Investigation of porous Si formed by metal-assisted chemical etching with Au as catalyst

O. Pyatilova1*, S. Gavrilov1, A. Savitskiy1, A. Dudin2, A. Pavlov2, Yu. Shiblyaeva1
1 National Research University of Electronic Technology, Zelenograd, Moscow, Russia
2 Institute of nanotechnology of microelectronics of the Russian academy of sciences, Moscow, Russia
*e-mail: Silova87@gmail.com

Abstract.
In this work, we investigated the effect of the reaction zone temperature and amount of catalyst on the reaction kinetics of Si chemical etching using Au clusters. The growth rates of the porous layer thickness ($V_p$) and pore diameter ($V_d$) was calculated. Influence of etching process parameters on the pore’s sidewall angle was established.

1. Introduction
Porous Si has a wide range of potential applications in nanoscale electronics [1, 2], optoelectronics [3], thermoelectrics [4], photovoltaics [5], biosensors [6], and as electrodes in Li-ion batteries [7]. Metal-assisted chemical etching (MACE) is a novel method that can be successfully used to form nanoscale structures in Si [8-10]. This approach is based on the use of metal films or clusters loaded on Si wafers as catalysts for etching of Si in HF/H$_2$O$_2$ aqueous solutions without external electrical power. Etching is initiated by the metal, thus the kinetics of process and the geometry of the porous layer are affected by the type and structure of metal catalyst. MACE process can be described by means of the galvanic corrosion in which Si is anode and Au is cathode [11, 12]. Therefore, the cathode area influences the anodic dissolution rate of silicon. On the other hand, MACE process can be described in terms of band theory, since there is a metal-semiconductor interface [13]. In this case, as is known, the temperature influences the concentration of charge carriers and injection of holes from a metal and this requires detailed study for MACE process. In this work, we investigate the effect of the reaction zone temperature and amount of catalyst on the reaction kinetics of Si chemical etching using Au clusters.

2. Experiment
Wafer of p-type Si (100), 0.01 Ω·cm was used as substrate. The single-crystalline wafers were rinsed with piranha etch (mixture of H$_2$SO$_4$ (98%) and H$_2$O$_2$ (30%) (1:2 in volume)) at 130°C during 10 min prior to etching. Then wafers were rinsed with deionized water and dried in the isopropyl alcohol vapor flow. After that, Si wafers were rinsed in HF/H$_2$O solution (1:5 in volumes) in order to remove native SiO$_2$. Au clusters were deposited on Si wafer using the vacuum thermal evaporation method. In order to prepare the samples, the two weights of Au were subsequently evaporated on 100 mm-Si wafer: 15 mg and 12 mg. Test samples covered with Au clusters were placed into solution containing HF (40%)/H$_2$O$_2$(30%)/H$_2$O (volume ratio 17/3/51) at 25°C, 40°C, 50°C and 70°C for 10-50 min [14]. Then samples were rinsed in ethanol and air-dried. Morphology of the sample surface was investigated by scanning electron microscopy (SEM) using Helios NanoLab 650. Surface composition of samples was analyzed by energy-dispersive X-ray spectroscopy (EDX). In order to estimate geometrical parameters of the metal catalyst, the cluster diameter distribution histograms were obtained by computer processing of the SEM images of the Au coated wafer surface using Axio Vision software.
3. Result
Figure 1 shows the SEM images of the Si surface covered with Au cluster array after the consecutive evaporation of 15 (Figure 1a) and 12 mg weight portions of gold (Figure 1b). The insets show the gold cluster diameter distribution histograms per 1 μm².

![Figure 1. SEM images of sample surface after the consecutive evaporation of 15 mg (a) and 12 mg (b) of gold and corresponded cluster diameter distribution histograms; Axio Vision dialog box while processing of SEM images (c)](image)

As it follows from the results of the microscopy, the subsequent evaporation of the 15 mg and 12 mg of gold leads to the formation of clusters with prevailing diameter of 100-120 nm; 30 nm and 50 nm, respectively. The SEM cross-sectional views of por-Si structures obtained after etching of Si/Au samples at different temperatures are shown in Figures 2-5. Evaporation weight portion of gold is 15 mg.

![Figure 2. SEM images of por-Si formed at 25°C during 10 min (a) and 50 min (b).](image)
The etching process at 25 °C leads to formation of the pores oriented along the crystallographic direction [100]. Additionally, the small side branches of pores are also formed. The geometrical parameters (thickness of porous layer and pores diameter) of the por-Si were determined on the basis of the results of computer processing of SEM images. Figure 6 illustrates that the thickness of the porous layer depends on the etching duration. In case of etching process at 25 °C, the thickness of the porous layer is 250 nm, 370 nm and 580 nm after 10 min, 30 min and 50 min etching, respectively. The growth rate of the porous layer increases threefold with increasing reaction zone temperature up to 40 °C. 30-min etching leads to formation of square pores with a side of 0.25-1.63 μm. Increasing
the solution temperature up to 50 °C and 70 °C promotes the formation of porous layer with the thickness of 2, 6 and 10 µm after 10 min, 30 min and 50 min etching, respectively.

**Figure 6.** Dependence of the thickness of porous layer and pore diameter on etching duration at different temperatures (from 25 °C to 70 °C).

Thus, the porous silicon layers were formed with a wide range of geometrical parameters: thickness from 0.24 µm to 10 µm; pore diameter from tens of nanometers to 3.5 µm. The thickness of the porous layer and the pore diameter increase with increasing temperature of the solution. This is due to the following factors:
- increasing charge carrier concentration on semiconductor-electrolyte interface;
- increasing diffusion coefficient of reagents and products in the solution;
- convective mass transfer occurring because of the temperature gradient;
- increasing hole current due to intensive injection h+ from metal by reducing the width of the potential barrier Au/Si.

In this work we calculated the etching rate of monocrystalline silicon at various temperatures. The etching rate of silicon means two parameters: the growth rate of the porous layer thickness (Vₜ) and the growth rate of the pore diameter (Vₚ). If reaction rate constant of silicon etching is known, one can then predict the geometry of the porous layer.

![Graph showing the dependence of thickness and pore diameter on etching duration](image)

**Figure 7.** Experimental plots for thickness of porous layer and pore diameter.

Accordingly, an activation energy (Eₐ) and pre-exponential factor (A) have been calculated using the Arrhenius equation [10]. The growth rate of the porous layer thickness is described by the following equation: $Vₜ = 2.6 \cdot 10^{10} \exp(-0.54/kT)$, where $Vₜ$ - reaction rate coefficient, $Eₐ=0.54$ eV - the
activation energy of growth, $A_1=2.6 \cdot 10^{10} \text{ nm/min}$ is pre-exponential factor at $E_{ad}$. The growth rate of the pore diameter is described by the following equation: $V_d=1.01 \cdot 10^{12} \cdot \exp (-0.66/kT)$, where $E_{ad}=0.66 \text{ eV}$, $A_2=1.01 \cdot 10^{12} \text{ nm/min}$ at $E_{ad}$.

Additionally, pore's sidewall angles have been measured for the samples of por-Si formed at 50°C and 70°C (corresponded SEM images are shown in Figures 4, 5). Figure 8a illustrates the evolution of the geometry of por-Si layers with increasing the etch temperature and the duration of etching.

![Figure 8. The evolution of the geometry of por-Si layers (a), SEM top view of por-Si (b)](image)

It is established that the pore's sidewall angle decreases with increasing duration of etching. This is due to the difference in the dissolution rates at the pore bottom and top because of the different concentrations of Au. Figure 8b presents SEM top view of por-Si after 30-min etching process at 70°C. It should be noted that the pores are formed with a bottom parallel to the crystallographic direction [100] for all samples after 50-min etching at 50°C and 70°C. It is established that Au clusters are present at the bottom of the pores. Since the etching process is Au-assisted, the concentration of Au affects the dissolution rate [15]. Therefore, the dissolution rate at the bottom of the pores is higher than at the surface of sample and $V_b>V_d$.

As the Au-assisted chemical etching in itself is local electrochemical etching, the cathode area contributes to the value of Si dissolution rate [16]. The thickness of por-Si layer depending on the duration of etching at different temperatures (from 25°C to 50°C) is shown in Figure 9. Evaporation weight portion of Au is 12 mg.

![Figure 9. Dependence of the thickness of porous layer on etching duration.](image)

It is shown, that the etching process at 25-50°C leads to formation of the structure with pores oriented along the crystallographic direction [100]. The thickness of the porous layer depends on the
etching time (10, 30 and 50 min) and is 197 nm, 200 nm and 234 nm for 25 °C; 106 nm, 369 nm and 447 nm for 40 °C; 177 nm, 230 nm and 529 nm for 50 °C, respectively. It was noted that the macroporous silicon began to form only after etching at 70 °C.

Thus, the growth rate of the porous Si layer is significantly affected by the evaporated weight portion of Au. This may be related to the dependence of cluster diameter on the amount of evaporated metal.

Conclusion
The reaction zone temperature and amount of catalyst on the reaction kinetics of Au-assisted chemical etching was investigated. The porous silicon layers were formed with a wide range of geometrical parameters: thickness from 0.24 µm to 10 µm; pore diameter from tens of nanometers to 3.5 µm. The growth rate of the porous layer thickness is described by the equation: $V_b=2.6 \times 10^{10} \exp (-0.54/kT)$. The growth rate of the pore diameter is described by the equation: $V_d=1.01 \times 10^{12} \exp (-0.66/kT)$. It is established that the pore's sidewall angle decreases with increasing duration of etching. This is due to the difference in the dissolution rates at the pore bottom and top because of the different concentrations of Au. Thus, the growth rate of the porous Si layer is significantly affected by the evaporated weight portion of Au.

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