High speed etching of silicon in KOH + NH_2OH solution at lower temperatures for the fabrication of through holes in silicon wafer

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In the fabrication of complicated MEMS inertial sensors, there are many instances where metallisation cannot be done by usual methods such as lift off or conventional metal etch. In such cases, a shadow mask needs to be used. A silicon shadow mask can be realised by the fabrication of through holes in silicon. This also can be used as a cover wafer for wafer level encapsulation by fabricating a cavity in the device region. The fabrication of the shadow mask is carried out by doing double side wet anisotropic etching using potassium hydroxide (KOH) + hydroxylamine (NH_2OH) solution at low temperatures of 50–60°C. The low temperature of etching is preferred so as to reduce the etching of thermal oxide used as a mask layer. This work focuses on the etching characteristics of the KOH + NH_2OH solution at low temperatures in terms of etch rate, undercutting, surface morphology, and selectivity of an oxide layer with silicon. This is very useful in through hole etching using silicon dioxide as a mask. The effect of aging on these characteristics is also studied and this is useful in continuous etching spread over few days especially during pilot production. The results are compared with those obtained using a pure KOH solution.

1. Introduction: In the fabrication of complicated MEMS inertial sensors, there are many instances where metallisation cannot be done by usual pattern methods such as lift off or conventional metal etch. In such cases, it is necessary to fabricate a shadow mask for the final metallisation of the sensor. Shadow mask fabrication in silicon (Si) using deep reactive ion etching (DRIE) is complicated as this necessitates the use of a support wafer to prevent Helium coolant leakage [1]. The support wafer needs to be glued on to the processing wafer using cool grease or by any other bonding techniques. This further complicates the process and increases the number of steps involved in the fabrication of the shadow mask. Owing to these reasons, the wet etching route is preferred for the through hole etching in Si for shadow mask fabrication. In order to reduce etching time to half, wet etching is performed from both sides of the Si wafer after accurate back side alignment of the mask pattern. This also helps the oxide mask layer to withstand the long duration of etching. However, wet etching has its own limitations such as an arbitrary structure with vertical sidewalls that cannot be fabricated.

Potassium hydroxide (KOH) and tetramethylammonium hydroxide (TMAH) are most commonly used as wet anisotropic etchants for wet bulk micromachining in MEMS [2–11]. When compared with TMAH, KOH provides a higher etch rate and higher etch anisotropy between Si{100}/Si{110} and Si{111}. This is especially useful in the fabrication of V-shaped holes for direct wire bonding with the device underneath the through hole wafer in wafer level encapsulated devices [12–14]. The high etch rate of Si is desirable to reduce the etching time. Although a higher etch rate can be obtained at a higher temperature (75–80°C), it increases the etch rate of thermally grown Si dioxide (SiO_2) which is commonly used as a mask layer. In order to overcome this problem, the etching is carried out at lower temperatures in the range of 50–60°C. However, at low temperatures, the KOH etch rate is very poor and this necessitates the addition of special additives such as hydroxylamine (NH_2OH) [15, 16].

The effect of different concentrations of NH_2OH on the etching characteristics of Si{100} using 20 wt% KOH and 5 wt% TMAH is studied [15–18]. 15% NH_2OH is found to be the optimal concentration in 20 wt% KOH to obtain improved etching characteristics. The etch rates, etched surface morphologies, and undercutting results in 15% NH_2OH-added 20 wt% KOH are presented in the literature [15, 16]. Etch rate of Si{100} in 15% NH_2OH + 20 wt% KOH solution is nearly three times higher than that in pure KOH at the same temperature. The etch rate of SiO_2 also increases but not significantly compared to that of Si. The etch selectivity, which is defined as the ratio of Si etch rate and SiO_2 etch rate, increases remarkably in NH_2OH + KOH solution. The addition of NH_2OH does not affect the etched surface roughness and morphology significantly [15, 16]. For through hole fabrication, etching needs to be carried out for long durations. Hence it is important to study the aging effect of KOH + NH_2OH solution as NH_2OH is an unstable alkaline solution [19]. At lower etch temperatures, the oxide etch rate is low and hence selectivity is high.

In this work, 15% NH_2OH-added 20 wt% KOH is used to first study the etchant characteristics and then their variation due to the aging effect at lower temperatures. The experiments are carried out at temperatures in the range of 50–60°C. The lower temperature is selected to achieve high etch selectivity between Si and SiO_2. The etching characteristics are then compared with etchant characteristics of 20 wt% pure KOH solution at the same temperatures. Furthermore, this study is used to fabricate a through hole wafer which will be used in the fabrication of a MEMS inertial sensor.

2. Experimental details: In the present work, firstly etching experiments on Si {100} and {110} are investigated to optimise the etching condition to achieve improved etch rate of Si and etch selectivity between Si and SiO_2. Optimal etching conditions are exploited for through hole fabrication in Si {100} wafer.

Four inch Czochralski-grown Si{100} and {110} oriented p-type wafers of resistivity 5–10 Ω-cm are used to study the etching characteristics of 15% NH_2OH added 20 wt% KOH solution. Thermal SiO_2 of 0.9 μm thickness is used as the masking layer. The oxide is patterned using photolithography and then followed by etching in buffered hydrofluoric acid (BHF). The photoresist is removed using acetone followed by rinsing in deionised (DI) water. The wafers are diced into small chips of $2 \times 2\ cm^2$ size. They are then cleaned in the Piranha bath (H_2O_2:H_2SO_4 1:1) followed by thorough rinsing in running DI water to ensure the removal of organic and particle contaminants. 20 wt% KOH solution is prepared by adding the required weight of KOH pellets in DI water. 50% aqueous NH_2OH solution is used as the additive. The experiments are carried out at different temperatures of 50, 55 and 60°C. The solution is heated in a Polytetrafluoroethylene (PTFE) make cylindrical container equipped with a glass reflux condenser arranged in a constant temperature water bath with an accuracy of ±1°C. The reflux condenser is used to avoid the change in etchant concentration due to the evaporation of water. The temperature variation of the bath is kept within ± 1°C automatically by the proportional–integral–derivative control of the PTFE heater. In addition, it is continuously monitored using a Teflon coated thermometer immersed in the solution. The aging effect of the etchant is studied by using the same solution continuously for 5 days. The etch depth and surface morphology are determined using an optical profiler attached to a micro system analyser (Polytec MSA 500), undercutting measurements are carried out using an optical microscope (Olympus MX61). Etching characteristics using pure KOH solution were also determined to compare the results.

To demonstrate the application of NH_2OH-added KOH for the fabrication of through hole in Si{100} wafer, oxidised four inch Si{100} wafer of $375 \pm 25\ \mu m$ thickness is patterned on both sides of the wafer with square openings of size $500 \times 500\ \mu m^2$ using standard photolithography with back side alignment of accuracy <3 µm, followed by etching in BHF. The etching is carried out at 55 ± 1°C. The etching progress is monitored at regular intervals to exactly stop at the point when all the through holes are opened. In order to compare the results, through hole etching is also carried out in 20 wt% pure KOH solution.

3. Results and discussion

3.1. Etch rate: Etch rate is defined as the vertical etch depth per unit time. It is computed from etch depth measurements using optical profilometry technique. The measurement is carried out at a time interval of 6 h on both Si{100} and Si{110} samples. The etch rate is studied at different temperatures for both NH_2OH-added KOH solution and pure KOH solution. The results are presented in Fig. 1. It can be observed that the etch rate of both Si{100} and Si{110} increases substantially with the addition of NH_2OH and further it increases with temperature. The etch rate changes due to the aging effects are studied by keeping the etchant at the etchant temperature continuously for 4 days. The results are presented in Fig. 2 for both Si orientations. In the first part of the graph, results are presented for one day by carrying out the etching for 1 h after every 6 h in the same solution. In the second part, the etch rates are presented for the samples etched for 1 h after every day. The aging effect of NH_2OH-added 20 wt% KOH solution is less for 1–2 days and so the solution can be used for continuous etching purposes with monitoring of etch rate in each batch. Beyond 4 days, the etch rate drops by ∼50%. This is observed to

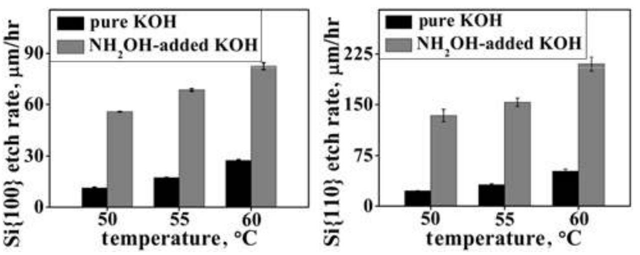

Fig. 1 *Etch rate of Si{100} and Si{110} in pure and 15% NH_2OH-added 20 wt% KOH for different etching temperatures*

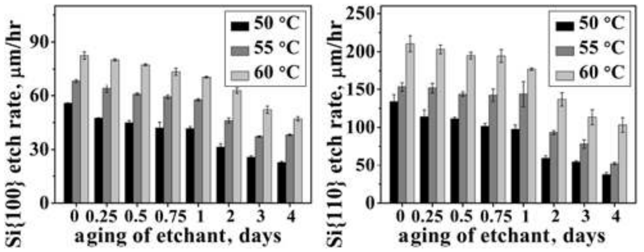

Fig. 2 *Aging effect of 15% NH_2OH-added 20 wt% KOH on the etch rate of Si{100} and Si{110} for different etching temperatures*

be the same for all temperatures in the range of 50–60°C. The magnitude of the etch rate is found to be higher in the case of Si{110} compared to that of Si{100} however, the trend of the aging effect is the same for both crystal orientations.

During Si etching, the etch rate of the solution decreases due to the consumption of the active species as well as due to the aging effect. According to Wei *et al.*, the addition of NH_2OH in KOH leads to the formation of NH_2O^-, NH_2NHOH, nitroxyl (HNO), and radical NH_2O [19]. In NH_2OH-added KOH, the main active species are NH_2O^-, OH^-, and H_2O. The aging effect of an etching solution is the result of the self-decomposing behaviour of the etchant chemical resulting in a reduction in the amount of active species available for etching that may lead to the decrease of the etch rate of Si. Thus, the aging of NH_2OH + KOH influences the etching characteristics. As the etch rate is influenced by etchant age, etch depth must be measured in between the etching process using dummy patterned samples for the fabrication of the controlled depth cavities.

3.2. Etch selectivity between Si and thermal oxide: As discussed in Section 2, thermally grown SiO_2 of 0.9 µm is used as the mask during wet etching. It is very important that the oxide mask remains during the entire etching duration. This is ensured by studying the etch rate of SiO_2 along with that of Si in both NH_2OH-added KOH and pure KOH solution for all temperatures of interest. The thickness of SiO_2 is measured using a SENTECH 500 ADV Combined FTP and Laser ellipsometer. The results are plotted in Fig. 3. It can be seen that the etch rate of SiO_2 increases with temperature and the values remain almost the same for both types of solution. The etch selectivity of NH_2OH + KOH solution is found to be almost three times that of pure KOH solution at lower temperatures as shown in Fig. 4. The etch rate of SiO_2 in the KOH solution is mainly affected by etchant concentration and etching temperature. The aging of the KOH does not influence the etch rate of SiO_2 and so is the case with NH_2OH + KOH solution as shown in Fig. 3.

3.3. Surface morphology: The surface morphology is important if cavities need to be fabricated with the near optical finish. Here

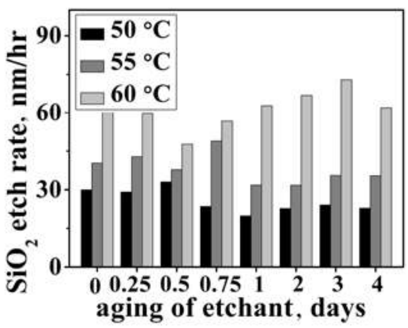

Fig. 3 *Aging effect of 15% NH_2OH-added 20 wt% KOH on the etch rate of SiO_2 for different etching temperatures*

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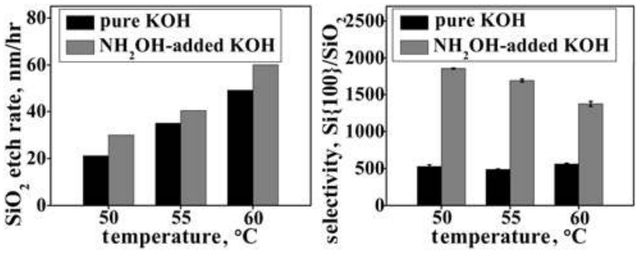

Fig. 4 *Etch rate of SiO_2 and its selectivity with Si{100} in pure and 15% NH_2OH-added 20 wt% KOH for different etching temperatures*

in this work, this is not an important characteristic as the etchant is being used to fabricate through holes in Si. Nevertheless, we studied the surface morphology of Si{100} and Si{110} for 15% NH_2OH-added 20 wt% KOH solution at three temperatures of interest and these are shown in Fig. 5. These are compared with surface morphology results when 20 wt% pure KOH solution is used under the same etching conditions. It is seen that there is not much variation with temperature or solution type for both crystal orientations of Si.

The aging effect of NH_2OH + KOH solution is studied for both Si {100} and Si {110} at different temperatures as shown in Figs. 6–9. From Figs. 6 and 7, it can be concluded that there is no significant aging effect on the etched surface morphology of Si{100} in the temperature range of 50–60°C and at the same time surface smoothness is high on Si{100} compared to Si{110} as expected. Similarly, surface morphology on Si{110} has not changed significantly as is evident from Figs. 8 and 9. This is because of the fact that at lower temperatures, the etch rate is less and hence the hydrogen bubbles get sufficient time to escape reducing the micro masking effect.

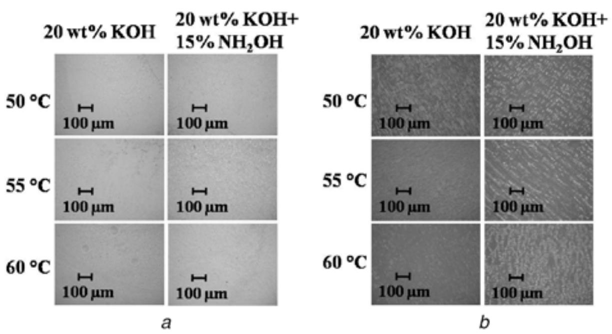

Fig. 5 *Surface morphology of*
a Si{100}
b Si{110} in pure and 15% NH_2OH-added 20 wt% KOH for different etching temperatures

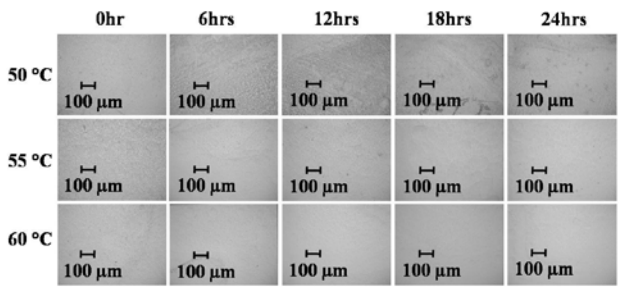

Fig. 6 *Aging effect of 15% NH_2OH-added 20 wt% KOH on the surface morphology of Si{100} for different etching temperatures and aging times spread over one day*

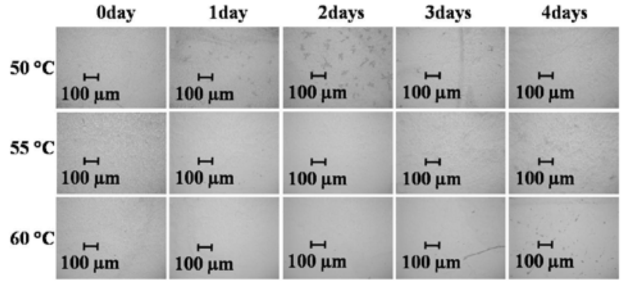

Fig. 7 *Aging effect of 15% NH_2OH-added 20 wt% KOH on the surface morphology of Si{100} for different etching temperatures and aging times spread over 4 days*

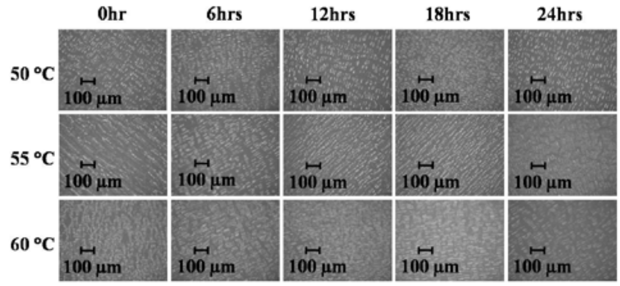

Fig. 8 *Aging effect of 15% NH_2OH-added 20 wt% KOH on the surface morphology of Si{110} for different etching temperatures and aging times spread over one day*

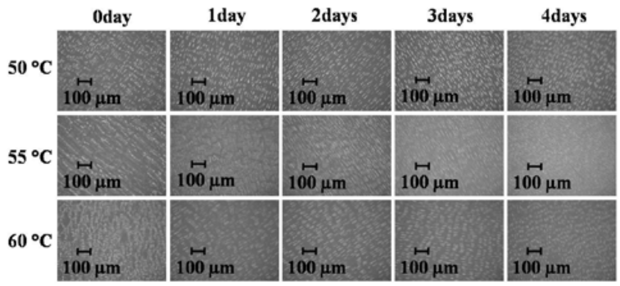

Fig. 9 *Aging effect of 15% NH_2OH-added 20 wt% KOH on the surface morphology of Si{110} for different etching temperatures and aging times spread over 4 days*

3.4. Undercutting at convex corner: The undercutting is an important concern in cases requiring the fabrication of sharp cornered mesa type structures in Si [20, 21]. In such cases, an undercutting is undesirable. However, in cases of sacrificial etch of Si to release suspended oxide structures, a higher undercutting is desirable. In the present work, undercutting has less effect as we could etch out through holes spaced as close as 300 µm. The undercut rate along ⟨110⟩ direction on Si{100} surface in pure and 15% NH_2OH-added 20 wt% KOH is studied for the temperatures of 50, 55 and 60°C. These are detailed in Fig. 10. As expected, the undercut rate of Si in NH_2OH-added KOH solution increases by 8–10 times compared to that of pure KOH solution. The aging effect of NH_2OH-added KOH solution on the undercut rate at the convex corner along ⟨110⟩ direction on Si {100} surface is shown in Fig. 11. The aging effect on the undercut rate is negligible in a day while it is observed to be reduced over 4 days of aging time of etchant solution.

3.5. Fabrication of through hole wafer: Though hole wafer fabrication can be done using other etching methods as well. DRIE, which is a plasma based dry etching process, can be used for the fabrication of through holes with vertical sidewalls. However, in this method, a support wafer needs to be bonded to the main wafer to prevent Helium coolant leakage and thereby prevent the abortion of the etch recipe automatically. This further complicates the process. In the case of wet etching, KOH and TMAH are used for the fabrication of through holes. To fabricate the through holes in the KOH solution, Si_3N_4 is the best mask and the etching should be done at high temperatures to achieve a high etch rate of Si [6]. In the case of the TMAH solution, SiO_2 can be used as an etch mask and high etching temperature is required to achieve a high etch rate [22]. The addition of NH_2OH into KOH increases the etch rate significantly and the lower etching temperature improves the etch selectivity between SiO_2 and Si. Hence 20 wt% KOH + 15 wt% NH_2OH at 55°C is an optimal condition to form through a hole in Si{100} wafer using thermally grown oxide layer as a mask.

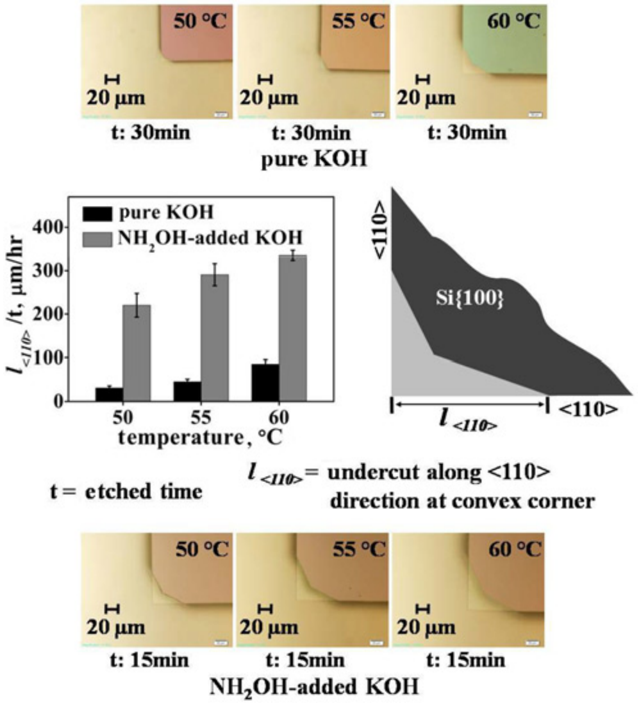

Fig. 10 *Undercut rate along ⟨110⟩ direction on Si{100} surface in pure and 15% NH_2OH-added 20 wt% KOH for different etching temperatures*

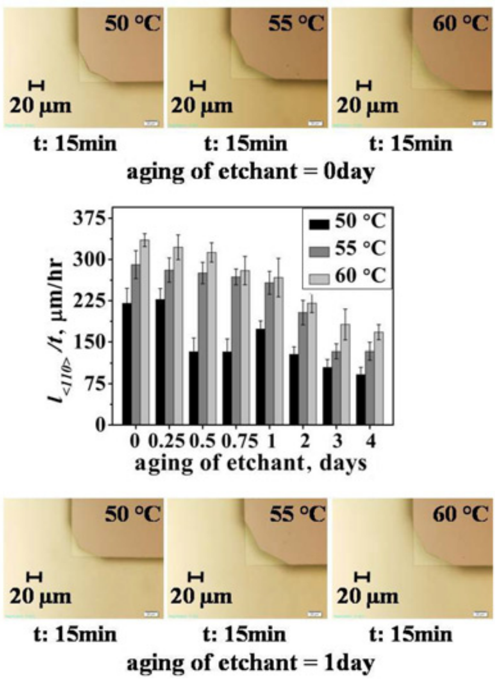

Fig. 11 *Aging effect of 15% NH_2OH-added 20 wt% KOH on the undercut rate at the convex corner along ⟨110⟩ direction on Si{100} surface for different etching temperatures*

Initially, the through hole fabrication is carried out using a pure 20 wt% KOH solution at 55°C. Fig. 12 shows the images of four inch Si{100} wafer at three different stages of though hole etching using a pure 20 wt% KOH solution at 55°C. It can be seen that the SiO_2 starts getting etched out from one side and it gets removed totally by the time through holes are formed. The total time of etching for realising through holes across the wafer is found to be 14 h. This confirms an application where we can effectively use 15% NH_2OH-added 20 wt% KOH solution at lower temperatures.

In the second part of the experiment, the through hole etching is carried out using 15% NH_2OH-added 20 wt% KOH solution at a

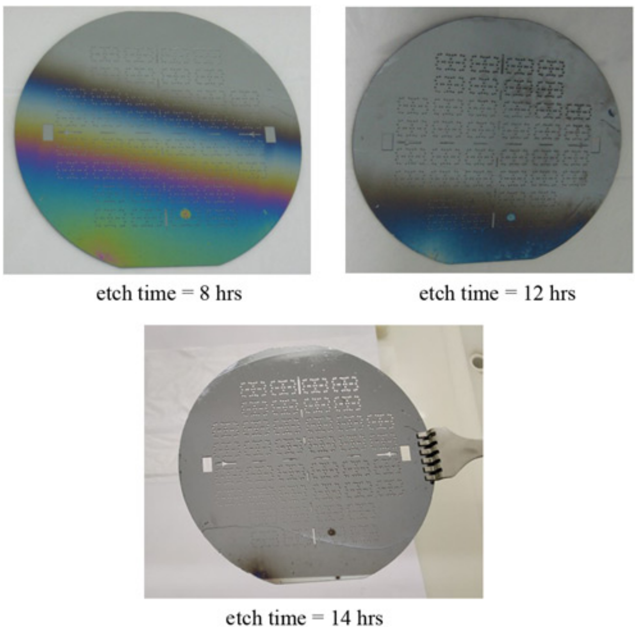

Fig. 12 *Different stages of through hole wafer fabrication in Si{100} wafer using pure 20 wt% KOH at 55°C*

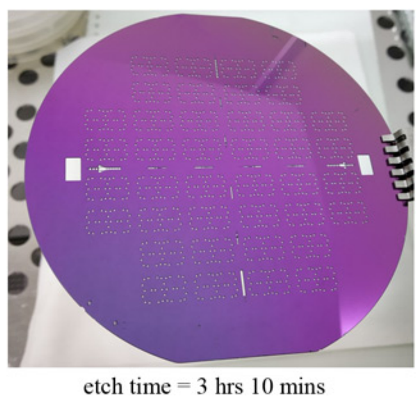

Fig. 13 *Through holes fabricated in Si{100} wafer using 15% NH_2OH + 20 wt% KOH at 55°C*

temperature of 55°C as this etchant composition and etching temperature exhibit reasonably high etch rate of Si and improved etch selectivity between Si and oxide as discussed in previous sections. Fig. 13 shows the image of four inch Si{100} wafer with through holes fabricated by etching from both sides. The SiO_2 mask is retained after the entire duration of etching. The total time of etching is found to be 3 h 10 min using 15% NH_2OH added 20 wt% KOH solution at 55°C.

4. Conclusion: The etching characteristics of Si{100} and Si{110} in 15% NH_2OH-added 20 wt% KOH and pure 20 wt% KOH solutions are studied in detail at lower temperatures in the range of 50–60°C. The aging effect of the NH_2OH-added KOH solution on etching characteristics is also studied over 5 days for both the crystal orientations. These studies are implemented in practical application towards the fabrication of through hole Si wafer. The same was carried out using pure KOH solution as well to compare the results. It was found that 15% NH_2OH-added 20 wt % KOH at 55°C is an optimal condition to form through a hole in Si{100} wafer using a thermally grown oxide layer as a mask. Hence this work can be directly used for wet bulk micromachining towards the production of MEMS devices.

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6 References

[1] Abhulimen I.U., Polamreddy S., Burkett S., ET AL.: 'Effect of process parameters on via formation in Si using deep reactive ion etching', *J. Vac. Sci. Technol. B, Microelectron. Nanometer Struct. Process. Meas. Phenomena*, 2007, **25**, (6), pp. 1762–1770

[2] Seidel H., Csepregi L., Heuberger A., ET AL.: 'Anisotropic etching of crystalline silicon in alkaline solutions I. Orientation dependence and behavior of passivation layers', *J. Electrochem. Soc.*, 1990, **137**, (11), pp. 3612–3626

[3] Pal P., Ashok A., Haldar S., ET AL.: 'Anisotropic etching in low-concentration KOH: effects of surfactant concentration', *Micro Nano Lett.*., 2015, **10**, (4), pp. 224–228

[4] Sato K., Shikida M., Matsushima Y., ET AL.: 'Characterization of orientation-dependent etching properties of single-crystal silicon: effects of KOH concentration', *Sens. Actuators A, Phys.*, 1998, **64**, (1), pp. 87–93

[5] Rola K.P., Zubel I.: 'Impact of alcohol additives concentration on etch rate and surface morphology of (100) and (110) Si substrates etched in KOH solutions', *Microsyst. Technol.*, 2013, **19**, (4), pp. 635–643

[6] Tanaka H., Yamashita S., Abe Y., ET AL.: 'Fast etching of silicon with a smooth surface in high temperature ranges near the boiling point of KOH solution', *Sens. Actuators A, Phys.*, 2004, **114**, (2–3), pp. 516–520

[7] Shikida M., Sato K., Tokoro K., ET AL.: 'Differences in anisotropic etching properties of KOH and TMAH solutions', *Sens. Actuators A, Phys.*, 2000, **80**, (2), pp. 179–188

[8] Zubel I., Kramkowska M.: 'The effect of isopropyl alcohol on etching rate and roughness of (100) Si surface etched in KOH and TMAH solutions', *Sens. Actuators A, Phys.*, 2001, **93**, (2), pp. 138–147

[9] Gosalvez M.A., Pal P., Ferrando N., ET AL.: 'Experimental procurement of the complete 3D etch rate distribution of Si in anisotropic etchants based on vertically micromachined wagon wheel samples', *J. Micromech. Microeng.*, 2001, **21**, (12), p. 125007

[10] Alvi P.A., Meel V.S., Sarita K., ET AL.: 'A study on anisotropic etching of (100) silicon in a aqueous KOH solution', *Int. J. Chem. Sci.*, 2008, **6**, (3), pp. 1168–1176

[11] Pal P., Sato K.: 'Silicon wet bulk micromachining for MEMS' (Pan Stanford, Boca Raton, USA, 2017), ISBN 978-981-4613-72-9

[12] Tang C.W., Young H.T., Li K.M.: 'Innovative through-silicon-via formation approach for wafer-level packaging applications', *J. Micromech. Microeng.*, 2012, **22**, (4), p. 045019 (8pp)

[13] Torunbalci M.M., Alper S.E., Akin T.: 'Advanced MEMS process for wafer level hermetic encapsulation of MEMS devices using SOI cap wafers with vertical feedthroughs', *J. Microelectromech. Syst.*, 2015, **24**, (3), pp. 556–564

[14] Torunbalci M.M., Alper S.E., Akin T.: 'Wafer level hermetic sealing of MEMS devices with vertical feedthroughs using anodic bonding', *Sens. Actuators A, Phys.*, 2015, **224**, pp. 169–176

[15] Narasimha Rao A.V., Swarnalatha V., Ashok A., ET AL.: 'Effect of NH_2OH on etching characteristics of Si{100} I KOH solution', *ECS J. Solid State Sci. Technol.*, 2017, **6**, (9), pp. P609–P614

[16] Narasimha Rao A.V., Swarnalatha V., Pal P.: 'Etching characteristics of Si{110} in 20 wt% KOH with addition of hydroxylamine for the fabricaiton of bulk micromachined MEMS', *Micro Nano Syst. Lett.*, 2017, **5**, (1), p. 23

[17] Swarnalatha V., Narasimha Rao A.V., Pal P.: 'Effective improvement in the etching characteristics of Si{110} in low concentration TMAH solution', *Micro Nano Lett.*, 2018, **13**, (8), pp. 1085–1089

[18] Swarnalatha V., Narasimha Rao A.V., Ashok A., ET AL.: 'Modified TMAH based etchant for improved etching characteristics on Si {100} wafer', *J. Micromech. Microeng.*, 2017, **27**, (8), p. 085003 (8pp)

[19] Wei C., Saraf S.R., Rogers W.J., ET AL.: 'Thermal runaway reaction hazards and mechanisms of hydroxylamine with acid/base contaminants', *Thermochim. Acta*, 2004, **421**, (1–2), pp. 1–9

[20] Pal P., Sato K.: 'A comprehensive review on convex and concave corners in silicon bulk micromachining based on anisotropic wet chemical etching', *Micro Nano Syst. Lett.*, 2015, **3**, pp. 1–42

[21] Pal P., Sato K., Chandra S.: 'Fabrication techniques of convex corners in (100)-silicon wafer using bulk micromachining: a review', *J. Micromech. Microeng.*, 2007, **17**, pp. R111–R133

[22] Tang B., Sato K., Zhang D., ET AL.: 'Fast Si (100) etching with a smooth surface near the boiling temperature in surfactant modified tetramethylammonium hydroxide solutions', *Micro Nano Lett.*, 2014, **9**, (9), pp. 582–584