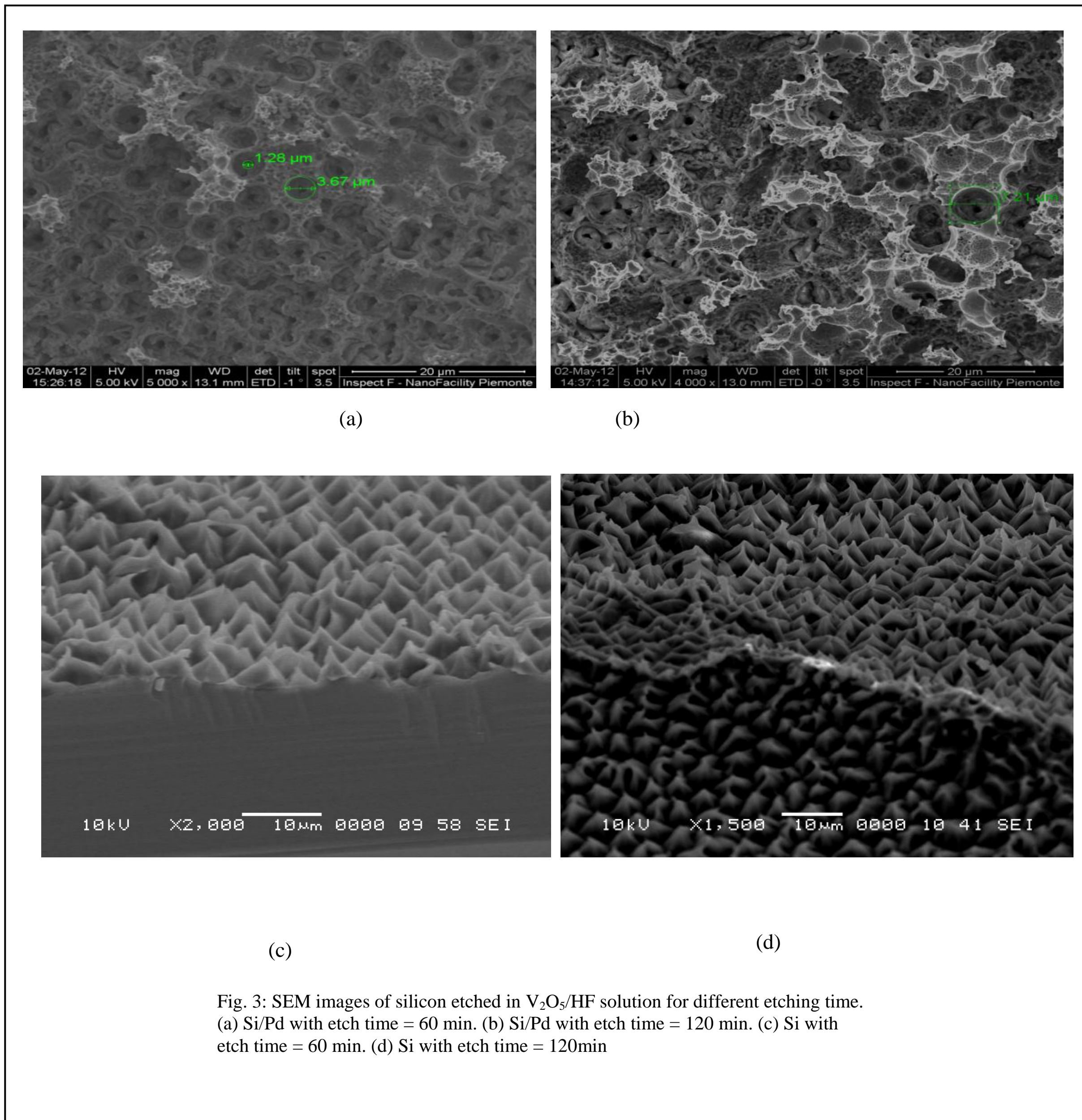

Fig. 3: SEM images of silicon etched in V_2O_5/HF solution for different etching time. (a) Si/Pd with etch time = 60 min. (b) Si/Pd with etch time = 120 min. (c) Si with etch time = 60 min. (d) Si with etch time = 120min

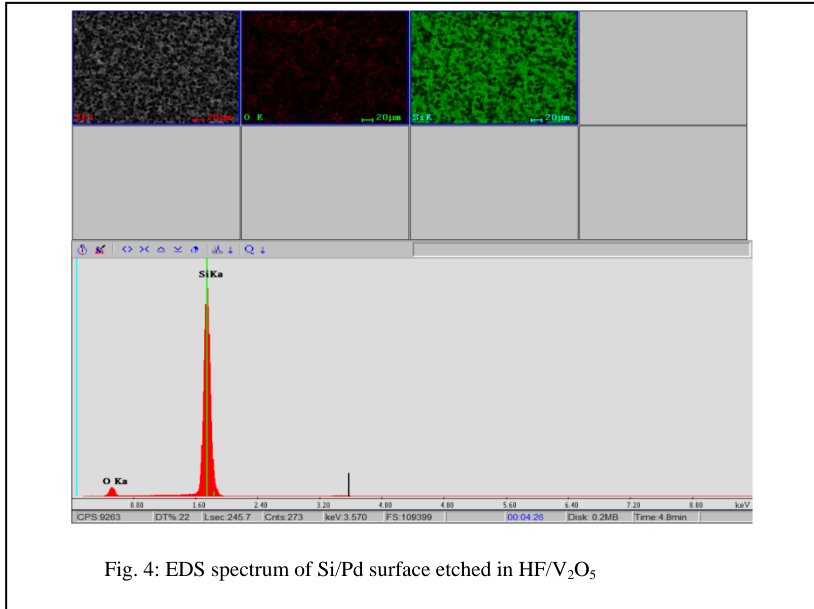

Fig. 4: EDS spectrum of Si/Pd surface etched in HF/V_2O_5

The analysis on the surface of the Pd/Si after etching was performed by EDS. Figure 4 shows that the etched surface consists only of silicon and oxygen, so we can deduce that most of the surface contains Si-O bonds and no trace of palladium.

The IR spectra were recorded at a resolution of 4 cm^{-1} by averaging 64 scans. The analysis (fig 5) show a shoulder at 2089 cm^{-1} which corresponds to the Si-H stretching and the appearance of three peaks at 2145, 2197 and 2245 cm^{-1} indicates the presence of oxygen on the silicon surface perhaps caused by the water after formation of porous silicon.

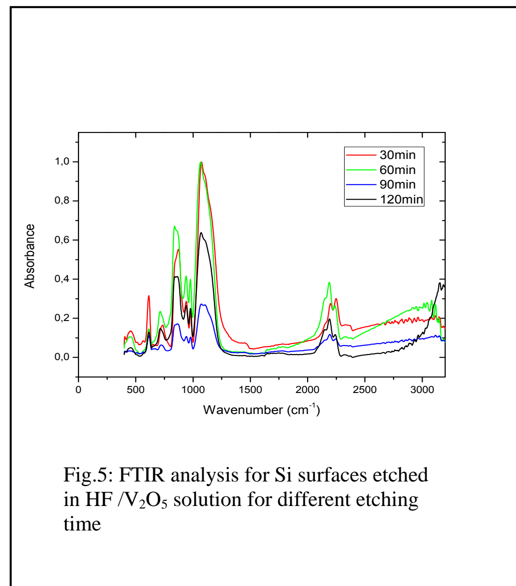

Fig.5: FTIR analysis for Si surfaces etched in HF /V_2O_5 solution for different etching time

Figure 6 shows the variation of the reflectance for etched Si samples in HF /V_2O_5 solution for different times observed at different etching time compared to that of corresponding to Si coated with Pd etched in the same conditions as previously. The Si bare sample etched for 120 min shows a reflectance around 2% for wavelengths ranging between 553 and 709 nm (fig.6) while the Pd coated Si sample shows a reflectance of 5% (fig.6)

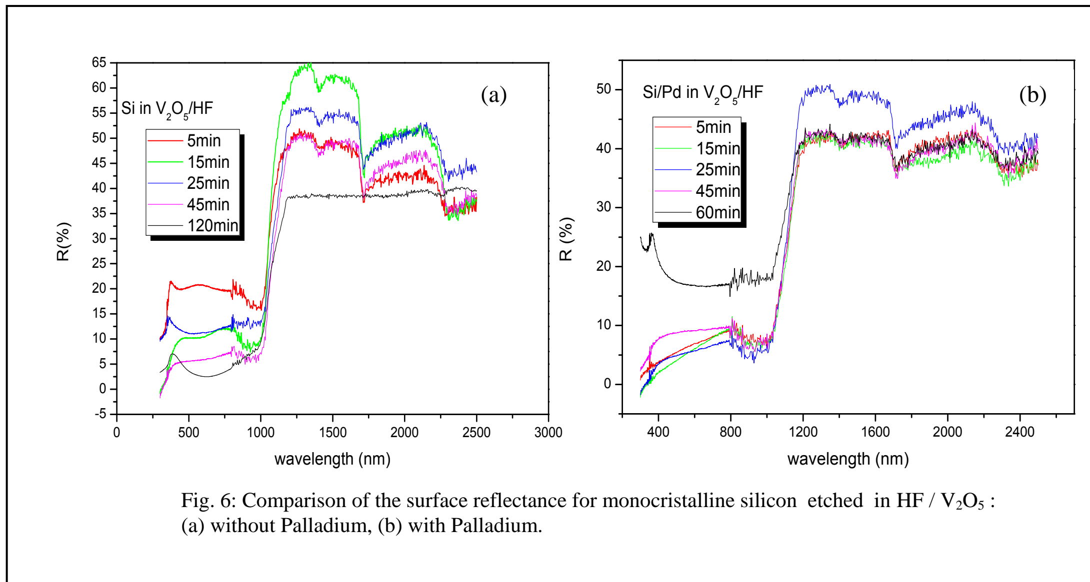

Fig. 6: Comparison of the surface reflectance for monocristalline silicon etched in HF / V_2O_5 :
(a) without Palladium, (b) with Palladium.

4. Conclusion:

The etching of silicon surfaces with and without Palladium deposit in V_2O_5/HF had shown different structures in both cases. Those structures had been investigated by SEM and EDS where we can deduce that the presence of palladium creates uniform pores on the Si surfaces and its role as catalyst accelerates the etching process, and the EDS spectrum revels that there is no traces of Pd on the surface after etching. The macropores created in the Pd coated Si samples after etching induces the high reflectance.

5. References:

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