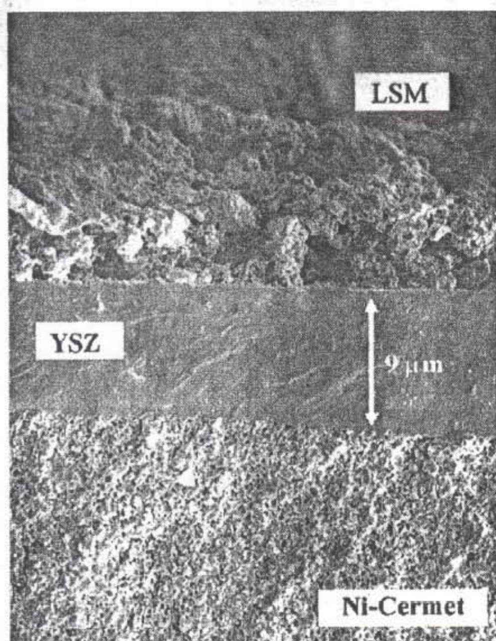

Fig. 5. SEM micrograph showing cross section of a Ni-Cermet/YSZ/LSM thin-film fuel cell that was thermally cycled and tested over 400 h.

Conclusions

A highly successful procedure has been developed which allows deposition of thin-film ceramics on highly porous substrates. The methodology is inexpensive and scalable. Thin-film SOFCs fabricated using these techniques demonstrate performances of close to 2 W/cm^2 at 800°C. Current interrupt techniques indicate the majority of the voltage loss at high current density is due to ohmic losses, most likely associated with cathode/electrolyte contact resistance (0.1 Ω cm^2). The exceptional performance of the thin-film SOFCs implies that reduced temperature operation is possible while still maintaining high power density.

Acknowledgment

This research was supported by the Laboratory Technology Research Program (ER-LTR), Office of Computational and Technology Research, U.S. Department of Energy under a CRADA (Cooperative Research and Development Agreement) between Ernest Orlando Lawrence Berkeley National Laboratory (Berkeley Lab) and The Electric Power Research Institute (EPRI), Palo Alto, CA 94303, under U.S. DOE Contract DE-AC03-76SF00098.

Manuscript submitted Sept. 23, 1996; revised manuscript received Oct. 20, 1996.

Lawrence Berkeley National Laboratory assisted in meeting the publication costs of this article.

REFERENCES

1. N. W. Minh, *J. Am. Ceram. Soc.*, **76**, 563 (1993).
2. A. Negishi, K. Nozaki, and T. Ozawa, *Solid State Ionics*, **3/4**, 443 (1981).
3. A. O. Isenberg, *ibid.*, **3/4**, 431 (1981).
4. T. Setogushi, T. Inou, H. Takebe, K. Eguchi, K. Morinaga, and H. Arai, *This Journal*, **139**, 2875 (1992).
5. U. B. Pal and S. C. Singhal, *ibid.*, **137**, 2937 (1990).
6. S. J. Visco, L.-S. Wang, S. Souza, L. C. De Jonghe, *Mater. Res. Soc. Symp. Proc.*, **369**, 683 (1995).
7. L. A. Chick, L. R. Pederson, G. D. Maupin, J. L. Bates, L. E. Thomas, and G. I. Exartos, *Mater. Lett.*, **10**, 6 (1990).

Highly Selective Chemical Etching of Si *vs.* $Si_{1-x}Ge_x$ Using NH_4OH Solution

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ABSTRACT

Highly selective chemical etching of Si *vs.* epitaxial $Si_{1-x}Ge_x$ in NH_4OH solution has been investigated. It was found the selectivity was better than 80:1 even for a $Si_{0.9}Ge_{0.1}$ in 10 weight percent (w/o) NH_4OH at 75°C. As the fraction x of Ge was increased, higher selectivity was obtained due to the decrease of the etch rate of the $Si_{1-x}Ge_x$. The achievement of the excellent selectivity in a $Si/Si_{1-x}Ge_x/Si$ heterostructure was clearly demonstrated by scanning electron microscopy. Surfaces of etched $Si_{1-x}Ge_x$ samples were analyzed using x-ray photoelectron spectroscopy. The high etch selectivity obtained in NH_4OH is essentially due to a passivation-film effect at the $Si_{1-x}Ge_x$ surface.

Introduction

Selective chemical etching of Si or $Si_{1-x}Ge_x$ has become a key technique in the fabrication of $Si_{1-x}Ge_x/Si$ heterojunction devices[1-4] and new kinds of structures.[5-7] In the fabrication process of the heterojunction device employing thin Si or $Si_{1-x}Ge_x$ layers, for example, it is often necessary to contact to buried Si or $Si_{1-x}Ge_x$ layers. To make contact to buried $Si_{1-x}Ge_x$ layers one needs to etch Si and vice versa. Thin film bond and etchback silicon on insulator (BESOI) of good quality was fabricated using a strained $Si_{0.7}Ge_{0.3}$ as an etch-stop layer. An important process of the fabrication was to selectively etch Si over the $Si_{0.7}Ge_{0.3}$.[5] Recently, we proposed and successfully fabricated Si quantum wires based on selectively removing $Si_{1-x}Ge_x$ from a $Si/Si_{1-x}Ge_x$ trench array.[7]

During the last several years, therefore, the characteristics of several chemical wet etchants for selectively etching $Si_{1-x}Ge_x$ and/or Si on $Si_{1-x}Ge_x/Si$ heterostructures have been investigated.[5-11] Among them, two aqueous etchants to selectively etch Si over $Si_{1-x}Ge_x$ were reported. One is the etchant composed of $KOH:K_2Cr_2O_7$:propanol:H_2O.[6,10] A selectivity of 40:1 was obtained recently in etching Si over B-doped $Si_{0.7}Ge_{0.3}$, but it is completely isotropic and requires the use of a hard mask.[10] Another is the mixture of ethylenediamines, pyrocatechol, and water (EPW), which was reported to etch Si over $Si/Si_{1-x}Ge_x$ ($x > 0.2$) with a high selectivity.[11] For a practical application, however, a selective chemical etching should be compatible with silicon integrated circuit (IC) processes. As a result, IC-compatible, nontoxic, anisotropic, simple, and highly selective etchants become important for processing high performance devices. Solutions based on ammonium hydroxide-water mixtures have been widely used in Si IC processes.[12] Koyama *et al.* investigated the etch characteristics of $Si_{1-x}Ge_x$ alloy in an ammoniac wet cleaning solution $NH_4OH:H_2O_2:H_2O$.[13] It was observed that the etch rate of $Si_{1-x}Ge_x$ was in the order of

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nanometers per minute and faster than that of Si, the result was suggested mainly because of the difference in microscopic reactions of Si and Ge with NH_4OH and H_2O_2. We first report here on highly selective chemical etching of Si with respect to epitaxial $Si_{1-x}Ge_x$ alloy in NH_4OH solution. The selectivity was better than 80:1 for various $Si_{1-x}Ge_x$ alloys with different fractions x of Ge ($0.1 \le x \le 0.3$). Actually, the $Si_{1-x}Ge_x$ acts as an etch-stop layer. Scanning electron microscopy (SEM) was used to observe the cross section of a selectively etched $Si/Si_{1-x}Ge_x/Si$ heterostructure. The change in the surface chemical states of etched $Si_{1-x}Ge_x$ was analyzed using x-ray photoelectron spectroscopy (XPS). The results observed suggest that a very thin porous oxide layer as passivation film forms at the $Si_{1-x}Ge_x$ surface in NH_4OH solution, effectively decreasing the etch rate of $Si_{1-x}Ge_x$ and consequently resulting in very high etch selectivity.

Experimental

Undoped $Si_{1-x}Ge_x$ (x = 0.1, 0.24, 0.3) epitaxial films were grown on p-type (100) Si wafers by very low-pressure chemical vapor deposition (VLPCVD). These as well as (100) Si wafers were used as samples. Beside these, a $Si/Si_{0.8}Ge_{0.2}/Si$ sandwich structure was grown and used for observation by SEM. The thickness of epitaxial $Si_{1-x}Ge_x$ and Si were about 150 nm. The details of the growth technique have been reported elsewhere.[14] SiO_2 patterns were formed by conventional SiO_2 chemical vapor deposition and photolithography technique on the top of the samples. Chemical etching was performed using 10 w/o NH_4OH solution at 75°C in a temperature-controlled system with a reflux condenser. SiO_2-patterned samples were first dipped in diluted HF for a few seconds to strip the native oxide, rinsed thoroughly in deionized water, and then immediately placed in the etch bath and etched with different etch times. After etching both SiO_2 patterns and the oxide formed on the surface of the etched parts in the etching procedure were removed completely by diluted HF. Etch depths of samples were measured using a Tencor Instrument Alpha step profilometer.

To analyze the cross section of $Si/Si_{1-x}Ge_x/Si$ etched under this condition, we carried out the experiment with a $Si/Si_{0.8}Ge_{0.2}/Si$ sandwich structure sample in the same etch condition. Here, lithography technique and reactive ion etching were carried out to generate line-and-space $SiO_2/Si/Si_{0.8}Ge_{0.2}/Si$ trench array along with [011] direction. SiO_2 pattern acted as a mask, protected the (100) facet of the sample from etching, while the two sides of the array consisting of (110) facets were exposed to etch.

Moreover, XPS study of etched $Si_{1-x}Ge_x$ surfaces was conducted. Three as-grown $Si_{0.7}Ge_{0.3}$ samples were HF cleaned first, washed in deionized water, and then two of those samples were put into the NH_4OH etchant for 0.5 and 1 h, and then were placed into a high vacuum chamber to perform measurement.

Results and Discussion

Figure 1a shows the results of the etch depth *vs.* the etch time in 10 w/o NH_4OH solution at 75°C. It can be seen that the relation between the etch depth and the etch time is almost linear for each sample with different Ge fractions ($x \le 0.3$). Consequently, the etch rate is derived from the slope of the plot. It gives the etch rates of about 640 Å/min for Si, 7.4 Å/min for $Si_{0.9}Ge_{0.1}$, 4 Å/min for $Si_{0.24}Ge_{0.76}$, and 2.4 Å/min for $Si_{0.3}Ge_{0.7}$ alloy, respectively, in 10 w/o NH_4OH at 75°C. The selectivity, defined as the etch rate ratio of the (100) Si to $Si_{1-x}Ge_x$ layer, as a function of Ge fraction x, is shown in Fig. 1b. Correspondingly, the selectivity is 86:1 for x = 0.1, 160:1 for 0.24, and 267:1 for 0.3, respectively.

Figure 2 shows a cross-sectional SEM image of an $SiO_2/Si/SiGe/Si$ trench array after etching, the top layer is the SiO_2 mask. It can be clearly seen that the epitaxial Si layer was partly etched, its width reduced from 7500 to about 2000 Å. The etching of the Si substrate stopped at two (111) facets, forming a triangle trench. As expected, the $Si_{1-x}Ge_x$ layer was almost unetched in this etch process. It is known that defects usually affect the characteristic of a wet chemical etch. There are many defects in the epitaxial Si compared with the substrate Si. The observation shows similarity in selective etch characteristics for both epitaxial and substrate Si which demonstrates clearly that $Si_{1-x}Ge_x$ alloy is an excellent etch-stop layer in NH_4OH solution.

Si 2p photoemission spectra of the $Si_{0.7}Ge_{0.3}$ samples are shown in Fig. 3. The photoemission peak at a binding energy about 99 eV is due to elemental Si, another peak near 102 eV is SiO_x.[15] The corresponding Ge $2p_{3/2}$ photoemission spectra are shown in Fig. 4. The peaks at about 1218 and 1222 eV are assigned to elemental Ge and GeO_x, respectively. The intensities of both SiO_x and GeO_x peaks increase with increasing etch time. Moreover, the SiO_x

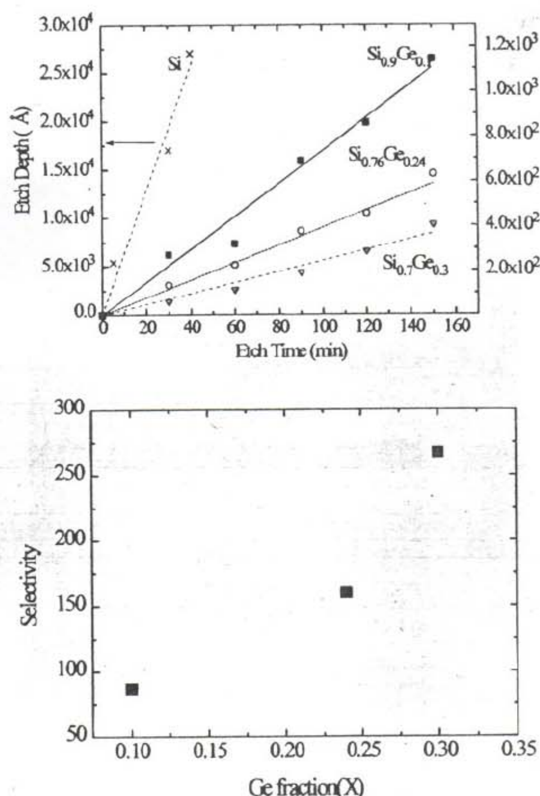

Fig. 1. (a, top) Etch depths *vs.* etch time in 10 w/o NH_4OH at 75°C; and (b, bottom) the dependence of the selectivity on the Ge fraction in $Si_{1-x}Ge_x$.

peaks increase more obviously than the GeO_x. At the same time, the intensities of elemental Si and Ge peaks decrease regularly. The above observations indicate that Si and Ge in samples were oxidized to form SiO_x and GeO_x in the etching process, and the oxides stuck on the surface of the $Si_{1-x}Ge_x$ sample. Furthermore,

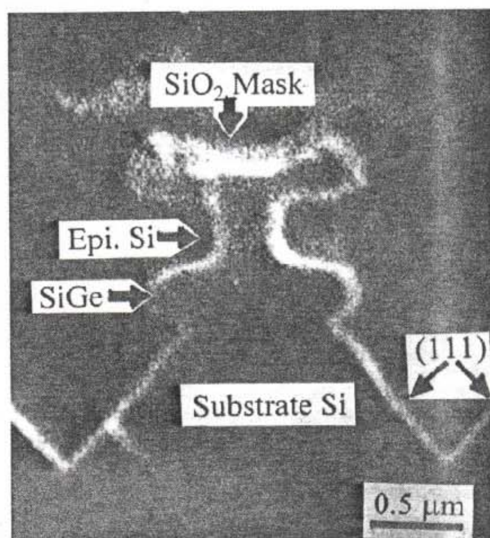

Fig. 2. The SEM cross-sectional image of a $Si/Si_{1-x}Ge_x/Si$ heterostructure etched in NH_4OH.

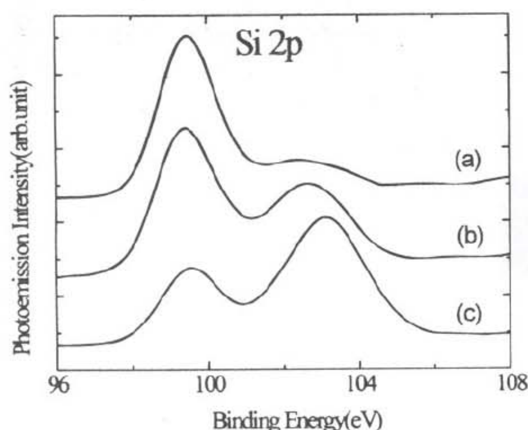

Fig. 3. Si 2p XPS of $Si_{0.7}Ge_{0.3}$ film (a) not etched, (b) etched for 0.5 h, and (c) etched for 1 h.

that the binding energy of SiO_x shifts gradually to high energy demonstrates that the oxygen fraction x increases slightly with etch time and the oxide becomes the prevalent constituent.[15] Being different from the thermal oxidation, the film composed with SiO_x and GeO_x formed in water was a layer of porous oxide.[16] Although porous, the oxide still acts as an effective passivation film on the surface of the $Si_{1-x}Ge_x$. In the etching process, hydroxide ions OH^- in the etchant must first diffuse through the porous oxide layer and attack the sample. The oxide effectively reduces the concentration of the OH^- at the sample surface. This, in turn, decreases the etching rate of the $Si_{1-x}Ge_x$ drastically. For comparison, we investigated the etch of $Si_{1-x}Ge_x$ in aqueous KOH solution; it was much higher than that in NH_4OH. One reason may be that the etch rate of Si oxide in NH_4OH is much lower than that in KOH. [17] Hence, the passive film throttles the etching because both the dissolution of the oxide film and the diffusion rate of OH^- in NH_4OH through the oxide film becomes rate limiting. It is suggested that the mechanism of the etch stop of $Si_{1-x}Ge_x$ in NH_4OH is a passivation-film effect.

With the observations above, the basis by which Si can be selectively etched from $Si_{1-x}Ge_x$ layers is through the difference of the oxidation between the Si and the $Si_{1-x}Ge_x$ surface in NH_4OH. Compared with a surface consisting of only Si-Si bonds, the presence of Ge in the film results in a substantial number of weak Si-Ge and weaker still Ge-Ge bonds at the surface. The Si-Ge bond and Ge-Ge bond are more easily broken to form Si-OH and Ge-OH at the surface. Moreover, the defects and strain in $Si_{1-x}Ge_x$ samples promote the oxidation process of Si and Ge to form SiO_x and GeO_x. This is supported by previous observations of enhanced oxidation at the surfaces of heavily doped silicon in KOH solution.[18]

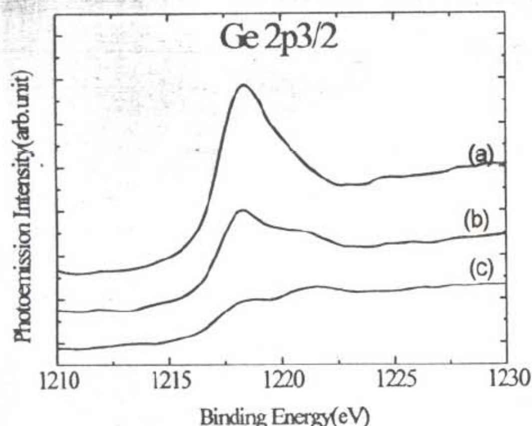

Fig. 4. Ge $2p_{3/2}$ XPS of $Si_{0.7}Ge_{0.3}$ film (a) not etched, (b) etched for 0.5 h, and (c) etched for 1 h.

Moreover, Ge has been reported to act like a catalytic agent, which promotes the decomposition Si-OH to form more SiO_x. [19,20] The more Ge fractions in $Si_{1-x}Ge_x$, the quicker the growth rate of SiO_x in NH_4OH, increasing both the coverage and the density of SiO_x on the surface of $Si_{1-x}Ge_x$. Consequently, the etch rate of $Si_{1-x}Ge_x$ decreases with increasing Ge fraction x.

Conclusion

We have reported on highly selective chemical etching of Si *vs.* epitaxial $Si_{1-x}Ge_x$ in NH_4OH solution. The selectivity for etching Si *vs.* the $Si_{0.9}Ge_{0.1}$ was better than 80:1, and higher selectivity was obtained as the Ge fraction x increased. The results presented here show that the NH_4OH solution is an excellent selective etchant for selectively etching Si *vs.* $Si_{1-x}Ge_x$, consequently, the $Si_{1-x}Ge_x$ acts as an etch-stop layer. The SEM observation of $Si/Si_{1-x}Ge_x/Si$ heterostructure demonstrated that the $Si_{1-x}Ge_x$ alloy is an effective etch-stop layer. Moreover, the change in the surface chemical state of etched $Si_{1-x}Ge_x$ surfaces measured by XPS showed that a passive layer composed mainly of SiO_x and GeO_x formed at the surface in the etching process. The etch stop of the $Si_{1-x}Ge_x$ layer may be because the presence of Ge enhances the oxidation at the $Si_{1-x}Ge_x$ surface, and consequently the SiO_x protects the $Si_{1-x}Ge_x$ from further etching in NH_4OH solution.

Acknowledgments

The authors acknowledge Professor J. J. Kelly and Dr. Ad.mens at Utrecht University, the Netherlands for helpful discussions and XPS measurement, Dr. D. A. Du and C. Y. Lin of Center for Materials Analysis at Nanjing University, and Z. H. Xie of Nanjing Electronic Device Institute for technical assistance. The work is supported by the Chinese National Nature Science Foundation and National High Technology Research and Development Foundation.

Manuscript submitted Aug. 12, 1996; revised manuscript received Dec. 16, 1996.

Nanjing University assisted in meeting the publication costs of this article.

REFERENCES

1. G. L. Patton, J. M. Comfort, B. S. Meyerson, E. F. Crabbe, G. J. Scilla, E. Defresart, J. M. Stork, J. Y. C. Sun, D. L. Harame, and J. N. Burghartz, *IEEE Electron Device Lett.*, **EDL-11,** 171 (1990).
2. R. Karunasiri, J. S. Park, and K. L. Wang, *Appl. Phys. Lett.*, **59,** 2588 (1991).
3. R. Karunasiri, J. Park, Y. Mii, and K. Wang, *ibid.*, **57,** 2585 (1990).
4. Y. Mii, Y. Xie, E. Fitzgerald, D. Monroe, F. Thiel, B. Weir, and L. Feldman, *ibid.*, **59,** 1611 (1991).
5. D. J. Dodbey, M. E. Twigg, and H. L. Hughes, *This Journal*, **137,** 3219 (1990).
6. D. J. Godbey, H. Hughes, F. Kub, M. Twigg, L. Palkuti, P. Leonov, and J. Wang, *Appl. Phys. Lett.*, **56,** 373 (1990).
7. J. L. Liu, Y. Shi, F. Wang, Y. Lu, R. Zhang, P. Han, S. L. Gu, and Y. D. Zheng, *ibid.*, **68,** 2137 (1996).
8. A. H. Krist, D. J. Godbey, and N. P. Green, *ibid.*, **58,** 1899 (1991).
9. T. K. Corns, M. O. Tanner, and K. L. Wang, *This Journal*, **142,** 1260 (1995).
10. L. Shang, S. A. Campbell, and W. H. Liu, *ibid.*, **141,** 507 (1994).
11. R. M. Finne and D. L. Klein, *ibid.*, **114,** 965 (1967).
12. W. Kern and D. A. Puotinen, *RCA Rev.*, **31,** 187 (1970).
13. K. Koyama, M. Hiroi, T. Tatsumi, and H. Hirayama, *Appl. Phys. Lett.*, **57,** 2202 (1990).
14. Y. D. Zheng, R. Zhang, L. Q. Hu, S. L. Gu, R. L. Jiang, R. H. Wang, P. Han, *Mater. Res. Soc. Symp. Proc.*, **263,** 227 (1992).
15. D. Graf, M. Grundner, and R. Schulz, *J. Vac. Sci. Technol. A*, **7,** 808 (1989).
16. E. D. Palik, J. W. Faust, Jr., H. F. Gray, and R. F. Greene, *This Journal*, **129,** 2051 (1982).
17. U. Schnakenberg, W. Benecke, B. Lochel, S. Ullerich, and P. Lange, *Sens. Actuators A*, **25-27,** 1 (1991).
18. E. D. Palik, V. M. Bermudes, and O. J. Glembocki, *This Journal*, **132,** 135 (1985).
19. D. K. Nayak, K. Kamjoo, J. S. Park, J. C. S. Woo, and K. L. Wang, *Appl. Phys. Lett.*, **57,** 369 (1990).
20. F. K. Legoues, R. Rosenberg, T. Nguyen, F. Himpsel, and B. S. Meyerson, *J. Appl. Phys.*, **65,** 1724 (1989).