Investigation of the Morphological Evolution and Etching Kinetics of black Silicon During Ni-Assisted Chemical Etching

To cite this article: OV Volovlikova et al 2018 J. Phys.: Conf. Ser. 987 012039

View the article online for updates and enhancements.

Related content

- Morphology of the porous silicon obtained by electrochemical anodization method
  S D Bertel H, A Dussán C and J M Diaz P

- Comparison of different etching methods on the morphology and semiconductor characters of black silicon
  Wenlin Meng, Hao Zhong, Wei Hou et al.

- Fabrication of black silicon by Ni assisted chemical etching
  Kai Gao, Hongjie Shen, Youwen Liu et al.
Investigation of the Morphological Evolution and Etching Kinetics of black Silicon During Ni-Assisted Chemical Etching

OV Volovlikova*, G O Silakov*, S A Gavrilov*, A A Dudinb, G O Diudbinb, Y I Shilyaevea*

a National Research University of Electronic Technology - MIET, Zelenograd, Moscow, Russia
b Institute of Nanotechnology of Microelectronics, Russian Academy of Sciences, Moscow, Russia
*e-mail: VolovlikovaOV@org.miet.ru

Abstract. Kinetics of contact angle of solutions contained HF (40%):H2O2(30%):C2H5OH:H2O on Si/Ni has been investigated. The effect of the ethanol concentration on the morphology of the porous silicon formed by Ni-assisted chemical etching is discussed. The influence of ethanol concentration on the morphology of the porous silicon was established by water contact angle and roughness factor.

1. Introduction

Superhydrophobic surfaces are a key technology for their ability to reduce friction losses in microchannels and their self cleaning properties [1-4]. Hydrophobicity is a property of a solid surface, which plays important roles in many industrial applications. Material with wide application is porous silicon [5-7]. The past decade has seen the rapid development of porous silicon (p-Si) in many applications including microelectronics, implantation, drug delivery, and biosensor [8]. Silicon surface chemistry is of fundamental importance because of the very relevant role of silicon in modern technology. The morphology of silicon wafer is modified by an electrochemical wet etching [9-11], galvanic etching [12-14], metal-assisted chemical etching (MACE) [15-17] to produce pores with controlled size and distribution and coated with a silane hydrophobic layer.

Perspective method for porous silicon formation is MACE using thin film of Ni [18]. There is no residual Ni on the surface of the por-Si after MACE with Ni films [19]. The effect of non-wetting the porous surface is achieved by creating a stable Cassie state on the surface. At this state there are air gaps between the liquid and the surface [20]. It is possible to obtain both hydrophilic and hydrophobic surfaces by changing the geometric parameters of the porous layer. Wettability of the surface is characterized by the water contact angle (CA). CA can be increased by increasing the surface roughness factor or the pore diameter [21]. One of the methods to change the surface roughness is to change the solutions composition for MACE contained HF (40%), H2O2(30%), and H2O. The addition of alcohol to the solution promotes an increase in the wettability of the surface and decrease in the roughness. The effect of the ethanol concentration on the morphology of the porous silicon formed by Ni-assisted chemical etching is not investigated.

Thus, the aim of the work is studying the kinetics of contact angle of solution contains ethanol on the initial surface Si/Ni. The effect of the ethanol concentration on the morphology of the porous silicon formed by Ni-assisted chemical etching was investigated.

2. Experimental details

Wafers of p-type Si ((100), 0.01 Ω·cm) are used as substrates. Preliminary to be etched single-crystalline wafers were washed with piranha etch (mixture of sulfuric acid H2SO4 (98%) and hydrogen
peroxide H$_2$O$_2$ (30%) (1:2 in volume) at 130°C during 10 min. Then they were rinsed in deionized (DI) water and dried by jet of isopropyl alcohol vapor. Si wafers were rinsed in HF-H$_2$O solution (1:4 in volumes) to remove native SiO$_2$. Subsequently, a 50 nm thick Ni thin film (99.99 % purity) was deposited by magnetron sputtering (Si/Ni samples). Then wafers were cut into 2×2 cm$^2$ pieces and used as samples. All solutions contained HF (40%):H$_2$O$_2$(30%):C$_2$H$_5$OH:H$_2$O. There were 14 solutions with various component concentrations (table 1).

| Solution number | volume part HF | volume part H$_2$O$_2$ | volume part C$_2$H$_5$OH | volume part H$_2$O | molar ratio HF/H$_2$O$_2$ | molar ratio HF/C$_2$H$_5$OH |
|-----------------|----------------|------------------------|-------------------------|-------------------|--------------------------|------------------------|
| I               | 8              | 8                      | 4                       | 40                | 1.60                     | 2.56                   |
| II              | 8              | 8                      | 8                       | 40                | 1.60                     | 1.28                   |
| III             | 8              | 8                      | 12                      | 40                | 1.60                     | 0.85                   |
| IV              | 8              | 12                     | 4                       | 40                | 1.06                     | 2.56                   |
| V               | 8              | 12                     | 8                       | 40                | 1.06                     | 1.28                   |
| VI              | 8              | 12                     | 12                      | 40                | 1.06                     | 0.85                   |
| VII             | 8              | 8                      | 0                       | 40                | 1.60                     | $10^7$ ($\times$)      |
| VIII            | 8              | 8.5                    | 4                       | 40                | 1.50                     | 2.56                   |
| IX              | 8              | 9                      | 8                       | 40                | 1.42                     | 1.28                   |
| X               | 8              | 10                     | 12                      | 40                | 1.28                     | 0.85                   |
| XI              | 8              | 12                     | 0                       | 40                | 1.06                     | $10^6$ ($\times$)      |
| XII             | 8              | 13                     | 4                       | 40                | 0.98                     | 2.56                   |
| XIII            | 8              | 14                     | 8                       | 40                | 0.91                     | 1.28                   |
| XIV             | 8              | 15                     | 12                      | 40                | 0.85                     | 0.85                   |

The solution was dripping on the Si/Ni surface for kinetics of contact angle investigation. Solution drop profile began to change immediately. We use a Fujifilm Finepix S4000 camera, to record images of millimeter size sessile solution drops, at rest over horizontal samples. Samples Si/Ni were immersed in the solutions presented in Table 1 for black silicon morphology investigation. Etching duration was 20, 40 and 60 min. Then samples were rinsed in ethanol and dried in air. Morphology of the samples surface were investigated by scanning electron microscopy (SEM) using a JSM-6010PLUS/LA (JEOL company) and Helios NanoLab 650. An atomic force Dimension Icon microscope (Bruker) was used for the morphological characterization of the samples by employing tapping mode AFM. We adopt the sessile drop method to measure the contact angles (CA) over the porous silicon samples. We also used a Goniometer LK-1 [22] to record images of sessile DI water (18.2 Ω) drops. Drop volume was 10 ml. We use freely available software, DropShape to process images and measure contact angles.

3. Results and Discussion

3.1 Kinetics of contact angle

Contact angles have been obtained from Si/Ni samples. The initial CA of VII, XI, XII and XIV solutions is 40°, 22°, 11°, and 1° respectively. Mean observed water CA evolution over 60 seconds of monitoring is presented in Figure 1.
The maximum value of the contact angle 40° is observed on the Si/Ni surface when an investigated solution contained no alcohol and minimum value of H₂O₂ (VII solution). The minimum value of the contact angle 1° is observed on the Si/Ni surface when an investigated solution contained 12 volume part of C₂H₅OH and 15 volume part of H₂O₂ (XIV solution).

Contact angle decreases with molar ratio HF/H₂O₂ decreasing. It can be explained by H₂O₂ increasing. The ratio of HF/H₂O₂ decreases due to a decrease in the concentration of HF and growth of the concentration of C₂H₅OH. Water has a high surface tension because it is strongly attracted to itself. However, at the adding alcohol, instead of water interacting only with other water molecules, it now interacts (less strongly) with alcohol, and the surface tension of the mixture will be lower (Figure 2) [9]. Extreme hydrophilicity has been observed for molar ratio HF/H₂O₂ = 0.91 and 0.85.

The kinetic curves of the solutions contact angle of the Si/Ni surface (Figure 1) can be divided into 3 sections. Each section characterizes the corresponding process takes place on the Si/Ni surface during etching with solutions of I-XIV (Figure 2).

Table 2 shows the CA value and the rate of CA decrease.
Table 2 – Decreasing contact angle (CA) rate vs. duration

|    | HF/H₂O₂ | 1.6 | 1.5 | 1.42 | 1.28 | 1.06 | 0.98 | 0.91 | 0.85 |
|----|---------|-----|-----|------|------|------|------|------|------|
| CA (1 s), °| 40 | 36 | 37 | 30 | 22 | 11 | 1 | 0.8 |
| CA (6 s), ° | 28 | 27 | 22 | 23 | 11 | 0 | 0 | 0 |
| CA, °/sec | 2.1 | 1.5 | 2.6 | 1.03 | 1.85 | 1.92 | 0.15 | 0.12 |

|    | HF/H₂O₂ | 1.6 | 1.5 | 1.42 | 1.28 | 1.06 | 0.98 | 0.91 | 0.85 |
|----|---------|-----|-----|------|------|------|------|------|------|
| CA (7 s), ° | 34 | 33 | 25 | 28 | 10 | 0 | 0 | 0 |
| CA (30 s), ° | 21 | 21 | 15 | 18 | 0 | 0 | 0 | 0 |
| CA, °/sec | 1.2 | 1.27 | 0.98 | 0.86 | 0.14 | 0 | 0 | 0 |

|    | HF/H₂O₂ | 1.6 | 1.5 | 1.42 | 1.28 | 1.06 | 0.98 | 0.91 | 0.85 |
|----|---------|-----|-----|------|------|------|------|------|------|
| CA (31 s), ° | 18 | 17 | 12 | 12 | 0 | 0 | 0 | 0 |
| CA (60 s), ° | 0.1 | 0.09 | 0.1 | 0.18 | 0 | 0 | 0 | 0 |

The behavior of a drop solution of each section is determined by the following processes:

1 section:
- duration up to 6 seconds;
- the contact angle depends on the surface energy of Si/Ni;
- H₂O₂ – constant value equals to 1.75 mol/L for molar ratio HF/H₂O₂ in the range of 1.28-1.6
  and 2.5 mol/L for HF/H₂O₂ in the range of 0.85-1.06;

2 section.
- duration from 7 to 30 seconds;
- the increasing of the CA is noted at 7 seconds. The obtained results indicate a change in the
  surface tension of the solution. This can be due to the dissolution of the metal film and the formation
  of porous silicon.
- the rate of decrease of the CA in section II is lower than in section I.

3 section.
- duration over 30 seconds;
- characterized by the absence of Ni and the formation of porous silicon;
- the rate of decrease of CA is practically equal to zero.

Ethanol concentration influence on the CA can be demonstrated in Figure 3.

The increasing of HF/C₂H₅OH and decreasing the C₂H₅OH concentration respectively in the
solution leads to increasing the CA throughout the duration of the treatment. At the initial time of
monitoring (Figure 3a) the difference between the contact angles for HF/H₂O₂ = 1.6 and 1.06 is ~ 7-8°.
The difference in CA is reduced to 2-3° at 30 seconds of monitoring. The difference in CA is reduced
to 1-2° at 60 seconds of monitoring.

![Figure 3. Initial contact angle (a), during 20 sec (b) and during 60 sec (c).](image-url)

Thus, it has been found that the addition of C₂H₅OH to the etching solution results in a
decreasing in CA and a surface tension of the solution. We investigate XIII and XIV solutions as
completely wetting solutions. In addition alcohol-containing solution, promotes the detachment of H$_2$ from Si during the formation of the porous layer. Such an etchant composition improves wetting of the surface during etching and leads to the uniformity of the modified Si.

3.2 Morphological Evolution

Figure 4 shows SEM images of the por-Si after 40 minute duration of treatment in HF (40%):H$_2$O$_2$(30%):C$_2$H$_5$OH:H$_2$O.

![Figure 4](image_url)

Figure 4. SEM images of por-Si after treatment in solution with HF/H$_2$O$_2$ and HF/C$_2$H$_5$OH: 1.6 and no ethanol (a), 1.6 and 0.85 (b), 1.06 and no ethanol (c), 1.06 and 0.85 (d).

The lower the concentration of H$_2$O$_2$ in the solution, the more uniform porous layer is formed (Figure 4 a, c). Macropores begin to form on the surface of porous silicon after etching with solution containing C$_2$H$_5$OH (Figure 4 b, d).

The porous silicon samples after 40 min treatment were characterized via Atomic Force Microscopy (AFM). The results obtained are shown in Figure 5.
Figure 5. AFM images for the formation of pores in Si in a solution of HF/C$_2$H$_5$OH=2.56 (b), HF/C$_2$H$_5$OH=1.28 (c), HF/C$_2$H$_5$OH=0.85 (d), image zoom of (a-d) 10×10 μm. The inset of Figure shows the silicon nanocrystal size distribution on the surface (left), water contact angle (right).

From Figure 5, we observe that the formation of macropores is feasible after etching in solution HF/C$_2$H$_5$OH=1.28 and HF/C$_2$H$_5$OH=0.85. Through section analysis with the AFM software, the diameter of the pores was obtained with values between 300 and 900 nm. Open pores contacting with the external environment leads to decreasing the solid-liquid contact in the Cassie state. Therefore the contact angle of wetting is increased. Water CA is 115° in the case of absence of ethanol in etching solution, at HF/C$_2$H$_5$OH=2.56 water CA is 134°, at HF/C$_2$H$_5$OH=1.28 water CA is 136°, at HF/C$_2$H$_5$OH=0.85 water CA is 138° (Figure 5 a, d). Thus, the higher the ethanol concentration in the solution, the higher the water CA on porous Si, because of pores formation on the surface. It is known that CA is one of the main techniques to indicate surface roughness. Roughness is determined by composition of a solution. Cassie–Baxter equation describes CA ($\theta_{CB}$) of roughness surface [23].

\[
\cos \theta_{CB} = f \cos \theta + f - 1,
\]

where $\theta_{CB}$ is the liquid–solid contact angle on the textured surface, $\theta$ is the static contact angle on the flat surface, and $f$ is the fraction of the liquid–solid contact area, $r$ - roughness ratio factor.

The results of calculations are shown in Figure 6.
It was established that the value of the roughness calculated from Cassie–Baxter equation has an inverse dependence on the ethanol concentration in the solution. Through roughness analysis with the AFM software, the distribution histograms of the silicon particles were obtained (Figure 6). It has been established that the smaller the particle size of the porous layer, the greater its roughness.

The chemical composition of the porous surface has influence on the CA in addition to roughness and pores. Chemically bonded hydrogen atoms forms during the formation of pores in contact with the HF-containing electrolyte. Porous silicon acquires hydrophobic properties. Thus, water CA on as-etched porous silicon is from 135° to 144° depending on the composition of the electrolyte. Due to the oxidation of the samples in air, the water CA is decreased due to formation of the hydrophilic Si-OH groups [24]. For the samples stored in air for 1 week, water CA is 117°-142°, depending on the composition of the electrolyte; for 3 weeks, water CA is 111°-136°, for 8 weeks, water CA does not exceed 125°. Since we assume that the value of the CA depends on the Si-H groups, it will be necessary to carry out an additional study.

4. Conclusion.
The addition of ethanol to the etching solution contained HF+H₂O₂ during Ni-assisted chemical etching leads to decreasing of etchant CA on Si/Ni. CA of etchant contained HF and H₂O₂ on Si/Ni is 40°, at HF/C₂H₅OH = 0.85 etchant CA is 1°. The lower the concentration of H₂O₂ in the solution, the more uniformly porous layer is formed. Macropores begin to form on the surface of porous silicon after etching with solution containing C₂H₅OH. We observe that the formation of macropores with diameter 300 - 900 nm is feasible after etching in solution HF/C₂H₅OH=1.28 and HF/C₂H₅OH=0.85.

Water CA on the porous silicon is 115° in the case of absence of ethanol in etching solution, at HF/C₂H₅OH=2.56 water CA is 134°, at HF/C₂H₅OH=1.28 water CA is 136°, at HF/C₂H₅OH=0.85 water CA is 138°. Thus, the higher the ethanol concentration in the solution, the higher the water CA on porous Si, because of pores formation on the surface. It was established that the value of the roughness ratio factor calculated from Cassie–Baxter equation has an inverse dependence on the CA and on the ethanol concentration in the solution, respectively. It has been established that the smaller the particle size of the porous layer, the greater its roughness.

Acknowledgment
This study was supported by the Russian Science Foundation, project no. 16-19-10625.
[1] Furstner R and Barthlott W 2005 Langmuir 21 956-61.
[2] Zhang M, Feng Sh, Wang L, Zheng Y 2016 Biotribology 5 31-43.
[3] Yang H, Jiang P 2010 Langmuir 26 12598-04.
[4] Bhushan B, Jung Y C, Koch K 2009 Langmuir 25, 3240-8.
[5] Gullis G, Canham L T, Calcott P D J 1997 J. Appl. Phys. 82, 909-65.
[6] Schmidt V, Riel H, Senz S, Karg S, Riess W, Gösele U. 2006 Small 2 85-8.
[7] Goldberger J, Hochbaum A I, Fan R, Yang P 2006 Nano Lett. 6 973-7.
[8] Foll H, Christoffersen M, Carstensen J, and Hasse G 2002 Materials Science and Engineering R: Reports 39 93-41.
[9] Barillaro G, Nannini A, Piotto M 2002 Sensors and Actuators A 102 195–01.
[10] Lehmann V and Full H 1990 J. Electrochem. Soc. 137 653-9.
[11] Gavrilov S A, Karavanskii V A, Sorokin I N 1999 Russian Journal of Electrochemistry 35 729-34.
[12] Ashruf C M A, French P J, Bressers P M M C, Sarro P M, and Kelly J J 1998 Sens. Actuators A: Phys. 66 284-91.
[13] Kolasinski K W 2014 Nanoscale Res. Lett. 9 432-40.
[14] Pyatilova O V, Gavrilov S A, Shilyaeva Yu I, Pavlov A A, Shaman Yu P, and Dudin A A 2017 Semiconductors 51 173–7.
[15] Qu Y, Liao L, Li Yu, Zhang H, Huang Yu, and Duan X 2009 Nano Lett. 9 4539-43.
[16] Lee Ch-L, Tsujino K, Kanda Yu, Ikeda Sh, and Matsumura M 2008 J. Mater. Chem. 18 1015-20.
[17] Huang Z, Geyer N, Werner P, Boor J, and Gösele U 2011 Adv. Mater. 23 285-08.
[18] Volovlikova O V, Gavrilov S A, Sysa A V, Savitskiy A I, Berezkina A Yu 2017 ElConRus 1213-6.
[19] Yue Z, Shen H, Jiang Y et al. 2014 J Mater Sci: Mater Electron 25 1559-63.
[20] Bracco G, Holst B 2013 Surface Science Techniques (Springer) 1 chapter 3-34.
[21] Yilei Zh 2007 Retrospective Theses and Dissertations. 15934.
[22] http://www.openscience.ru/chem/index.php?page=wetting&item=003.
[23] Zhang T, Zhang P, Li Sh, Li W, Wu Zh and Jiang Y Nanoscale Research Letters 2013 8 351-6.
[24] Jiang L, Li S, Wang J, Yang L, Sun Q, and Li Zh 2014 Journal of Nanomaterials, ID 526149, 6 pages.