Structure of Porous Si Formed by Metal-Particle (Pt, Pd) Enhanced HF Etching

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Metal-particle-enhanced HF etching of Si can produce micrometer-sized macroporous and nanometer-sized microporous Si by simple immersion of metal-particle-modified Si in a HF aqueous solution without a bias or a particular oxidizing agent. The etching rate of Si and the structure of produced porous Si are changed by the dissolved oxygen concentration of the HF solution and the photoillumination intensity on Si during etching. In this study, we found that strong photoillumination promotes the etching of Pt-modified n-Si under the absence of dissolved oxygen in the HF solution. Pd particles show a unique behavior in which the etching of n-Si proceeds at a high rate accompanying hydrogen evolution under dark conditions and the absence of dissolved oxygen.

Key words: Porous silicon, Chemical etching, Metal particles, Electroless deposition, Solar cell, Photoelectrochemistry

1. INTRODUCTION

Porous silicon (Si) has a wide range of pore nanometers sizes between and sub-millimeters [1-3]. Microporous Si that consists of nanometer-sized pores has attracted considerable attention due to its visible light emissions and large net surface areas. Light emitting devices [4], silicon-on-insulator devices [5], and sensors [6,7] are expected to be applications of porous Si [1]. Macroporous Si that consists of micrometer-sized pores can function as a textured surface to improve the conversion efficiency of solar cells equipped not only with single-crystalline [3,8,9] but also multicrystalline Si wafers [10,11] by reducing the reflectivity of Si. Porous Si, which is usually prepared by electrochemical etching under anodic bias in a fluoride-containing solution, can be produced by metal-enhanced (galvanic) etching in a HF solution [7,10]. Recently, we reported a preparation process of porous Si using the modification of Si wafers with fine metal particles, followed by simple immersion in a HF solution in which we dispense with a bias or a particular oxidizing agent [8,9,11,12]. This simple process is advantageous to improve solar cell efficiency, as mentioned above [8,9,11]. Such etching behaviors as the etching rate and the structure of porous Si are changed with photoillumination intensity on the Si surface and dissolved oxygen concentration in the HF solution during etching [9,12]. We described the etching mechanism of n-Si using a local galvanic cell that consists of a local cathode reduction of oxygen and a local anode oxidation of Si. In the present study, we found that the reduction of protons can function as a local cathode reaction of the metal-particle-enhanced etching of n-Si, and especially Pd-particle-modified n-Si can be etched at a high rate under the absence of oxygen even in the dark.

2. EXPERIMENTAL

Single-crystalline n-Si wafers (CZ, (100), ca. 1 Ω cm, 525 μ m thick, Yamanaka Semiconductor) were used as substrates and cut into $1.0 \times 1.0 \text{ cm}^2$ pieces. Just before the modification of n-Si wafers with fine metal particles, the wafers were washed with acetone and etched with CP 4A (a mixture of HF, HNO₃, CH₃COOH, and H₂O) and a 7.3 M (M = mol dm⁻³) HF solution. The electroless displacement deposition method was used to modify the n-Si wafers with fine metal (Pt or Pd) particles [13]. The n-Si wafers were immersed in a 1 mM metal salt (H₂PtCl₆ or PdCl₂) solution containing 0.15 Μ HF at 313 K for 120 s. The metal-particle-deposited n-Si wafers were immersed in a 7.3 M HF aqueous solution at 298 K for 24 h in a dark room. In some cases, argon (Ar) gas (>99.99% purity) bubbling was applied to the HF solution, and/or the n-Si wafers were irradiated with a tungsten-halogen lamp (ELH 120 V, 300 W) during immersion. Illumination intensity was adjusted by measuring the photocurrent of solid-state pn-Si solar cells. The photocurrent was converted to illumination intensity by a proportional calculation from the photocurrent under simulated solar illumination (AM 1.5G, 100 mW cm⁻²). The mass of the n-Si wafers was measured with an analytical balance (Mettler Toledo, AG245 or XS105DU), and the photoluminescence of n-Si wafers was visually examined under UV irradiation (ca. 1 mW cm⁻² with a San-ei Electric UVP-365 power meter) using a black light (Toshiba, FL4BLB). Surface and cross-sectional inspections of n-Si wafers were performed with a scanning electron microscope (SEM, Hitachi, S 900).

3. RESULTS AND DISCUSSION

Figure 1 shows a SEM image of the Pt-particle-deposited n-Si wafer immersed in a 7.3 M HF solution for 24 h with Ar gas bubbling into the solution (absence of dissolved oxygen in the solution) under photoillumination of 1 mW cm^{-2} . The surface shows no change from before immersion. The decrease in the mass of the samples was less than 0.04 mg. Under dark conditions with Ar gas bubbling, identical results were obtained except for a 0.00 mg mass change. These results are different from those obtained without gas bubbling (dissolved oxygen concentration was expected to be ca. 5 ppm) that we reported previously [9]. Under dark conditions without gas bubbling, the Pt-particle-deposited n-Si wafers were etched for 0.1-0.2 mg, and micrometer-sized pores were formed on the sample surfaces. Photoillumination of 1 mWcm⁻² without gas bubbling increased the etching rate to mg and formed 0.7 - 1.1a luminescent microporous layer on the photoilluminated surface of the samples.

Under photoillumination of 40 mW cm^{-2} with Ar gas bubbling, the Pt-particle-deposited n-Si wafers were etched for 0.1–0.4 mg by immersing them in a 7.3 M HF solution for 24 h. The photoilluminated surface of the n-Si wafer partly changed color. No photoluminescence was obtained on either side of the samples photoilluminated and nonilluminated



Figure 1. SEM image of Pt-particle-deposited n-Si wafer after immersion in 7.3 M HF solution for 24 h with Ar gas bubbling under photoillumination of 1 mW cm⁻².



Figure 2. Typical SEM image of etched part of Pt-particle-deposited n-Si wafer after immersion in 7.3 M HF solution for 24 h with Ar gas bubbling under photoillumination of 40 mW cm⁻².

during immersion in the HF solution, indicating that no microporous layer was formed on the samples. Figure 2 shows a typical SEM image of the color-changed part on the photoilluminated surface of the etched n-Si sample. A macroporous layer was formed that consists of many macropores much larger than those formed in the dark without gas bubbling [9]. No change in surface morphology was obtained for the nonilluminated side of the samples by SEM inspection. A n-Si wafer only modified with Pt particles on one side was etched for 0.05 mg by immersion in a 7.3 M HF solution for 24 h under photoillumination of 40 mWcm⁻² onto a Pt-particle-deposited surface with Ar gas bubbling. Relatively strong photoillumination promotes the metal-particle-enhanced HF etching of Pt-modified n-Si under the absence of dissolved oxygen in the HF solution.

The above results are explained based on our previously reported discussion [9,12]. The metal-particle-enhanced HF etching of silicon proceeds by a local cell mechanism consisting of metal-particle cathodes and Si anodes. Figure 3 shows a schematic potential diagram of n-Si in the HF solution based on the literatures [1,14-16]. There are two possible local cathode reactions in the HF aqueous solution: reduction of protons and reduction of dissolved oxygen. While the potential of proton reduction is between the conduction band and the valence band edges of n-Si, the potential of oxygen reduction is more positive than the potential of the valence band edge. Only oxygen can inject positive holes into the valence band of n-Si by reduction on Pt particles. Thus, under dark conditions, the absence of dissolved oxygen in the HF solution





Figure 3. Schematic potential diagram of n-Si in a HF solution.



Figure 4. Schematic energy diagram of Pt-particle-deposited n-Si in HF solution under high intensity photoillumination with absence of dissolved oxygen.

prohibits the etching of n-Si. Under low intensity photoillumination, almost all of photogenerated holes in the valence band of n-Si recombined with electrons from the conduction band at the surface of n-Si. Thus, the potential of Pt particles on the n-Si does not reach the potential of sufficient proton reduction, i.e., hydrogen evolution, and the etching rate is almost zero. Under high intensity photoillumination, the Fermi level of n-Si shifts toward the negative by the photovoltaic effect to balance the flows of photogenerated electrons and holes [17,18], and the potential of Pt particles reaches the potential of sufficient hydrogen evolution. Figure 4 shows a schematic energy band diagram of n-Si under such conditions. Since the holes in the valence



Figure 5. SEM image of Pd-particle-deposited n-Si wafer after immersion in 7.3 M HF solution for 24 h with Ar gas bubbling in the dark.

band of n-Si are minority carriers, they recombine with the electrons of the conduction band in the interior of n-Si. The holes cannot reach the nonilluminated surface of n-Si. Therefor (2007)ne electrons in the conduction band reduce protons on the Pt particles at the nonilluminated surface of n-Si. The corresponding amount of positive holes dissolves Si at the photoilluminated surface, although most holes recombine with electrons from the conduction band at the surface. Thus, a тасторотоць layer is formed on the photoilluminated surface of n-Si, and the absence of catalytic Pt particles on the nonilluminated surface attenuates the etching rate.

Palladium particles yielded a high etching rate of 0.3-4.8 mg for 24 h immersion in a 7.3 M HF solution under dark conditions with Ar gas bubbling. This is much different not only from the Pt case of 0.00 mg but also from Ag, Cu, and Au less than 0.08 mg. Figure 5 shows a SEM image of Pd-particle-deposited n-Si after HF immersion where mass decrease was 2.9 mg corresponding to 12 µm of Si thickness. Dimples of several micrometers sizes were formed. No photoluminescence was obtained. Thus, neither a macroporous nor a microporous layer was formed on Pd-particle-deposited n-Si by HF immersion under the present conditions. Gas evolution only occurred on the Pd-particle-deposited area of n-Si (Fig. 6). The mass of Pd-particle-deposited n-Si decreased by 1.6 mg when ultra pure Ar gas (>99.9999% purity) was used whose oxygen concentration was less than 0.1 ppm. This value is in the range of mass decrease when a regular Ar gas including less than 10 ppm of oxygen was used. Thus, the oxygen included in the Ar gas



Figure 6. Photograph of partly-Pdparticle-deposited n-Si in 7.3 M HF solution just after immersion in identical solution for 30 min with Ar gas bubbling in the dark. The bottom half of n-Si wafer was modified with Pd particles

cannot be an oxidant of the local cathode reaction.

The mechanism of this unique behavior of Pd particles is not clear. Possible mechanism is the following. According to thermodynamics, water can oxidize bare Si with hydrogen evolution, and HF can dissolve bare Si with production of silicon hexafluoride and hydrogen evolution [19]. However, the etching rate of Si in HF solution is very low due to stable hydrogen termination of Si surface [19,20]. Pd enhances native oxide growth on Si surface [20]. Thus, Pd can activate Si surface in the HF solution. On the activated Si surface, Si can be dissolved in the HF solution via chemical or electrochemical reactions accompanying hydrogen evolution. The chemical reaction can be oxidization by water or dissolution by HF. The electrochemical reaction can be electron injection into the conduction band of Si due to anodic oxidization or dissolution of Si involving cathodic hydrogen evolution on catalytically active Pd particles.

In conclusion, in the present study of metal particle enhanced HF etching of Si, we revealed that strong photoillumination promotes the etching of Pt-modified n-Si under the absence of dissolved oxygen in the HF solution. Pd particles show unique behavior in which the etching of n-Si proceeds at a high rate accompanying hydrogen evolution under dark conditions and the absence of dissolved oxygen.

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References

[1] V. Lehmann, "Electrochemistry of Silicon", Wiley-VCH, Weinheim (2002).

[2] C. Lévy-Clément, A. Lagoubi, and M. Tomkiewicz, J. Electrochem. Soc., 141, 958-967 (1994).

[3] K. Kawakami, T. Fujii, S. Yae, and Y. Nakato, J. Phys. Chem. B, 101 4508-4513 (1997).

[4] L. T. Canham, Appl. Phys. Lett., 57, 1046-1048 (1990).

[5] N. Sato, K. Sakaguchi, K. Yamagata, Y. Fujiyama, and T. Yonehara, J. Electrochem. Soc., 142, 3116-3122 (1995).

[6] K. Watanabe, T. Okada, I. Choe, and Y. Sato, Sens. Actuators B, 33, 194-197 (1996).

[7] J. J. Kelly, X. H. Xia, C. M. A. Ashruf, and P. J. French, *IEEEE Sens. J.*, 1, 127-142 (2001).

[8] S. Yae, Y. Kawamoto, H. Tanaka, N. Fukumuro, and H. Matsuda, *Electrochem. Comm.*, 5, 632-636 (2003).

[9] S. Yae, H. Tanaka, T. Kobayashi, N. Fukumuro, and H. Matsuda, *Phys. Stat. Sol. (c)*, 2, 3476–3480 (2005).

[10] K. Tsujino, M. Matsumura, and Y. Nishimoto, Sol. Energy Mater. Sol. Cells, 90, 100-110 (2006).

[11] S. Yae, T. Kobayashi, T. Kawagishi, N. Fukumuro, and H. Matsuda, *Solar Energy*, **80**, 701-706 (2006).

[12] S. Yae, T. Kobayashi, T. Kawagishi, N. Fukumuro, and H. Matsuda, "Pits and Pores III: Formation, Properties and Significance for Advanced Materials", Electrochem. Soc. Proc. Vol. 2004-19, Ed. by P. Schmuki et al., The Electrochemical Society, Pennington (2006) pp. 141-146.

[13] S. Yae, K. Matsumoto, N. Nasu, N. Fukumuro, and H. Matsuda, "Extended Abstracts of the 2004 Joint International Meeting 206th Meeting of The Electrochemical Society and 2004 Fall Meeting of The Electrochemical Society of Japan", Hawaii, 2004, abst. #1558.; S. Yae, N. Nasu, K. Matsumoto, T. Hagihara, N. Fukumuro, and H. Matsuda, Electrochim. Acta, submitted for publication.

[14] M. Fujitani, R. Hinogami, J. G. Jia, M. Ishida, K. Morisawa, S. Yae, and Y. Nakato, *Chem. Lett.*, **1997**, 1041-1042.

[15] A. J. Bard, R. Parsons, and J. Jordan (Eds.), "Standard Potentials in Aqueous Solution", IUPAC, Marcel Dekker, New York (1985).

[16] S.M. Sze, "Physics of Semiconductor Devices", 2nd ed. John Wiley & Sons, New York (1981) pp. 22-32.

[17] K. Rajeshwar, "Fundamentals of Semiconductor Electrochemistry and Photoelectrochemistry" in "Encyclopedia of Electrochemistry Vol. 6 Semiconductor Electrodes and Photoelectrochemistry", Ed. by S. Licht, WILEY-VCH, Weinheim (2002) pp. 29-33. [18] J. Nelson, "The Physics of Solar Cells", Imperial College Press, London (2003) pp.9-11. [19] K. Osseo-Asare, D. Wei, and K. K. Mishra, J.

Electrochem. Soc., 143, 749-751 (1996).

[20] X. G. Zhang, "Electrochemistry of Silicon and Its Oxide", Kluwer Academic/Plenum Publishers, New York (2001) Ch. 2 and 7.

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