Formation and Dissolution of Mesoporous Layer during Metal-Particle-Assisted Etching of n-Type Silicon

Ayumu MATSUMOTO,1,4,5 Keishi IWAMOTO, Yuki SHIMADA, Kyohei FURUKAWA, Shun MAJIMA, and Shinji YAE

Department of Chemical Engineering and Materials Science, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan
* Corresponding author: matsumoto.ayumu@eng.u-hyogo.ac.jp

ABSTRACT
Metal-assisted etching has attracted increasing attention as a method to produce porous silicon (Si). We previously found that gold (Au)-particle-assisted etching and platinum (Pt)-particle-assisted etching cause general corrosion of the Si substrate, but not in the case of silver (Ag)-particle-assisted etching [A. Matsumoto, et al., RSC Adv., 10, 253 (2020)]. In this work, we discussed the mechanism of the general corrosion with electrochemical approaches. We demonstrated that potentials of the Au- and Pt-deposited Si during the metal-particle-assisted etching are higher than that of the bare Si in the etchant, but not in the case of the Ag-deposited Si. We also performed electrochemical etching of the bare Si by applying the potential during the Pt-particle-assisted etching, resulting in the formation of a mesoporous layer which was dissolved in the etchant. We concluded that the general corrosion occurs during the metal-particle-assisted etching due to the dissolution of the mesoporous layer formed by anodic polarization of the Si substrate.

Keywords: Metal-Assisted Chemical Etching, Porous Silicon, Anodic Polarization, General Corrosion

1. Introduction

As one of methods to produce porous silicon (Si), metal-assisted etching (metal-assisted chemical etching) is under intense investigation. In the metal-assisted etching, porous Si is electrolessly formed by immersing a metal-modified Si in a mixture solution of hydrofluoric acid (HF) and oxidizing agent (e.g. hydrogen peroxide (H2O2), dissolved oxygen (O2), and metal ions). The metal-assisted etching proceeds with a local cell mechanism consisting of cathodic reduction of the oxidizing agent on the metal catalyst and anodic oxidation of Si. The reduction of the oxidizing agent injects positive holes into the valence band of Si, and the Si surface is dissolved by the reaction with the injected holes and fluoride species in the etchant. The greatest feature of this method is selective etching of the Si surface under the metal catalyst that enables us to produce porous Si reflecting the catalyst pattern, e.g. nanowire arrays and nanohole arrays. As a recent progress, zigzag and helical structures have also been reported.

Various applications utilizing the metal-assisted etching have been proposed so far, from energy conversion and storage (e.g. solar cells, thermoelectric devices, and lithium-ion batteries) to biomedicine (e.g. sensors, tissue engineering, and drug delivery), and it is expected to be used for semiconductor microfabrication. Our group has applied the porous Si in solar cells, electroless plating, and laser plasma spectroscopy. Meanwhile, it is required to control the etching behavior for the improvement of processing accuracy.

Metal catalyst plays an essential role for determining the etching behavior. Recently, Tamarov et al. comprehensively studied the etching behavior using various kinds of metal particles, and demonstrated that the difference of the band structure formed at the metal/Si interface results in the difference of the porous structures. Our group demonstrated that the etching rate is determined by the catalytic activity of the metal for the reduction of the oxidizing agent by etching n-Si in HF-O2 systems with various kinds of metal particles. In the previous work, we etched n-Si in a HF-H2O2 system using silver (Ag), gold (Au), and platinum (Pt) particles, and found that general corrosion (Fig. 1) is caused by the Au- and Pt-assisted etching but not by the Ag-assisted etching. We should know the degree of the general corrosion for practical applications. However, the mechanism of the general corrosion has not been fully clarified yet.

In recent years, electrochemical measurements and application of external bias during the metal-assisted etching have been
performed. For example, Torralba et al. performed electrochemical measurements during the Pt-particle-assisted etching of p-Si in a HF-H2O2 system with a simulation of the band structures at the Pt/p-Si/etchant interfaces. According to them, the injected holes spread into the bulk Si that induces anodic polarization of the Si substrate and mesopore formation around straight pores formed under the Pt particles. In addition, it is known that mesoporous Si is dissolved in HF solutions. On the basis of these reports above, it is expected that the general corrosion occurs due to the dissolution of a mesoporous layer formed by the anodic polarization. In this work, we confirmed this hypothesis with electrochemical approaches. We measured open circuit potentials of n-Si during the Ag-, Au-, and Pt-particle-assisted etching in the dark. We also reproduced the mesoporous layer with electrochemical etching of bare Si under illumination by applying the potential during the Pt-particle-assisted etching, and immersed it in the etchant to confirm the dissolution of the mesoporous layer.

2. Experimental

We prepared n-type Si (100) substrates (CZ, 0.5–10 Ω cm, 725 ± 25 μm) (Miyoshi Co., Ltd., T8NFL-6Z26) modified with Ag, Au, and Pt particles through electrodeless displacement deposition. For the modification of the Ag, Au, and Pt catalysts, the Si substrates were immersed in mixture aqueous solutions of 1 mM (M: mol dm⁻³) AgNO₃ and 0.15 M HF at 278 K for 20 s, 1 mM HAuCl₄ and 0.15 M HF at 278 K for 25 s, and 3 mM K₂PtCl₄ and 0.15 M HF at 313 K for 180 s, respectively. Under these conditions, the metal particles were separately deposited on the Si surface and the metal coverage on the Si surface was approximately 30% regardless of the kind of metal particles (deposition results can be seen in Ref. 35).

Figure 2 shows a schematic illustration of an electrochemical cell. The cell was made of polychlorotrifluoroethylene. As a working electrode (WE), the bare, Ag-, Au-, or Pt-deposited Si was used. A rubber packing was inserted between the cell and the WE to prevent liquid leakage. The inner diameter of the rubber packing was 1.0 cm and the effective surface area of the WE was 0.785 cm². An indium-gallium alloy was applied to the back side of the Si substrate to make an ohmic contact with a copper (Cu) plate (current collector). As a counter electrode (CE), a Pt ring was used. As a reference electrode (RE), a silver/silver chloride (Ag/AgCl) electrode (HORIBA, Ltd., 2060A-10T) was used. The reference electrode was connected to the etchant through a saturated potassium chloride (KCl) aqueous solution and a salt bridge. For the measurement of open circuit potentials and the electrochemical etching, a potentiostat (BioLogic Science Instruments, VSP) was used.

We prepared a mixture aqueous solution of 6.6 M HF and 0.08 M H₂O₂ as an etchant. The temperature of the etchant was kept at 298 K in a water bath immediately before the electrochemical experiments which were performed at room temperature. Open circuit potentials of the bare, Ag-, Au-, and Pt-deposited Si substrates in the etchant were measured in the dark. We also conducted the electrochemical etching of the bare Si in the etchant under the illumination of a halogen lamp (FUJI LAMP, ELH 120V300W) to reproduce the mesoporous layer formed by the Pt-particle-assisted etching. We immersed the Si substrate after the electrochemical etching in the etchant for 60 s at 298 K in the dark and confirmed the change of the mesoporous layer. The cross section of the samples was observed by a scanning electron microscope (SEM) (JEOL Ltd., JSM-7001F).

3. Results

3.1 Open circuit potential

Figure 3 shows temporal variations of open circuit potentials of the bare, Ag-, Au-, and Pt-deposited Si in the etchant. We started the potential measurement immediately after pouring the etchant in the electrochemical cell, i.e. the potential at 0 s can be roughly regarded as the potential when the etching reaction started. Since we found that the general corrosion occurs by the metal-particle-assisted...
etching for 60 s, we investigated the potential at the same time scale (the potential was measured for 120 s). The potential was different depending on the kind of metal particles. The potentials of the Au- and Pt-deposited Si were higher than that of the bare Si. On the other hand, the potential of the Ag-deposited Si was lower than that of the bare Si.

3.2 Formation and dissolution of mesoporous layer

In general, porous Si is produced by anodic polarization of Si substrates in HF solutions, namely electrochemical etching. By applying a positive potential lower than that for electropolishing, a porous layer is formed on the Si surface. It is also known that a mesoporous (and/or microporous) layer can be formed by the metal-assisted etching (e.g. Refs. 3–5, 9, 12, 16, 23, 31, 32, 35, 36, 41). In this section, for the reproduction of the mesoporous layer formed by the metal-assisted etching, the bare Si was etched by the electrochemical etching under the condition simulating the Pt-particle-assisted etching which forms a thick mesoporous layer. In addition, we confirmed whether the mesoporous layer is dissolved in the etchant or not by immersing the porous Si substrate produced by the electrochemical etching in the etchant.

The electrochemical etching was performed at the potential corresponding to the Pt-assisted etching (−0.25 V vs. Ag/AgCl) under the halogen lamp illumination of 17.3 mW cm⁻². Note that the photoillumination is needed to generate positive holes in the valence band of n-Si (positive holes are minority carriers). The irradiance was fixed so that the current density during the electrochemical etching corresponded to the amount of electricity consumed for the formation of the mesoporous layer during the Pt-assisted etching. The amount of electricity was estimated by the following calculation. We assumed that the general corrosion is caused by that the mesoporous layer is chemically dissolved during the metal-assisted etching. The mass loss of substrate (Δm) is the sum of the mass losses for the formation of the mesoporous layer, for the formation of the straight pores under the metal particles, and for the dissolution of the mesoporous layer as follows (see Fig. 4):

\[
Δm = Δm_{\text{meso}} + (d_{\text{obs}} + d_{\text{cor}})Sx + d_{\text{cor}}(1 - p_{\text{meso}})Sx(1 - x)
\]

where \(Δm_{\text{meso}}\) is the mass loss for the formation of the mesoporous layer, \(d_{\text{obs}}\) is the observed depth of the straight pores, \(d_{\text{cor}}\) is the depth of the general corrosion, \(p\) is the density of Si (2.33 g cm⁻³), \(S\) is the surface area of the Si substrate on which the electrole deposited was conducted, \(x\) is the metal coverage on the Si surface, and \(p_{\text{meso}}\) is the porosity of the mesoporous layer. The amount of electricity consumed for the formation of the mesoporous layer \((Q_{\text{meso}})\) is obtained from the mass loss as follows:

\[
Q_{\text{meso}} = nF \frac{Δm_{\text{meso}}}{M}
\]

where \(n\) is the number of electrons transferred in the reaction, \(F\) is the Faraday constant \((9.65 × 10^4 \text{ C mol}^{-1})\), and \(M\) is the molar mass of Si \((28.1 \text{ g mol}^{-1})\). The current density for the formation of the mesoporous layer \((i_{\text{meso}})\) is as follows:

\[
i_{\text{meso}} = \frac{Q_{\text{meso}}}{t(1 - x)}
\]

where \(t\) is the time for the metal-assisted etching. Using the equations above, we calculated the current density for the formation of mesoporous layer. In Eq. (1), we used the experimental conditions (\(S = 1.0 \text{ cm}^2\), \(x = 0.29\), experimental results \((Δn = 75.9 \mu g, d_{\text{obs}} = 630 \text{ nm}\), and estimated result \((d_{\text{cor}} = 100 \text{ nm})\) with an assumption \((p_{\text{meso}} = 0.5)\) in the previous work. Then, the mass loss for the formation of the mesoporous layer was obtained \((Δn_{\text{meso}} = 18 \mu g)\). Note that, in the previous work, we performed the Pt-assisted etching by immersing the 1 cm × 1 cm piece of the Si substrate (metal particles were deposited only on one side and thus \(S = 1.0 \text{ cm}^2\)) in the etchant, and the thickness of the mesoporous layer left after the etching was 120 nm. In Eq. (2), we assumed that the mesoporous layer is formed by the two-electron reaction \((n = 2)\), and the amount of electricity was obtained \((Q_{\text{meso}} = 0.12 \text{ C})\). Using Eq. (3) and the experimental conditions \((t = 60 \text{ s}, S = 1.0 \text{ cm}^2)\) in the previous work, the current density was obtained \((i_{\text{meso}} = 2.9 \text{ mA cm}^{-2})\). The irradiance of the halogen lamp was adjusted to be 17.3 mW cm⁻² so that the current density during the electrochemical etching was 2.9 mA cm⁻².

Figure 5a shows a cross-sectional SEM image of the porous Si substrate produced by the photoelectrochemical etching simulating the Pt-particle-assisted etching. The porous Si substrate was immersed in the etchant for 60 s in the dark without external bias (Fig. 5b). We can see a mesoporous layer with a thickness of 150 nm before the immersion. After the immersion, we can also see the mesoporous layer with a thickness of 70 nm. Thus, the mesoporous layer was dissolved during the immersion.

---

**Figure 5.** (a) Cross-sectional SEM image of the porous Si substrate produced by the photoelectrochemical etching under the condition simulating the Pt-particle-assisted etching (etchant: 6.6 M HF and 0.08 M H₂O₂, applied potential: −0.25 V vs. Ag/AgCl, irradiance: 17.3 mW cm⁻², etching time: 60 s). (b) After the immersion in the etchant for 60 s in the dark without external bias.
layer of 80 nm was removed. Note that, for the SEM observation, a sample piece of the porous Si (ca. 3 mm × 5 mm) was prepared and it was immersed in the etchant after the first SEM observation, i.e. the same cleavage plane of the same sample piece was observed before and after the immersion. This means that the sample-to-sample variability was eliminated and that not only the top-surface but also the side of the mesoporous layer was exposed to the etchant during the dissolution test, which is similar to the situation of the metal-particle-assisted etching.

4. Discussion

4.1 Anodic polarization

As shown in Fig. 3, the potential was higher in the order of the Au-deposited Si, Pt-deposited Si, bare Si, and Ag-deposited Si. Meanwhile, a degree of the general corrosion (d_{OUTH}/d_{OUTH} + d_{OUTH}) was higher in the order of the Au-deposited Si, Pt-deposited Si, and Ag-deposited Si, and the general corrosion of the Ag-deposited Si was negligible (etching results can be seen in Ref. 35). These results imply that the general corrosion is related to the potential of the Si substrate during the metal-assisted etching.

Here, we discuss the open circuit potential of the Si substrate in the etchant based on the mixed potential theory. In the case of the bare Si, the open circuit potential should be dominated by the mixed potential of the H_2O_2 reduction at cathodic sites and the Si oxidation at anodic sites on the Si surface, as the Si surface is electrolessly dissolved in HF-H_2O_2 solutions. By the modification of metal catalyst, both the cathodic and anodic polarization characteristics of the Si substrate can change and the degree of change is different in the cathodic and anodic reactions. Thus, the open circuit potential is shifted by the metal deposition. The result in Fig. 3 indicates that the changes of the polarization characteristics depend on the kind of metal particles deposited on the Si surface. Liu measured cathodic and anodic polarization curves of bare Si and Ag-deposited Si in HF and HF-H_2O_2 solutions, and showed that both the cathodic and anodic currents of the moderately doped n-Si (2–2.7 Ω cm) in the HF-H_2O_2 system increase by the Ag deposition. Then, the enhancement of the anodic reaction is more significant than that of the cathodic reaction, i.e. the increase rate of the anodic current from the bare Si to the Ag-deposited Si is higher than that of the cathodic current. Such changes result in the increase of the corrosion current and the negative shift of the corrosion potential. The negative shift of the potential by the Ag deposition is in agreement with our result in Fig. 3. The increase of the anodic current by the Ag deposition under the anodic polarization of n-Si can be explained by that the Ag particles work as the catalyst not only for the cathodic reaction but also for the anodic reaction. Even though the metal-assisted etching proceeded, the potential of the Ag-deposited Si was lower than that of the bare Si. This indicates that the overpotential of the Si oxidation reaction is reduced in the vicinity of the Ag particles. Regarding palladium (Pd), for example, our group showed that Pd particles work as the catalyst for the Si oxidation, i.e. electroless etching of Si. In this case, the anodic current under the anodic polarization of n-Si is obviously increased by the Pd deposition. Current doubling effect can also be a factor to increase the anodic current. Assuming that the H_2O_2 reduction occurs on the Ag catalyst even under the anodic polarization due to its high electrode potential, the Si surface can be dissolved by the positive holes injected into the Ag/Si interface. Then, electrons can be injected into the conduction band of Si through the current doubling pathway during the two-electron dissolution reaction. 47, 48

In contrast to the case of the Ag-deposited Si, the potentials of the Au- and Pt-deposited Si were higher than that of the bare Si (see Fig. 3). This indicates that the enhancement of the cathodic reaction is more significant than that of the anodic reaction, i.e. the Au and Pt particles mainly work as the catalyst for the H_2O_2 reduction. The positive shift of the potential by the Pt deposition has also been reported in the case of p-Si by Torralba et al. 34 Chourou et al. measured anodic polarization curves of p-Si modified with different kinds of metal particles in HF solutions with and without H_2O_2. They showed that the anodic current increases by the metal deposition in the HF-H_2O_2 system and that the onset potential of the Pt-deposited Si is more positive than that of the Ag-deposited Si. Meanwhile, we previously measured cathodic polarization curves of Ag, Au, and Pt electrodes in the etchant and the onset potential of Pt was more positive than that of Ag, indicating that the catalytic activity of Pt for the H_2O_2 reduction is higher than that of Ag. Thus, we can predict that the potential of the Pt-deposited Si is higher than that of the Ag-deposited Si. We should also mention that the potential of the Au-deposited Si was higher than that of the Pt-deposited Si. On the other hand, there is a possibility that the H_2O_2 reduction proceeds under diffusion limited conditions during the metal-assisted etching. Assuming that H_2O_2 is sufficiently consumed by the metal-assisted etching during the potential measurement, the potential of the metal-deposited Si becomes lower than the mixed potential estimated from the cathodic polarization curve of the metal electrode and the anodic polarization curve of the Si electrode. This is explained by the decrease of the cathodic current due to the lack of H_2O_2 near the Si surface. Considering the consumption of H_2O_2, the cathodic current of the Pt-deposited Si is significantly reduced due to the high catalytic activity of Pt for the H_2O_2 reduction and consequently the potential becomes lower than the estimated mixed potential. This can also be a reason that the potential of the Pt-deposited Si is lower than that of the Au-deposited Si.

Band structure at the metal/Si interface is a key factor in the metal-assisted etching. 31, 36, 37, 60, 61, 63, 64 For example, Kolasinski's group showed that, for both the n- and p-Si, the band structures at the Au/Si and Pt/Si interfaces are favorable for the hole injection to the valence band of Si, but not at the Ag/Si interface. In the case of Au-assisted etching, positive holes produced by the H_2O_2 reduction can be consumed at the Ag/Si interface without the hole injection into bulk Si enough to induce the anodic polarization. They also proposed a possibility that the Ag particles are positively charged by the H_2O_2 reduction and the electric field induces the etching of Si in the vicinity of them. As another possibility, we suppose that the Si oxidation is catalyzed by the Ag particles, i.e. the Si oxidation with the electron injection can be a driving force of the Ag-assisted etching. In this case, the potential of the Ag-deposited Si can be lower than that of the bare Si.

Regarding the Pt-assisted etching, Torralba et al. 31 simulated the band structure at the p-Si surface around the Pt particle in the HF-H_2O_2 system. According to their simulation, the Pt particle forms an ohmic contact and a strong accumulation layer of positive holes at the Pt/p-Si interface, while a Schottky contact is formed at the etchant/p-Si interface away from the Pt particle. They mentioned that the injected holes have two contributions: preferential etching under the Pt particles with the accumulation at the Pt/Si interface and formation of the mesoporous layer with the spread into the bulk Si that causes the anodic polarization (i.e. barrier height for the hole transfer from Si to the etchant is reduced). In the case of n-Si (positive holes are minority carriers) accompanied with the general corrosion, injected holes should be consumed at the location away from the metal catalyst. This indicates that excess holes at the metal/Si interface are diffused through the bulk Si, i.e. anodic polarization is induced as it is also seen in Fig. 3. Here, we focus on the
accumulation of holes at the metal/Si interface, which plays an important role for the preferential etching under the metal catalyst.30 According to the calculation by Kolaskiński’s group,36,45 the accumulation layer of holes is formed at the valence band of Si by the contact with Au and Pt. Then, the accumulation layer under the Au catalyst is smaller than that under the Pt catalyst, indicating that the spread of excess holes into the bulk Si during the Au-assisted etching is more significant than that during the Pt-assisted etching. This can be a reason that the potential of the Pt-deposited Si is lower than that of the Au-deposited Si.

For detailed discussion on the open circuit potential, further investigations (e.g. polarization curve measurements, theoretical simulations, and application of external bias) will be required with the control of catalyst pattern. It is also interesting that the potential of the Au-deposited Si changed significantly over time (see Fig. 3). The reason of the temporal change of the potential and its influence on the etching behavior should be investigated in future work.

4.2 General corrosion

We can confirm in Fig. 5a that the thickness of the mesoporous layer produced by the electrochemical etching was 150 nm. Meanwhile, the thickness of the mesoporous layer produced by the Pt-particle-assisted etching was 120 nm.35 Since the mesoporous layer of similar thickness was obtained under the condition simulating the potential and the current density, we believe that the mesoporous layer was roughly reproduced by the photoelectrochemical etching. In the photo electrochemical etching, electron-hole pairs are generated by the photoexcitation. The holes are consumed for the formation of mesoporous layer, while the electrons are consumed at the counter electrode through the external circuit which is a substitute of the catalyst in the metal-assisted etching.

As shown in Fig. 5, the mesoporous layer of 80 nm was removed after the immersion in the etchant, which is comparable with the estimated depth of the general corrosion (120 nm).35 This indicates that the general corrosion is caused by the metal-particle-assisted etching as a consequence of the dissolution of the mesoporous layer. As reasons of the general corrosion, electrochemical etching, galvanic dissolution, and chemical dissolution can be considered, which are respectively explained by that the top-surface of the mesoporous layer is dissolved due to positive holes given by the anodic polarization, given by the H2O2 reduction, and without the charge transfer. Note that it is difficult to compare the difference of the dissolution reactions contributing the general corrosion between the Au- and Pt-assisted etching showing the different open circuit potentials. The porosity of the mesoporous layer and the dissolution rate on the top-surface by the reactions consuming the holes can change depending on the applied potential, and the dissolution rate by the chemical dissolution can change depending on the porosity. The hole supply to the top-surface of Si is different between the Au- and Pt-assisted etching due to the differences of the catalytic activity for the H2O2 reduction and the band modulation at the Si surface. Since the inter-particle distance depends on the kind of metal particles, the lateral size of the Si walls left after the particle sinking is also different.35 However, from the fact that the dissolution test was conducted without applying the external bias to the sample piece of the porous Si, we can say that at least the galvanic and/or chemical dissolution of the mesoporous layer plays a significant role in the general corrosion during the Pt-particle-assisted etching.

5. Conclusion

We discussed the mechanism of the general corrosion in the metal-particle-assisted etching of n-Si with the electrochemical approaches. We measured the open circuit potentials of the Si substrates modified with different kinds of metal particles in the etchant. The potential of the Ag-deposited Si of which general corrosion is negligible was lower than that of the bare Si. The potentials of the Au- and Pt-deposited Si of which general corrosion is significant were higher than that of the bare Si. We also performed the photoelectrochemical etching of the bare Si by applying the anodic potential during the Pt-assisted etching, resulting in the formation of the mesoporous layer. The mesoporous layer was dissolved in the etchant and the depth of the dissolution was comparable with the depth of the general corrosion caused by the Pt-particle-assisted etching. These results suggest that the general corrosion occurs due to the formation and dissolution of the mesoporous layer during the metal-particle-assisted etching.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Numbers JP19K05082 and JP20K15314.

References

1. Z. Huang, N. Geyer, P. Werner, J. de Boer, and U. Gösele, Adv. Mater., 23, 285 (2011).
2. X. Li and P. W. Bohn, Appl. Phys. Lett., 77, 2572 (2000).
3. T. Tsuijino and M. Matsumura, Adv. Mater., 17, 1045 (2005).
4. C. Chauvet, S. Basistie, and C. Levy-Clement, Electrochem. Acta, 53, 5508 (2008).
5. S. Yae, Y. Kawamoto, H. Tanaka, N. Fukumuro, and H. Matsuda, Electrochem. Commun., 5, 632 (2003).
6. K.-Q. Peng, Y.-J. Yan, S.-P. Gao, and J. Zhu, Adv. Mater., 14, 1164 (2002).
7. R. Liu, C. Zhang, C. Con, B. Cui, and B. Sun, Nanoscale Res. Lett., 8, 155 (2013).
8. K. Yamakawa, S. Sakamoto, N. Fukumuro, and S. Yae, ECS Trans., 69(2), 185 (2015).
9. L. Kong, Y. Zhao, B. Dasgupta, Y. Ren, K. Hippalgaonkar, X. Li, W. K. Chim, and S. V. Chauhan, ACS Appl. Mater Interfaces, 9, 20981 (2017).
10. Y. Chen, L. Li, C. Zhang, C.-C. Tuan, X. Chen, J. Guo, and C.-P. Wong, Nano Lett., 17, 1014 (2017).
11. Y. Chen, C. Zhang, L. Li, C.-C. Tuan, F. Wu, X. Chen, J. Guo, Y. Ding, and C.-P. Wong, Nano Lett., 17, 4304 (2017).
12. K. Tsuijino and M. Matsumura, Electrochem. Solid-State Lett., 8, C193 (2005).
13. O. I. Hildreth, A. G. Fedorov, and C. P. Wong, ACS Nano, 6, 10004 (2012).
14. B. Jiang, M. Li, Y. Liang, Y. Bai, D. Song, Y. Li, and J. Luo, Nanoscale, 8, 3085 (2016).
15. T. Yasuda, Y. Maeda, K. Matsuaki, Y. Okazaki, R. Oda, A. Kitada, K. Murase, and K. Fukami, ACS Appl. Mater Interfaces, 11, 48604 (2019).
16. T. Yasuda, T. Yasuda, K. Matsuaki, Y. Okazaki, E. Pouget, R. Oda, A. Kitada, K. Murase, G. Raffy, D. M. Bassani, and K. Fukami, Electrochem. Commun., 114, 106714 (2020).
17. H. Han, Z. Huang, and W. Lee, Nano Today, 9, 271 (2014).
18. H. Alhnomd, B. Drodosceana, R. Elhanathan, T. Kraus, and N. H. Voelkeger, Prog. Mater. Sci., 116, 106036 (2021).
19. M. Zabedinejad, S. D. Farimani, M. Khajee, H. Mehrara, A. Erfanian, and F. Zeinali, J. Micromech. Microeng., 23, 055015 (2013).
20. L. Li, G. Zhang, and C.-P. Wong, IEEE Trans. Components, Packag. Manuf. Technol., 5, 1039 (2015).
21. L. Romano and M. Stampanoni, Micromachines, 11, 589 (2020).
22. Y. Asano, K. Matsuho, H. Ito, K. Higuchi, K. Shimokawa, and T. Sato, Proceedings of 2015 IEEE 65th Electronic Components and Technology Conference (ECTC), 853 (2015).
23. S. Yae, H. Tanaka, T. Kobayashi, N. Fukumuro, and H. Matsuda, Phys. Status Solidi C, 2, 3476 (2005).
24. S. Yae, T. Kobayashi, T. Kawagishi, N. Fukumuro, and H. Matsuda, Sol. Energy Mater. Sol. Cells, 80, 701 (2006).
25. S. Yae, T. Hirano, T. Matsuda, N. Fukumuro, and H. Matsuda, Appl. Surf. Sci., 255, 4670 (2009).
26. S. Yae, K. Sakabe, N. Fukumuro, S. Sakamoto, and H. Matsuda, J. Electrochem. Soc., 158, D573 (2011).
27. A. Matsumoto, Y. Shimizu, S. Yoshizumi, H. Nakano, and S. Yae, J. Anal. At. Spectrom., 35, 2239 (2020).
28. C.-L. Lee, K. Tsuijino, Y. Kanda, S. Ikeda, and M. Matsumura, J. Mater. Chem., 18, 1015 (2008).
29. H. Asob, F. Arai, and S. Ono, Electrochem. Acta, 54, 5142 (2009).
30. S. Yae, M. Tashiro, M. Abe, N. Fukumuro, and H. Matsuda, J. Electrochem. Soc., 157, D90 (2010).
31. M. L. Chourou, K. Fukami, T. Sakka, S. Virtanen, and Y. H. Ogata, Electrochem. Acta, 55, 903 (2010).
32. C. Chiappini, X. Liu, J. R. Fakhoury, and M. Ferrari, Adv. Funct. Mater., 20, 2231
33. S. Yae, Y. Morii, N. Fukumuro, and H. Matsuda, *Nanoscale Res. Lett.*, 7, 352 (2012).
34. S. Yae, Y. Morii, M. Enomoto, N. Fukumuro, and H. Matsuda, *ECS Trans.*, 50(37), 31 (2013).
35. A. Matsumoto, H. Son, M. Eguchi, K. Iwamoto, Y. Shimada, K. Furukawa, and S. Yae, *RSC Adv.*, 10, 253 (2020).
36. K. Tamarov, R. Kiviluoto, J. D. Swanson, B. A. Unger, A. T. Ernst, M. Aindow, J. Riikonen, V.-P. Lehto, and K. W. Kolasinski, *ACS Appl. Mater. Interfaces*, 12, 48969 (2020).
37. Z. P. Huang, N. Geyer, L. F. Liu, M. Y. Li, and P. Zhong, *Nanotechnology*, 21, 465301 (2010).
38. L. Li, X. Zhao, and C.-P. Wong, *ACS Appl. Mater. Interfaces*, 6, 16782 (2014).
39. L. Liu, *Sci. China Technol. Sci.*, 58, 362 (2015).
40. C. Q. Lai, W. Zheng, W. K. Choi, and C. V. Thompson, *Nanoscale*, 7, 11123 (2015).
41. E. Torralba, S. Le Gall, R. Lacharme, V. Magnin, J. Harari, M. Halbwax, J.-P. Vilcot, C. Cachet-Vivier, and S. Bastide, *ACS Appl. Mater. Interfaces*, 8, 31375 (2016).
42. A. Halimaoui, *Surf. Sci.*, 306, L550 (1994).
43. S. Yae, N. Nasu, K. Matsumoto, T. Hagihara, N. Fukumuro, and H. Matsuda, *Electrochim. Acta*, 53, 35 (2007).
44. V. Lehmann, *Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications*, Wiley-VCH, Weinheim (2002).
45. K. W. Kolasinski, *Nanoscale Res. Lett.*, 9, 432 (2014).
46. R. A. Lai, T. M. Hymel, V. K. Narasimhan, and Y. Cui, *ACS Appl. Mater. Interfaces*, 8, 8875 (2016).
47. H. Gerischer and M. Lübke, *Ber. Bunsen-Ges. Phys. Chem.*, 91, 394 (1987).
48. H. Gerischer, P. Allongue, and V. Costa Kieling, *Ber. Bunsen-Ges. Phys. Chem.*, 97, 753 (1993).
49. K. W. Kolasinski, *Phys. Chem. Chem. Phys.*, 5, 1270 (2003).
50. K. W. Kolasinski, *Surf. Sci.*, 603, 1904 (2009).