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Electrochemical Etch-Stop Characteristics of TMAH:IPA:Pyrazine Solutions

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In this paper, the authors present the electrochemical etch-stop characteristics of single-crystal silicon in tetramethyl ammonium hydroxide (TMAH):isopropyl alcohol (IPA): pyrazine solutions. The addition of pyrazine to TMAH:IPA solutions increased the etch rate of (100) silicon; thus the time required by the etch-stop process was shortened. The current-voltage (*I-V*) characteristics of n- and p-type silicon in TMAH:IPA:pyrazine solutions were obtained. The open circuit potential (OCP) and passivation potential (PP) of n- and p-type silicon were obtained and the applied potential was selected between n- and p-type silicon PPs. The electrochemical etch-stop method was applied to the fabrication of 801 microdiaphragms of 20 μm thickness on a 5-inch silicon wafer. The average thickness of 801 microdiaphragms fabricated on one wafer was 20.03 μm and the standard deviation was $\pm$0.26 μm. The silicon surface of the etch-stopped microdiaphragm was extremely flat with no noticeable taper or nonuniformity. The benefits of the electrochemical etch-stop method for the etching of silicon in TMAH:IPA:pyrazine solutions become apparent when reproducibility of microdiaphragm thickness for mass production is realized. The results indicate that use of the electrochemical etch-stop method for the etching of silicon in TMAH:IPA:pyrazine solutions provide a powerful and versatile alternative process for fabricating high-yield silicon microdiaphragms.

1. Introduction

There has been increasing interest in the development of microelectromechanical systems (MEMS) using silicon micromachining technology. Because of its superior electrical and mechanical properties,[1] single-crystal silicon has been applied to various MEMS. Bulk micromachining is a very important technique, and making three-dimensional microstructures by anisotropic wet etching of single-crystal silicon is of even greater importance. For example, the sensitivities of piezoresistive and capacitive pressure sensors, respectively, are inversely proportional to the square and the cube of the thickness of diaphragms formed by anisotropic wet etching.[2,3] In the case of microdiaphragms, in particular, if there exists a significant irregularity or nonuniformity on the etched microdiaphragm surface, the stress distribution in the microdiaphragm will be disturbed. This causes significant variations in the sensitivity, the offset and the dynamic range of the resulting devices.[4] Therefore, accurate control of microdiaphragm thickness with a uniformly etched surface is very important for using micromachined silicon structures as sensing or active elements.

Anisotropic etchants that are frequently used for single-crystal silicon are KOH, NaOH, ethylenediamine pyrocatechol water (EDP), hydrazine water and tetramethyl ammonium hydroxide (TMAH). Hydrazine water and EDP are toxic and unstable. Consequently, they are not easy to handle. The bases KOH and NaOH have excellent anisotropic etching properties, but the use of KOH is usually restricted to postprocessing treatment. In terms of process compatibility, the etchant must be compatible with the CMOS manufacturing process. Since TMAH contains no alkaline ion impurity, it can be used in IC processing. The TMAH is similar to KOH in terms of anisotropic etching characteristics and low toxicity.[5–7] TMAH is also used in the removal of positive photoresists. However, roughly etched surfaces at low concentrations and serious undercutting at high concentrations are drawbacks. To overcome these disadvantages, investigations of TMAH:isopropyl alcohol (IPA) solutions were conducted.[8] Though the addition of IPA improved the smoothness of the surface and reduced the undercutting, it also reduced the etch rate of TMAH. On the other hand, when pyrazine ($C_3H_4N_2$) was added to TMAH:IPA solutions, we found for the first time that the etch rate of single-crystal silicon is enhanced and flatness of the etched surface and compensation of undercutting are improved simultaneously.[9]

As stated above, the accurate control of microdiaphragm thickness using anisotropic wet etchants is very important. Widely used methods to control the microdiaphragm to the desired thickness are the etched-time stop, the boron etch-stop,[10] the silicon-on-insulator (SOI) substrate[11] and the electrochemical etch-stop methods.[12] One disadvantage of the etched-time stop method is that the variation of etch rate which occurs with certain etchants and the variation in silicon thickness can lead to errors in thickness which may be a large percentage of the desired diaphragm or beam thickness. One disadvantage of the boron etch-stop method is that single-crystal silicon heavily doped with boron introduces compressive stress into other structures and is not compatible with circuit processing techniques. The SOI substrate method shows good etch-stop characteristics but is not practical because of the price of SOI wafers. Therefore, we focus on the

electrochemical etch-stop method, which is based on the anodic passivation characteristics of silicon with a reverse-bias pn junction, to provide large etching selectivity for p-type silicon over n-type silicon in an anisotropic wet etchant.[13] This method has the advantage that it can easily control impurity concentration and the thickness of epitaxial layers.

In this paper, we describe the electrochemical etch-stop characteristics of single-crystal silicon in TMAH:IPA:pyrazine solutions. The etch-stop method is used for the fabrication of microdiaphragms at reverse-biased pn junctions. The reproducibility in the thickness of 801 microdiaphragms fabricated on a 5-inch silicon wafer and the surface smoothness of the etch-stopped microdiaphragms are presented.

2. Experimental

2.1 *Samples*

The starting materials consisted of 550-μm-thick, <100>-oriented 5-inch p- and n-type wafers. The electrical resistivities were 13 – 18 Ω·cm and 4 – 6 Ω·cm, respectively. Since the thermal oxide etch rate of TMAH is very low, a 4000-Å-thick thermal oxide was used as masking material for all samples.

Depending upon the experiment, two groups of wafer samples were prepared:

(a) For current-voltage (*I-V*) measurements, one side contact metallized n- and p-type wafers were used. Rectangular openings (801 in number) 1.5 mm × 1.5 mm in size were made on the other side of the wafer.

(b) For etching diaphragms, we used wafers that had 20-μm-thick n-type silicon grown epitaxially on a p-type substrate. In the n-type silicon layer, we implanted boron to form a contact, and 801 diaphragm patterns were also made on the other side of the wafer.

The optimum solution anisotropic etching is TMAH (20 wt.%):IPA (8.5 vol.%):pyrazine (0.5 g/100 ml). Under these conditions, the etch rate is higher than that in TMAH:IPA solutions and the surface quality is excellent.[9] Therefore, the electrochemical etch-stop characteristics of Si are analyzed in the optimum anisotropic etching conditions of TMAH:IPA:pyrazine solutions.

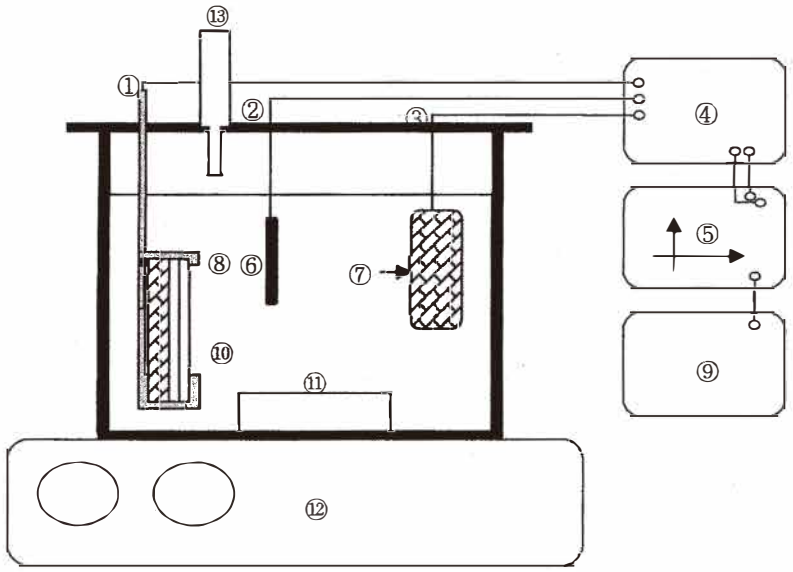
2.2 *Setup for etching*

Electrochemical etching was controlled using an EG&G 362 potentiostat. An Ag/AgCl-type electrode, whose working temperature extends up to 100°C, was used as the reference electrode and a Pt mesh, which supports high currents, was used as the counter electrode. All voltages presented in the paper are referred to the Ag/AgCl electrode.

Etching was performed in the dark using a tank equipped with a reflux condenser into which nitrogen was bubbled. A temperature of 80°C was chosen for all experiments and was controlled during the process to within ±1°C.

The experimental setup is shown in Fig. 1. The *I-V* curves were obtained using a three-electrode system with the voltage sweep rate set at 2 mV/s. The holder that prevented leaking out of the solution to the back of the wafer was made of Teflon and an O-ring.

The etch-stop voltage was selected between n- and p-type silicon passivation potentials (PPs), and the electrochemical etch-stop characteristics of a 5-inch silicon wafer



① Working electrode ② Reference electrode
③ Counter electrode ④ Potentiostat ⑤ PC
⑥ Ag/AgCl ⑦ Pt mesh ⑧ Teflon holder
⑨ Plotter ⑩ Sample ⑪ Magnetic stirrer
⑫ Hot plate ⑬ Reflux con

Fig. 1. Experimental setup for electrochemical etch-stop.

were studied. The thickness variation of microdiaphragms fabricated by the etch-stop method and the sufrace roughness of etch-stopped microdiaphragms were evaluated using scanning electron microscopy (SEM) and atomic force microscopey (AFM), respectively.

3. Results and Discussion

3.1 *I-V characteristics*

By conventional *I-V* measurements, the open circuit potential (OCP) and PP were determined in a three-electrode configuration. The sweep rate was 2 mV/s and the range was from –2 V to 0 V. Figure 2 shows the *I-V* characteristics of n- and p-type silicon obtained in the TMAH:IPA:pyrazine solutions. The etchant is TMAH (20 wt.%):IPA (8.5 vol.%):pyrazine (0.5 g/100 ml) solutions at 80°C. The addition of pyrazine to the TMAH:IPA solutions shifted both the OCP and PP of silicon toward the positive direction.

The OCPs for n-type and p-type silicon were –1.4 V and –1.1 V, respectively, and the

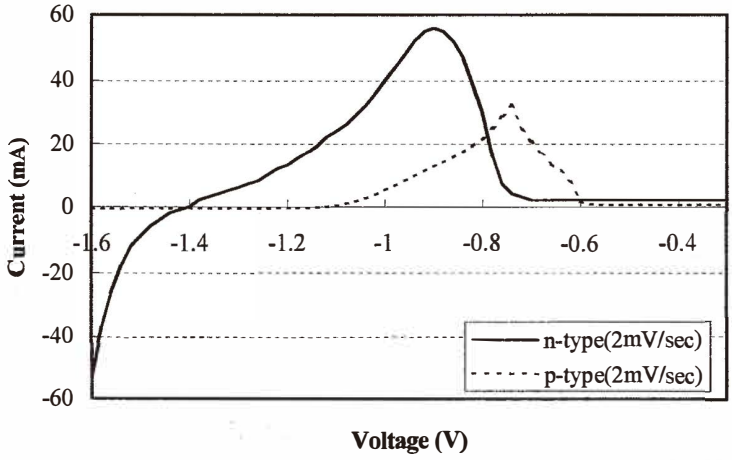


Fig. 2. Current-voltage characteristics of n- and p-type silicon obtained in TMAH:IPA:pyrazine solutions.

PPs were – 0.9 V and – 0.74 V, respectively. Thus, we have selected a potential, at which selective etching is realized. Since this potential is determined between the two PPs, one must choose the potential from values between – 0.9 V and – 0.74 V.

3.2 *T-I characteristics*

When etching reached the space-charge layer of the n-region, a typical current peak appeared to indicate the end of the process. After the peak appeared, the wafers were overetched for 10 min. Figure 3 shows the typical time-current (*I-T*) characteristics for a 5-inch silicon wafer with a 20-μm-thick epitaxial layer in TMAH:IPA:pyrazine solutions sduring the electrochemical etch-stop process. The increase in the etch rate due to the addition of pyrazine reduced the time required by the etch-stop process.[14] The current peak indicates increasing current with decreasing thickness of the diaphragms. Thus, the leakage current under reverse bias was increased. The n-type silicon that was exposed to the etchant when all p-type silicon was etched off, behaved as a resistor only. Therefore, large current flow occurred. This current induced anodic oxidation at the surface of n-type silicon.[15] Hydroxide ions in the etchant react with the silicon surface to form silicon dioxide (SiO_2). Since the etch rate of SiO_2 in TMAH solutions is very low, etching does not proceed further and finally stops. Moreover, because SiO_2 is a good insulator, the current decreases to zero.

3.3 *Flatness of etched surfaces*

Surface smoothness of the etch-stopped microdiaphragms is one of the main requirements for the fabrication of high-quality micromachining devices. Figure 4 shows a cross-sectional SEM image of a cleaved silicon microdiaphragm fabricated by the electrochemical etch-stop method in TMAH (20 wt.%):IPA (8.5 vol.%):pyrazine (0.5 g/100 ml)

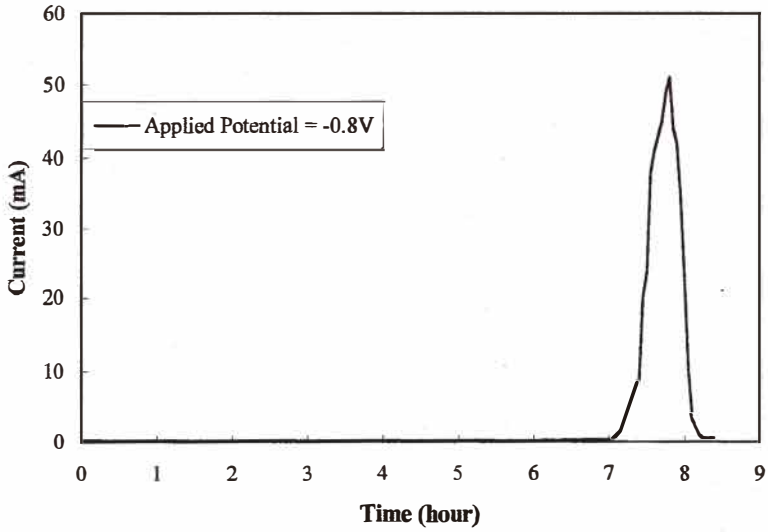


Fig. 3. Time-current characteristics for a 5-inch silicon wafer in TMAH:IPA: pyrazine solutions during the electrochemical etch-stop process.

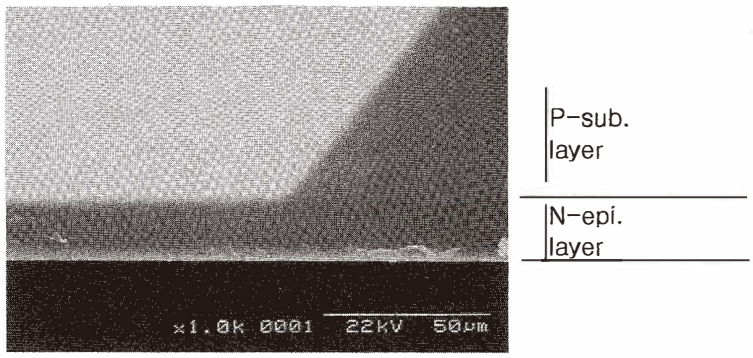


Fig. 4. Cross-sectional SEM image of an etch-stopped microdiaphragm.

solution at 80°C. Etching was stopped precisely at the pn junction and a microdiaphragm of approximately 20 μm thickness was fabricated. In spite of the initially unpolished back of the silicon wafer, the etch-stopped microdiaphragm surface was extremely flat and had no noticeable taper or nonuniformity. The etched-stopped surface smoothness in TMAH (20 wt.%), TMAH (20 wt.%):IPA (8.5 vol.%) and TMAH (20 wt.%):IPA (8.5 vol.%):pyrazine (0.5 g/100 ml) solutions, respectively, was 13.55, 5.48 and 5.42 nm. In spite of the decrease in etch rate, the addition of IPA to TMAH solution improved the

etch-stopped surface flatness.[8] On the other hand, the addition of pyrazine to TMAH:IPA solutions increased the etch rate and improved the etch-stopped surface simulateously.[9] Figure 5 shows an AFM image of the etch-stopped silicon surface in which the microdiaphragm from the unpolished surface was etched in TMAH (20 wt.%):IPA (8.5 vol.%):pyrazine (0.5 g/100 ml) solutions. The inital surface roughness of about 5 μm was reduced to less than 5.42 nm after the etch-stop process. The very good flatness of the etched silicon surface and the accurate electrochemical etch-stopped characteristics in TMAH:IPA:pyrazine solutions are significant improvements over these of the conventional method of etch monitoring and control.[16] Therefore, the etch-stop approach using the electrochemical etch-stop method in TMAH:IPA:pyrazine solutions shows great promise due to its ability to achieve a very flat and highly uniform microdiaphragm surface.[17]

3.4 *Distribution in thickness of diaphragms*

All devices produced by mass production should have identical mechanical properties. Hence, the reproducibility of the thickness of microdiaphragm is an important fabrication feature. To evaluate the reproducibility of the thickness of the microdiaphragm across a wafer, 801 microdiaphragms were fabricated, equally spaced over a 5-inch silicon wafer with 20-μm-thick n-type silicon grown epitaxially on a p-type substrate. After the electrochemical etch-stop process in the TMAH:IPA:pyrazine solutions at a reverse bias of 0.8 V, the thickness of the microdiaphragms was measured by microscopy. Figure 6 shows a histogram of variation in thickness of microdiaphragms on one silicon wafer. Microdiaphragms with a thickness of 20±0.2 μm comprise 77.9% of the total number of

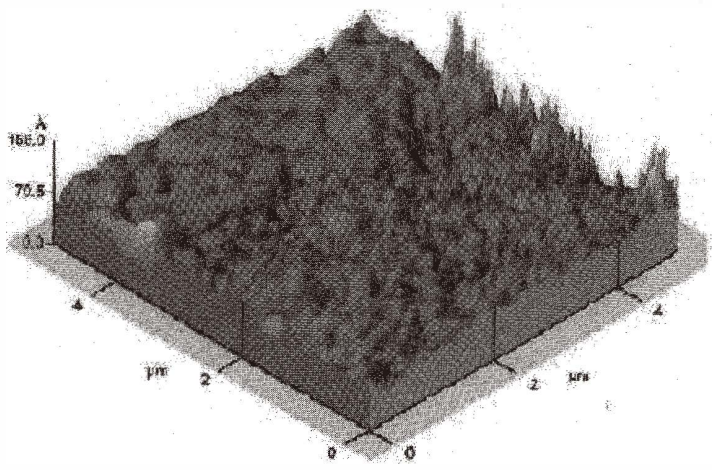


Fig. 5. AFM image of an electrochemical etch-stopped microdiaphragm surface in TMAH:IPA:pyrazine solutions.

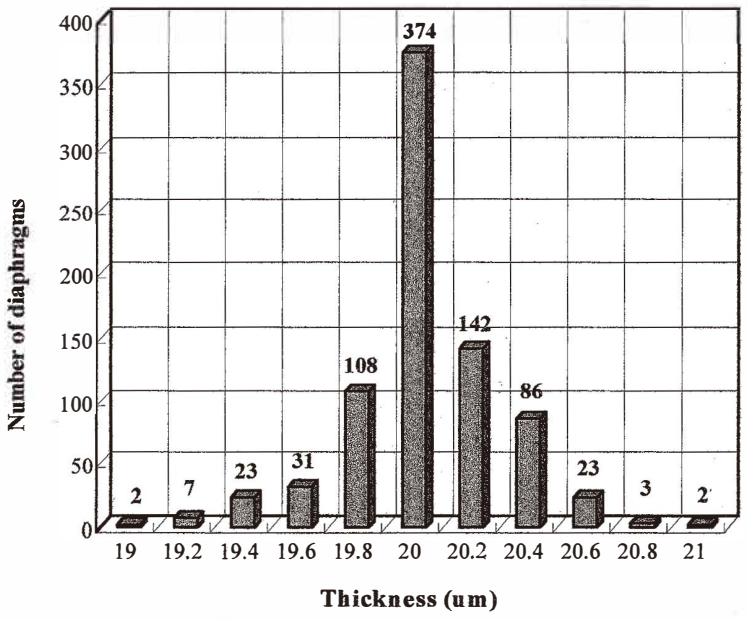


Fig. 6. Thickness distribution of 801 microdiaphragms fabricated on a 5-inch silicon wafer using the electrochemical etch-stop process in TMAH:IPA:pyrazine solution.

microdiaphragms on one wafer. The average thickness of the 801 microdiaphragms is 20.03 μm, and the standard deviation is only $\pm$0.26 μm. This result is markedly improved from that of previous fabrication methods.[18] In this work, the thickness of microdiaphragms in the central part of the silicon wafer was slightly less than 20 μm as a result of electrical contacts. Because of the attachment of four point electrodes on each of the corners of the silicon wafer, the central part of the silicon wafer is not passivated to sufficiently n-type silicon at the pn junction. The thickness of microdiaphragms at the edge of the silicon wafer was greater than 20 μm because of the etching holder. Since hydrogen bubbles generated during etching were not eliminated completely, they gathered around the holder. If an additional point electrode were added and the structure of the etching holder changed, these problems would be solved. Moreover, this distribution in thickness reflects the variation in thickness of the epitaxial silicon layer in the wafers used in these experiments, which is about 0.2 μm. Among different wafers, the thickness of the epitaxial layer can vary by more than 0.5 μm, yielding a large variation in the thickness of the microdiaphragms. Therefore, the reproducibility of the electrochemical etch-stop method is limited only by the reproducibility of the growth of the epitaxial layer.

4. Conclusions

The electrochemical etch-stop characteristics of single-crystal silicon in a TMAH (20 wt.%):IPA (8.5 vol.%):pyrazine (0.5 g/100 ml) solutions at 80°C are presented. The *I-V* curves, OCP and PP were also obtained for n- and p-type silicon. Selective etching of p- and n-type silicon is possible by electrochemical etching at – 0.8 V. This potential is between n- and p-type silicon PPs. The *T-I* curve indicates the etch-stop point. The increase in etch rate by the addition of pyrazine reduces the time required by the for etch-stop process. The variation in the thickness of 801 microdiaphragms fabricated on a 5-inch wafer by the etch-stop method and the sufrace roughness of etch-stopped microdiaphragms were evaluated using SEM and AFM, respectively. The average thickness of the microdiaphragms is 20.03 μm, and the standard deviation is ±0.26 μm. The etch-stopped microdiaphragm surface is extremely flat without any noticeable taper or nonuniformity. These results are satisfactory for fabricating high-yield microdiaphragms for MEMS applications.

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