Sensors and Materials, Vol. 10, No. 7 (1998) 425–433
MYU Tokyo

S & M 0344

CAD for Silicon Anisotropic Etching
— Effect of Etching Products and Diffusion —

Osamu Tabata

Ritsumeikan University, Department of Mechanical Engineering,
Faculty of Science and Engineering
1-1-1 Nojihigashi, Kusatsu-city, Shiga 525-8577, Japan

(Received March 18, 1997; accepted December 10, 1997)

***Key words*:** silicon, anisotropic etching, simulation, etching products, diffusion

Recently, an anisotropic etching simulation program for silicon based on the Wulff-Jaccodine graphical method has been successfully developed. The experimentally measured distribution of etch rates for all crystallographic orientations is required for this program. In this study, the dependence of etching rates on the amount of dissolved silicon and on resulting changes in pH and conductivity of tetramethyl ammonium hydroxide (TMAH) etchants was investigated. The experimental results strongly suggested that the products formed during the etching reaction affect the etching characteristics. Next, an etching experiment using a small etching hole was carried out to investigate the diffusion effect. The results suggested that the influence of diffusion should also be taken into account in the simulation program. Finally, an idea for a simulation program based on a graphical approach combined with the physics of atomic-scale phenomena is proposed to take the effects of etching parameters such as additives, etching products and diffusion into account.

1. Introduction

Anisotropic etching of silicon is a key technology for fabricating various 3-dimensional structures for micro electro mechanical systems (MEMS). Many etchants including inorganic aqueous solutions of KOH, NaOH, CsOH and NH_4OH, as well as organic aqueous solutions containing ethylenediamine, hydrazine, choline and tetramethyl ammonium hydroxide (TMAH, $(CH_3)_4NOH$) have been proposed. The characteristics such as etching rate of silicon, etching rate dependencies on crystallographic orientations, etched surface roughness and etching rate of silicon dioxide depend on the etchant and its temperature and concentration. In particular, the etching rate of silicon and its dependency on crystallographic orientations are of great interest since they strongly affect results such as the dimensions of the etched 3-D structure. Therefore, many experiments regarding etching rate and its dependence on temperature and concentration for the three principle crystallographic planes, (100), (110) and (111), have been performed. However, it is very difficult to predict the result of etching empirically from only these three etching rates. Thus, many time-consuming experiments have been required to design and implement new structures.

Recently, several attempts have been made to develop anisotropic etching simulation programs which enable device design engineers to accurately predict etched results. These programs would reduce the need for time-consuming experiments and thus reduce the time and cost of development. One simulation program is based on the Wulff-Jaccodine graphical method.(1,2) This approach gives fairly accurate predictions if etching rate information for all crystallographic orientations is available. Therefore, an attempt to measure etching rate information for all crystallographic orientations under typical concentrations and temperatures with KOH has been initiated,(3) since KOH is the most commonly used etchant for MEMS fabrication. On the other hand, etching rates of all crystallographic orientations do not depend only on concentration and temperature but also on practical parameters, such as stirring conditions, additives and degradation of the etchant. It is not practical to measure etching rate for all crystallographic orientations under all of these parameters. If we can identify a few parameters that dominate etching rate for all crystallographic orientations, it will be possible to reconstruct etching rates for all crystallographic orientations from these parameters, which can be fitted for every etching condition by comparing etched structures with predicted structures for a number of experiments. For the extraction of the dominant parameters, a simulation based on the physics of atomic-scale phenomena(4–6) is promising. In this approach, few parameters are required to predict the etching rate for all crystallographic orientations. However, up to now, the definition and combination of parameters that can be used to reconstruct etching rates for all crystallographic orientations are not unique.

In the first part of this paper, experiments to determine the effect of etching products on etching characteristic are described. The pH and conductivity were used as to characterize the etchant conditions. The results of an etching experiment using a small etching hole, which was carried out to observe the diffusion effect during the etching process, are shown. Finally, an idea for a simulation based on a graphical approach combined with the physics of atomic-scale phenomena is proposed.

2. Effect of Etching Products

The hydroxide ion is thought to play an important role in anisotropic etching. Therefore, much attention has been paid to its concentration in etching solutions. However, less attention has been paid to the concentration of the etching products. In this experiment, the etching rates of (100) silicon in two different TMAH etchants having the same pH value but different amounts of etching products were measured. The concentration of products was varied by dissolving silicon in TMAH. The pH of the control etchant was adjusted by dilution with DI water. At equal values of pH, the conductivity (σ) of the etchant was taken to characterize the mobility of the hydroxide ion in the experimental etchants.

The σ of a solution is defined by the charge, mobility and concentration of all ionic species in the solution. Major ions in the etching solution are hydrated cations and hydroxide ions. Because the mobility of hydrated cations is thought to be smaller than that of hydroxide ions, the measured value of σ is thought to reflect the concentration and mobility of hydroxide ions. Because the concentration of hydroxide ions can be determined from pH values, differences in hydroxide ion mobility can be monitored by measuring both pH and σ.(7)

TMAH at a concentration of 22 wt.% (TCL-22, Kanto Chemical Corp.) was used, and solutions with lower concentrations were prepared by dilution with DI water. Dissolved silicon experiments were carried out with silicon dissolved at 0.3 to 4.0 mol/l in TMAH. The pH and σ of the TMAH were measured using a pH meter (Horiba Corp.) and a conductivity meter (Yokogawa Corp.). Etching was carried out with no stirring in a glass vessel thermostated in a temperature bath at 80°C.

Figure 1 shows the dependence of the Si (100) etching rate on pH for diluted TMAH and Si dissolved in TMAH. The etching rates decreased with increasing pH value. These

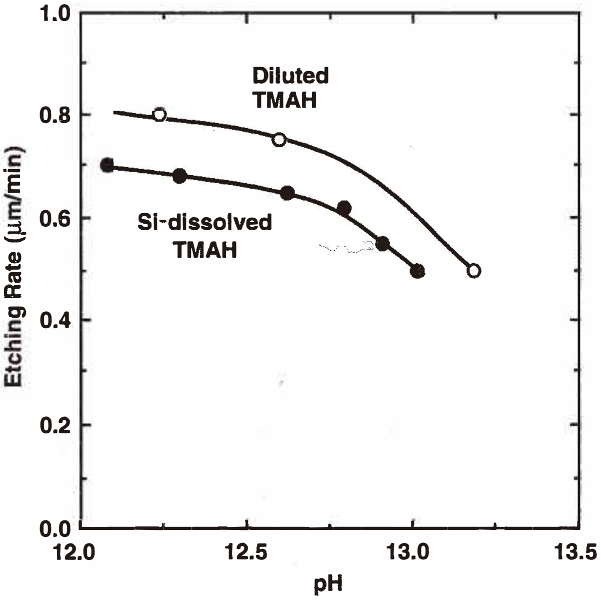

Fig. 1. Dependence of Si (100) etching rate on pH for diluted TMAH and Si-dissolved TMAH.

dependencies coincide with the fact that the etching rate decreases with increasing TMAH concentration above 5 wt.%. However, etching rates for diluted TMAH and TMAH with dissolved silicon did not coincide.

To clarify the reason for this difference in Si (100) etching rate, the relationships between pH and σ for silicon dissolved in 22 wt.% TMAH and diluted 22 wt.% TMAH were investigated. Figure 2 shows the dependence of pH and σ on the TMAH concentration. Both pH and σ increased with increasing TMAH concentration because the number of hydroxyl ions increases. Figure 3 shows an inverse dependence of pH and σ on the amount of dissolved silicon. These changes in pH and σ are caused by the consumption of hydroxyl ions during the etching reaction. The σ first decreased and then maintained a nearly constant value. The constant value of σ is thought to be defined by the concentration and the mobility of the hydrated TMA^+ ions. The relationship between pH and σ for silicon dissolved in 22 wt.% TMAH was compared with that for diluted 22 wt.% TMAH. The results are shown in Fig. 4. In a certain pH range, values of σ for TMAH with dissolved silicon were lower than those of diluted TMAH at the same pH. This suggests that the mobility of the hydroxide ion in the TMAH with dissolved silicon is lower than that in the diluted TMAH. This difference in mobility is thought to be caused by the etching products in the solution. This difference in mobility of the hydroxide ion is thought to affect the Si (100) etching rate.

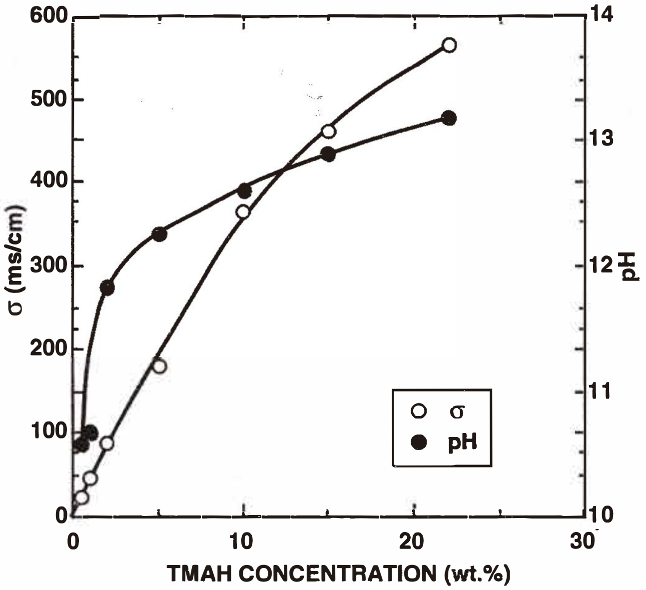

Fig. 2. Dependence of the pH and σ on TMAH concentration.

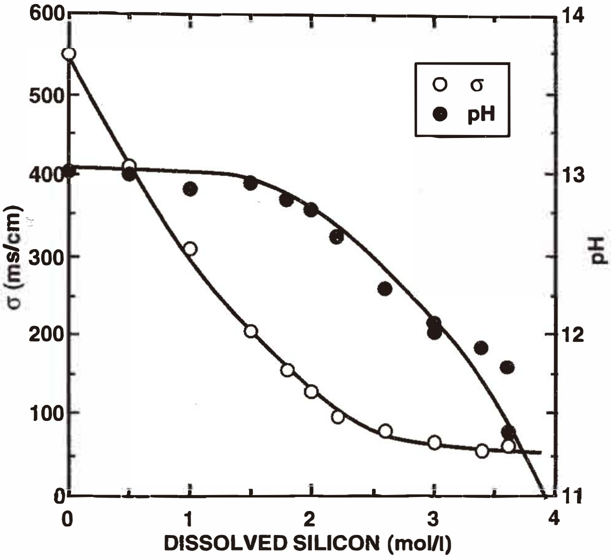

Fig. 3. Dependence of the pH and σ on the amount of dissolved silicon.

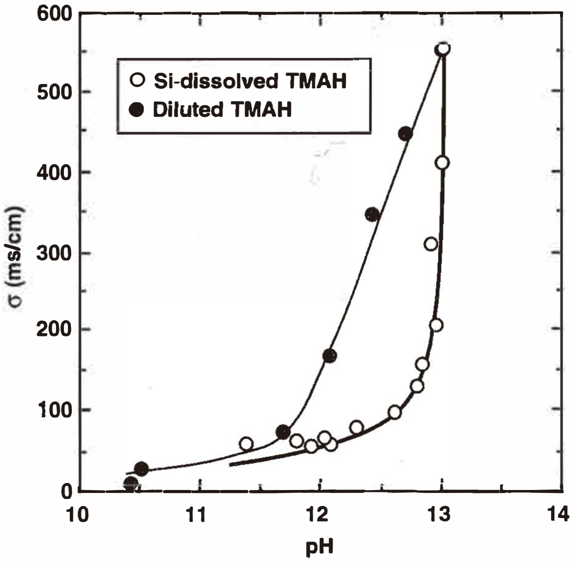

Fig. 4. Relationship between pH and σ for silicon dissolved in 22 wt.% TMAH and diluted 22 wt.% TMAH.

3. Diffusion Effect

In this section, the effect of diffusion on etching characteristics is illustrated using an experimental result. This result is difficult to predict with current etching simulation software, which does not take into account diffusion processes in the solution that affects the supply of etching solution and etching product removal as etching proceeds.

The cross-sectional structure of the sample used in this experiment is shown in Fig. 5. A 200-nm-thick polysilicon sacrificial layer covered with silicon nitride having an etching hole with a diameter of 2, 3, 4 or 8 μm was formed on a (100) silicon substrate. Etching of the polysilicon sacrificial layer and underlying silicon substrate was carried out simultaneously through this etching hole using 5 wt.% KOH at 80°C. The fabricated structure was a deep V-shaped cavity with an overlying circular membrane. The inclination of its side wall was almost 45 degrees. Figure 6 shows the diameter obtained. A smaller etching hole resulted in a smaller membrane diameter.

These results can be explained as follows. The amount of reactant required for the etching reaction increases with the area to be etched, which is almost proportional to the square of the radius of the membrane. On the other hand, the supply of etching solution is limited by diffusion through the small etching hole. Therefore, the concentration of etching solution in the cavity decreases as etching proceeds. The etching rate of polysilicon by KOH at 80°C depends strongly on the concentration of the etchant and has a maximum value of 1.4 μm/min at a concentration of approximately 20 wt.%. This behavior is very similar to that measured for a single-crystal silicon plane. From these results, it is obvious that if we use an etching solution with a concentration of less than 20 wt.%, the etching rate

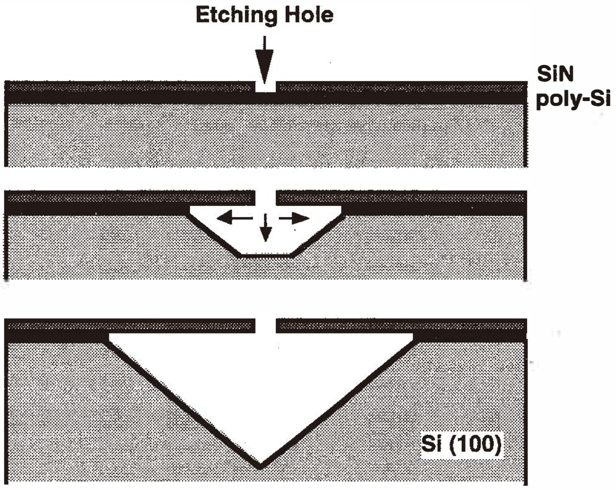

Fig. 5. Schematic diagram of simultaneous polysilicon sacrificial layer and silicon substrate etching.

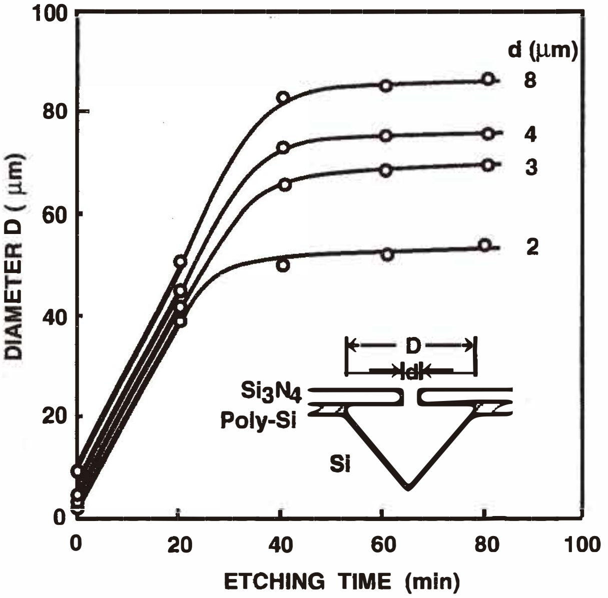

Fig. 6. Measured membrane diameter as a function of etching time using a polysilicon sacrificial layer with a small etching hole pattern.

decreases with the concentration of the etching solution in the cavity. At the same time, the amount of etching product increases as etching proceeds. The etching rate decreases as the concentration of etching product in the cavity increases, as shown in section 2 for TMAH.

4. Idea for a New Simulation Procedure

It is very difficult to predict the experimental results shown in Fig. 6 using a current anisotropic etching simulation program because the characteristics of the etching solution, such as concentration, are not taken into account in the simulation. However, with increasing demand for a high aspect ratio and/or sophisticated 3-dimensional structures, this effect will become more pronounced and thus should be included in simulation algorithms.

From a practical point of view, the idea for a simulation program based on the graphical approach combined with the physics of atomic-scale phenomena is promising. This idea is shown schematically in Fig. 7. A module to be developed will calculate the etching rates for all crystallographic orientations from a few parameters. To minimize the difference between simulated and experimental results, the parameters can be tuned by comparing

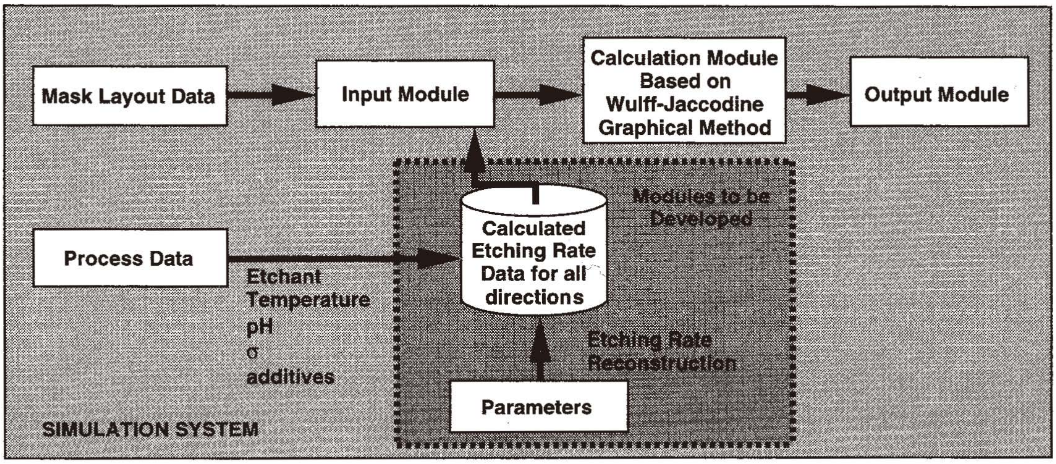

Fig. 7. Idea for a simulation program based on the graphical approach combined with the physics of atomic-scale phenomena.

experimentally etched structures fabricated using a certain test pattern with simulations. Once this is done, better results can be obtained from simulations using tuned parameters.

The key point is the selection of parameters. It makes sense to select parameters from the viewpoint of crystallographic growth science. By analogy to the crystallographic growth mechanism, etching rates are thought to be limited by (1) etching kinetics at the crystal surface and (2) diffusion in the solution. Concerning etching kinetics, the importance of surface free energy is obvious. The etched (111) and (100) planes have smooth surfaces, and the etching rates of these orientations show minima in all crystallographic orientations. These (111) and (100) planes coincide with singular surfaces for diamond lattice crystals such as silicon. If the surface free energy is plotted as a function of crystallographic orientation, it shows sharp minima, so-called "cusps", at the singular surface.

However, surface free energy alone does not fully determine the dependency of etching characteristics on etching conditions such as the concentration of etching products. Therefore, some parameters are required to describe the condition of the etchant. These should be based preferably on measurable values such as pH and conductivity. The importance of diffusion was also shown using experimental results. It is expected that calculation of the concentration of etchant and etching products in the cavity will become possible using a simulation program based on fluid dynamics. By combining the calculation of fluid flow with the anisotropic etching simulation program, it will be possible to predict the structure shown in Fig. 5. I propose use of the structure shown in Fig. 5 as a challenging problem for simulation.

5. Conclusion

The dependence of etching rate on the amount of dissolved silicon and resulting pH and conductivity changes of TMAH etchants was investigated. The experimental results strongly suggest that products of etching affect the etching reaction. The effect of diffusion on etching characteristics was shown. The structure used for this experiment was proposed as a challenging problem for an anisotropic etching simulation program. An idea for a simulation program based on a graphical approach combined with the physics of atomic scale phenomena was proposed.

References

1 K. Asaumi, Y. Irie and K. Sato: Proceedings of the 10th International Workshop on Micro Electro Mechanical Systems, 1997, p. 412.
2 A. Koide and S. Tanaka: Proceedings of the 10th Internaional Workshop on Micro Electro Mechanical Systems, 1997, p. 418.
3 K. Sato, M. Shikida, Y. Matsushima, T. Yamashiro, K. Asaumi, Y. Irie and Y. Yamamoto: Proceedings of the 10th Internaional Workshop on Micro Electro Mechaninal Systems, 1997, p. 406.
4 H. Camon, M. Djafari-Rouhani, D. Esteve, A. M. Gue and Z. Moktadir: Microsystem Technologies **1** (1995) 163.
5 P. J. Hesketh, C. Ju and S. Gowda: Journal of Electrochemical Society **140** (1993) 1080.
6 C. H. Sequin: International Conference on Solid State Sensors and Actuators, 1991, p. 801.
7 O. Tabata: Sensors and Actuators A **53** (1996) 335.

About the Author

Osamu Tabata received both his M.S. and Ph.D. from Nagoya Institute of Technology, Nagoya, Japan, in 1981 and in 1993, respectively.

Since 1981, he has been with the Toyota Central Research and Development Laboratories, Inc., Aichi, Japan. In 1996, he joined the Department of Mechanical Engineering, Ritsumeikan University, Shiga, Japan. He is currently engaged in the research of micro/nano processes, LIGA processes, thin-film mechanical property evaluation and MEMS.

He is an associate editor of *Journal of Micro Electro Mechanical Systems* and an editorial board member of *Sensors and Actuators.* He is also an active program committee participant for numerous international conferences.

He has been honored with the Science News Award for research in "Monolithic Pressure-Flow Sensors" in 1987, the Presentation Paper Award for research in "Anisotropic Etching of Silicon in TMAH Solutions" in 1992, the R&D 100 Award for research in "Thin-Film Young's Modulus Measurement Apparatus" in 1993 and the R&D 100 Award for research in "Thin Film Tensile Tester" in 1998.

He is a member of the Institute of Electrical Engineers of Japan, the Japan Society of Mechanical Engineers and the Institute of Electrical and Electronics Engineers.