**Wet chemical etching of SiGe(100) surface: an atomic force microscopy study**

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***Abstract –* An experimental study based on atomic force microscopy of the influence of wet chemical etching on Si0.77Ge0.23(100) surface morphology has been carried out. Etching experiments were performed in stirred aqueous tetramethylammonium hydroxide (TMAH) [(CH3)4N]OH solution kept at 70 ˚C. The effect of etching time, isopropyl alcohol additive, TMAH concentration, and the application of discontinuous etching procedure on resulting substrate morphology was investigated. The etching procedure was optimized to achieve small surface roughness.**

**needed for**

**in order to employ extremely fine local anodic oxidation patterns as etching masks.**

**Additional information about the etching process was extracted from the height-height correlation function. The developed etching technique may be applied for nanostructures fabrication on SiGe surface by local anodic oxidation technique.**

**A was developed and**

**on the final surface texture was also investigated**

**The variation of the RMS surface roughness vs. the TMAH concentration and etching time was investigated. Additional information about the etching process was extracted from the surface height histograms and surface skewness and kurtosis parameters. HHCF analysis?**

Abstract

* SiGe
* TMAH
* IPA
* discontinious etching
* AFM topography analysis
  + RMS
  + Height histograms
    - Height of the kredenses
    - unimodal, bimodal distribution
  + surface skewness, kurtosis
  + HHCF, surface is homogenius

Keywords: Silicon-germanium, wet chemical etching, TMAH?, local anodic oxidation, atomic force microscopy, ellipsometry

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**1. Introduction**

SiGe alloys have received enormous attention due to their potential abilities to introduce strain in the active regions of the complementary metal-oxide-semiconductor (CMOS) devices and thus improve the performance of very large scale integrated circuits [1],[2]. The strain introduced in CMOS devices modifies the electronic band structure and improves the mobility of charge carriers, consequently enhancing the speed of modern microprocessors [3]. The progress in strain engineering demands for fast and non-destructive methods for strain measurements [4]. Tip-enhanced Raman scattering (TERS) is a promising technique for high-resolution strain measurements since it permits to bypass the diffraction limit for lateral resolution by near-ﬁeld approaches. In order to apply TERS for strain characterization, the lateral sensitivity of this technique with respect to the strain distribution in silicon has to be improved, and adequate strained test calibration structures are needed [5]. In our previous work we showed that one of the methods capable of fabricate the fine calibration structures is local anodic oxidation (LAO) by using atomic force microscopy (AFM) [6]. In the approach the material contrast between LAO induced oxide and the SiGe substrate was employed for selective wet etching with the oxide pattern acting as a mask. Our experimental data proved that in order to fabricate high quality nanostructures the etching procedure must provide substrate with low surface roughness. This paper focuses on the optimization of the etching procedure what in turn leads to satisfy the need for a small surface roughness.

For fabrication of diverse microelectronic and microelectromechanical structures etching of Si in alkaline solutions has been commonly used for many years [7]. To the most popular solutions involved in the etching process belong potassium hydroxide (KOH), and tetramethylamonium hydroxide (TMAH) [(CH3)4N]OH [8], [9]**.** In general, the choice of etching solution influences numerous aspects including etching rate, anisotropy, and selectivity [10]. The etching in TMAH has several advantages over etching in KOH, to be precise: TMAH delivers better selectivity between Si and SiO2, shows reduced surface roughness and contamination, and moreover fulfills the requirements of CMOS-compatibility [11], [12]. In our previous investigations we successfully used TMAH for fabrication of the nanostructures on strained Si substrates [4].

For SiGe alloy etching mainly a mixture of HF:H2O2:CH3COOH=1:2:3 is used [13]. However, the extremely fragile oxide mask pattern which consist mainly of SiO2 [14], [15] may easily be dissolved by HF acid [16],[17],[18]. Additionally, as the LAO patterns are about 2 nm in height and below 100 nm in width [19] the etching solution must deliver very high selectivity between SiGe substrate and the oxide mask. Preliminary etching experiments performed in 12M KOH solution confirmed the lack of selectivity between SiGe and the oxide and the mask patterns were damaged after the process. Due to these factors we decided to employ TMAH as our main SiGe etching solution [6].

**2. Experimental details**

AFM measurements were performed using a Veeco Dimension 3100 microscope at a room temperature in a tapping-mode. A closed loop conﬁguration of the AFM scanner was used to compensate for actuator drift and hysteresis. The instrument was isolated from vibration, thermal, and acoustic disturbances by locating it within an integrated isolation enclosure on an air table. The ambient air humidity of the laboratory room was maintained at 40%. Silicon cantilevers, with typical tip radius of curvatures of less than 8 nm, were utilized. The average spring constant and resonance frequency were about 48 N/m and 275 kHz, respectively. The images were recorded at the scan frequency of 1 Hz with the resolution of 256×256 pixels. The Scanning Probe Image Processor 4.4.6.0 (SPIP, Image Metrology, Denmark) was used for the AFM data evaluation.

. For the nanostructures' fabrica-

tion we used the commercially available 25% TMAH aqueous solution.

In some etching experiments the isopropyl alcohol (IPA) was added to

TMAH solution. All experiments were carried out with a stirrer

running at 100 rpm in a thermostated vessel allowing the tempera-

ture stabilization within ±0.5 °C. The process was performed at 70 °C.

After etching, the fabricated test structures were investigated by both

a tapping-mode AFM and a Philips XL30 scanning electron microscope

(SEM) operating at an accelerating voltage of 2 kV.

Before performing LAO the quality of the SiGe substrate was

investigated by scanning the nanofabrication area in tapping-mode

AFM. As a general rule, after etching in HF solution the root mean

square roughness of the SiGe surface was lower than 0.2 nm across a

2×2 μm

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surface area.

In AFM data analysis, we focused on the variations of

RMS surface roughness (S q ) and on the surface height histo-

grams evolution during the ALD growth. These two charac-

teristics are related and S q , which for normally distributed

surface heights equals the standard deviation of the height

histogram, describes the spread of the height distribution

(HD) about the mean value.

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In general, analysis of the HD

can be applied to characterize the surface texture in AFM

measurements. The HD study can deliver complex informa-

tion regarding the evolution of the surface texture during

growth.

25 zotero://attachment/20266/

The experiments were performed on the samples with a 55 nm

thick epitaxial layer of strained SiGe with a Ge content of 23 at.%,

deposited onto a bulk Si(100) wafer.

In order to perform the AFM nanolithography the sample surface

was preprocessed. A strained wafer was cleaned in deionized water

and dried with pure nitrogen. After cleaning, the native oxide was

removed by dipping in 5% hydroﬂuoric acid (HF) for 120 s. Afterwards

the silicon surface was once again cleaned in deionized water and dried with pure nitrogen. Besides removing the oxide, the HF bath also

passivates the surface [27,28].

For the nanostructures' fabrica-

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In some etching experiments the isopropyl alcohol (IPA) was added to

TMAH solution. All experiments were carried out with a stirrer

running at 100 rpm in a thermostated vessel allowing the tempera-

ture stabilization within ±0.5 °C. The process was performed at 70 °C.

After etching, the fabricated test structures were investigated by both

a tapping-mode AFM

The experiments were performed on the samples with a 155 nm thick epitaxial layer of strained SiGe with a Ge content of 20 at.%, deposited onto a bulk Si(100) wafer.

For the TERS experiments, a patterned sample consisting of a

strained SiGe ﬁlm with 23 at.% Ge content was used. After patterning,

SiGe lines corresponding to the original ﬁlm thickness of 55 nm were

obtained, whereas the surrounding surface region was etched down to

a remnant SiGe ﬁlm thickness of 30 nm, resulting in a line height of

about 25 nm.

Before etching experiments the native oxide was removed by immersing the substrate in 5 % HF acid for 60 s (LAB 5 min).

The RMS roughness of the SiGe surface after HF treatment and before etching procedures was about 0.13 nm. Native oxide cleaning zotero://attachment/21161/ The standard deviation of the RMS roughness is estimated to about 4 %.

**For morphology investigation at least three images in different**

**positions on the samples were acquired and ﬂuctuations of the**

**root mean square (RMS) surface roughness (Sq) of less than 76%**

**were observed.**

**2. 1. Sample Preparation**

**2.2. Etching (temperature vs. RMS, we added IPA and the temp was 70 C because the IPA evaporated around 82 C)**

**3. Results and discussion**

Zaczac od sige przed trawieniem w TMAHU



7.18 nastepnie opisac ze generalnie RMS zmniejsza się ze wzrostem koncentracji dlatego przeprowadzono jeszcze eksperymenty w 50 i 83 % Wtedy uniknie się ponowneo umieszczania rysuku 60s NoIPA CONT

Fig1SiGe_FLAT_ART copy.tif

Fig. 1. T (t) (IPA / No IPA)etching procedure[DEP (Disc.) / continuous etching (Cont.)] measured by TM-AFM for parameters: (a) t 60 s, No IPA, continuous etching, (b) t 340 s, No IPA, continuous etching, (c) t 60 s, No IPA, DEP, (d) t 340 s, IPA, DEP, (e) t 60 s, IPA, continuous etching, (f) t 340 s, IPA, continuous etching, (g) t 60 s, IPA, DEP, (h) t 340 s, IPA, DEP. In all experiments temperature of 25 % aqueous TMAH solution was kept at 70 ˚C and mechanical stirring was used. Additionally *Sq* and colour scale (*Cs*) parameters are reported.

The increase of the roughness during etching is a complex phenomenon and was investigated in details for Si surface [Plaik] [zubel] [cos]. Some roughness properties were explained by a pseudo-masking model which pointed out that the main cause of the roughness increase is due to etching by-products formation (H2 bubbles) [palik] [20]. From the many parametrers that may be varied in order to obtain smooth surface [palik] we chosen to investigate in more details the following: (1) etching time, (2) influence of surfactant additives, (3) solution concentration.

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Additionally, all the experiments were performed in etching solution being robustly stirred with a magnetic stirrer as in this manner H2 bubbles are efficiently removed from the surface what helps to reduce roughness [palik].

Hydrophilic surface which may be obtained by application of surfactants to etching solution reduces the number of H2 bubbles nucleation sites leading to smoother surface.

We also performed experiments in so called discontinuous etching procedure (DEP). The idea behind DEP is breaking the overall etching time into smaller periods (pieces) quanta. For all the experiments the smallest etching time was fixed to 20 s. The whole etching process was carried out in the following steps: (1) immersing the substrate into etching solution for 20 s, (2) removing the substrate out of the solution, (3) immersing the substrate in deionized water for 2 s, (4) drying the substrate in N2 flow for 2 s. The steps (1-4) (one etching cycle) were repeated until the required etching depth was achieved.

The obtained results may be explained by taking into account the pseudo-masking model

The explanation of this phenomenon can be based on the pseudo-masking theory in which the surface is masked by H2 bubbles that are produced during the etching reaction. Typical nucleation sites for N2 bubbles are locally hydrophobic regions of the surface and micro-cavities with trapped air. N2 diffuses into these sites and the bubble volume begins to increase. At some point the buoyancy force realises the bubble ~~is from the surface~~ leaving some gas behind on the surface and new bubble starts to grow in the same place. Once a nucleation site for N2 is formed it will mask the surface at that point during the whole etching process leading to increased roughness. The usage DEP in which the etched substrate is removed from etching solution, immersed in deionised water, and re-immersed in etchant helps to reconfigure the N2 nucleation sites. After one DEP cycle is performed it is unlikely that hydrogen bubbles reappear in the same places what explains the reduced RMS surface roughness

Etching rates were calculated based on measurements by means of J.A. Woollam M-2000 elipsometer. In the experiments

those determined thickness of the material before digestion and after digestion.

In Fig. 2 we present the summary of the influence of different etching procedures on the RMS surface roughness. In general, the RMS roughness increases with time of etching. Only for DEP with IPA admixture the roughness slightly decreases.

Table 1 reports the roughness decrease values (RDV) as the ratio between continuous and DEP. The most favourable is applying the DEP for long etching times as in this way the smallest RDV are reached.

Fig2SiGe_concentration_FLAT_ART copy.tif

Fig 3. TM-AFM surface morphology of Si0.77Ge0.23(100) after etching in aqueous TMAH solution with a concentration of a) 50 %, b) 83 %. Variation of the RMS surface roughness and etching rate vs. TMAH concentration. For all experiments etching time and temperature were equal to 340 s and 70 ˚C, respectively.

The surface roughness decreases with increasing TMAH concentration for Si substrate []. Fig XX presents surface morphology after SiGe etching experiments with 50 % and 83 % of TMAH concentration. The surface roughness increases for increased TMAH concentration and for 50 % has a maximum value of 7.54 nm. For higher concentration the roughness decreases significantly to a value of 0.34. This experiment also confirms a the pseudo-masking model as we observed no H2 bubbles formation for 83 % TMAH concentration. However we also obserwed linear decrease of the etching rate with increase of the TMAH concentration (Fig. XXc)

# **4. Conclusions**

We demonstrated that it is possible to use TMAH aqueous solution for SiGe etching and for nanostructures fabrication. The main sources of surface roughness increase were analysed and some were examined and the results can be explained by a pseudo-masking model. Both the used surfactant and the developed discontinuous etching procedure reduce surface roughness and is helpful for fabrication of nanostructures. The reduction of roughness is well explained by a pseudo-masking model.

**Acknowledgment**

**References**

[1] M. L. Lee, E. A. Fitzgerald, M. T. Bulsara, M. T. Currie, and A. Lochtefeld, ‘Strained Si, SiGe, and Ge channels for high-mobility metal-oxide-semiconductor field-effect transistors’, *J. Appl. Phys.*, vol. 97, no. 1, pp. 011101–28, Jan. 2005.

[2] G. Sun, Y. Sun, T. Nishida, and S. E. Thompson, ‘Hole mobility in silicon inversion layers: Stress and surface orientation’, *J. Appl. Phys.*, vol. 102, no. 8, pp. 084501–7, Oct. 2007.

[3] Y. Sun, S. E. Thompson, and T. Nishida, ‘Physics of strain effects in semiconductors and metal-oxide-semiconductor field-effect transistors’, *J. Appl. Phys.*, vol. 101, no. 10, pp. 104503–22, May 2007.

[4] P. Hermann, M. Hecker, F. Renn, M. Rölke, K. Kolanek, J. Rinderknecht, and L. M. Eng, ‘Effects of patterning induced stress relaxation in strained SOI/SiGe layers and substrate’, *J. Appl. Phys.*, vol. 109, no. 12, p. 124513, 2011.

[5] L. Zhu, C. Georgi, M. Hecker, J. Rinderknecht, A. Mai, Y. Ritz, and E. Zschech, ‘Nano-Raman spectroscopy with metallized atomic force microscopy tips on strained silicon structures’, *J. Appl. Phys.*, vol. 101, no. 10, pp. 104305–6, May 2007.

[6] K. Kolanek, P. Hermann, P. T. Dudek, T. Gotszalk, D. Chumakov, M. Weisheit, M. Hecker, and E. Zschech, ‘Local anodic oxidation by atomic force microscopy for nano-Raman strain measurements on silicon-germanium thin films’, *Thin Solid Films*, vol. 518, no. 12, pp. 3267–3272, Apr. 2010.

[7] K. E. Petersen, ‘Silicon as a mechanical material’, *Proceedings of the IEEE*, vol. 70, no. 5, pp. 420–457, 1982.

[8] M. Shikida, K. Sato, K. Tokoro, and D. Uchikawa, ‘Differences in anisotropic etching properties of KOH and TMAH solutions’, *Sensors and Actuators A: Physical*, vol. 80, no. 2, pp. 179–188, Mar. 2000.

[9] I. Zubel and M. Kramkowska, ‘The effect of isopropyl alcohol on etching rate and roughness of (1 0 0) Si surface etched in KOH and TMAH solutions’, *Sensors and Actuators A: Physical*, vol. 93, no. 2, pp. 138–147, Sep. 2001.

[10] W. Menz, J. Mohr, and O. Paul, *Microsystem technology*. Wiley-VCH, 2001.

[11] O. Tabata, R. Asahi, H. Funabashi, K. Shimaoka, and S. Sugiyama, ‘Anisotropic etching of silicon in TMAH solutions’, *Sensors and Actuators A: Physical*, vol. 34, no. 1, pp. 51–57, Jul. 1992.

[12] P.-H. Chen, H.-Y. Peng, C.-M. Hsieh, and M. K. Chyu, ‘The characteristic behavior of TMAH water solution for anisotropic etching on both Silicon substrate and SiO2 layer’, *Sensors and Actuators A: Physical*, vol. 93, no. 2, pp. 132–137, Sep. 2001.

[13] T. K. Cams, M. O. Tanner, and K. L. Wang, ‘Chemical Etching of Si[sub 1−x]Ge[sub x] in HF:H[sub 2]O[sub 2]:CH[sub 3]COOH’, *J. Electrochem. Soc.*, vol. 142, no. 4, p. 1260, 1995.

[14] O. W. Holland, C. W. White, and D. Fathy, ‘Novel oxidation process in Ge+‐implanted Si and its effect on oxidation kinetics’, *Appl. Phys. Lett.*, vol. 51, no. 7, pp. 520–522, Aug. 1987.

[15] A. R. Srivatsa, S. Sharan, O. W. Holland, and J. Narayan, ‘Nature of interfaces and oxidation processes in Ge+‐implanted Si’, *J. App. Phys.*, vol. 65, no. 10, pp. 4028–4032, May 1989.

[16] D. J. Monk, D. S. Soane, and R. T. Howe, ‘A review of the chemical reaction mechanism and kinetics for hydrofluoric acid etching of silicon dioxide for surface micromachining applications’, *Thin Solid Films*, vol. 232, no. 1, pp. 1–12, Sep. 1993.

[17] D. M. Knotter, ‘Etching Mechanism of Vitreous Silicon Dioxide in HF-Based Solutions’, *Journal of the American Chemical Society*, vol. 122, no. 18, pp. 4345–4351, May 2000.

[18] Y. Sun, Z. Liu, S. Sun, and P. Pianetta, ‘The effectiveness of HCl and HF cleaning of Si[sub 0.85]Ge[sub 0.15] surface’, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 26, no. 5, pp. 1248–1250, 2008.

[19] X.-Z. Bo, L. P. Rokhinson, H. Yin, D. C. Tsui, and J. C. Sturm, ‘Nanopatterning of Si/SiGe electrical devices by atomic force microscopy oxidation’, *Appl. Phys. Lett.*, vol. 81, no. 17, pp. 3263–3265, Oct. 2002.

[20] C. R. Yang, C. H. Yang, and P. Y. Chen, ‘Study on anisotropic silicon etching characteristics in various surfactant-added tetramethyl ammonium hydroxide water solutions’, *Journal of Micromechanics and Microengineering*, vol. 15, p. 2028, 2005.