SURFACE SMOOTHNESS OF ANISOTROPICALLY ETCHED (100) SILICON

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Abstract: Preferential etching of (100) oriented silicon in aqueous KOH solutions with special emphasis on surface roughness was performed and results are presented. The surface quality is of great importance for devices utilizing thin membranes, cantilevers and other micromachined structures. The final surface smoothness is strongly dependent on parameters such as etching temperature, molarity and stirring of the solution as well as initial surface condition of silicon wafers. The influence of iso-propyl alcohol (IPA) and n-propanol additives is also shown. Resulting data were applied to the fabrication of the thin, square silicon diaphragm suitable for piezoresistive pressure sensor.

Gladkost anizotropno jedkane površine (100) silicija

Ključne besede: mikroelektronika, silicij, senzorji tlaka, senzorji piezouporovni, membrane tanke, oblike kvadratne, kakovost površine, obdelava površine, gladkost površine, obdelava najfinejša, jedkanje mokro, jedkanje anizotropno, KOH lug kalijev, raztopina vodna, orientacija kristalov

Povzetek: V članku je predstavljena problematika anizotropnega jedkanja silicija kristalne orientacije (100) v KOH vodni raztopini s posebnim poudarkom na doseganju gladke jedkane površine. Končna kvaliteta površine tanjšanega silicija je mono odvisna od naslednjih parametrov jedkanja: temperature jedkala, molarnosti raztopine, mešanja raztopine in od začetne kvalitete silicijeve površine. Prikazan je tudi vpliv dodatka izopropil-alkohola in n-propanola v KOH vodno raztopino na gladkost površine. Končna aplikacija raziskave je izdelava tanke silicijeve membrane, uporabne za piezoresistivni senzor tlaka.

INTRODUCTION

The micromachining of silicon has become a large field of interest for many researches and producers of sensors and actuators in the last decade. Silicon single crystal exhibits diverse physical and chemical properties along different crystal planes. Certain etching solutions attack different crystal planes with various etch rates. Anisotropical behaviour of (100) and (110) oriented silicon is one of the fundamental properties that enables the micromachining of silicon single crystal /1/. Along with conventional microelectronic technologies it leads toward fabrication of numerous miniaturized sensors, actuators and other micromechanical devices like gears and micromotors /1,2,5,6,8,9/. Most of these sensors are integrated with supporting on-chip interface circuitry enabling temperature compensation, linearization and other functions /9/. The etching anisotropy also differs with a type of the etching solution as well as with concentrations of etchants and additives /2/. Orientation dependent etch solutions are numerous such as ethylenediamine- pyrocathechol-water (EDP), hydrazine, KOH or similar alkaline solutions and recently reported anisotropic etching behaviour of NH_3-H_2O_2 solution with low H_2O_2 content. The difference between them is in the etch rate, anisotropy, operating hazard and masking materials. Different initial surface preparation of the silicon after long etching leaves various roughness of the final silicon wafer surface. For very thin structures (silicon diaphragms for pressure sensors, mass flow sensors or microphones, cantilevers or bridges for accelerometers) the surface roughness is of great importance because it can cause false response or severely damage the sensor device. To avoid this, it is desirable to fabricate sensor structures with very smooth surface.

The most commonly used bath for anisotropic etching of silicon nowadays is still aqueous KOH solution which represents the best compromise between etching anisotropy, (100) etch rate, dopant dependency of etch rate and most of all it is much safer to handle compared to the others /3/. By some authors we can achieve even an etch rate ratio 200:1 between (100) and (111) planes /2/. Backdraws are perhaps in the first place the possible process contamination with potassium and the fact that Si_3N_4 is inevitable as an etching mask for deep grooves. SiO_2 etch rate is about ten times higher than that of Si_3N_4, therefore SiO_2 mask is suitable only for short etching times. Emphasis were put on its influence on the surface smoothness regarding the concentration and bath temperature. The work conducted is mostly experimental and provides some observations on the behaviour of (100) silicon material thinned in KOH solutions.

EXPERIMENTAL DETAILS

All work presented here was performed on CZ grown silicon wafers, [100] crystal orientation, 3" in diameter, phosphorus doped, resistivity of 8-10 Ωcm, with mechanically mirror polished front side and caustic chemically polished back side. The wafers were RCA cleaned and prior to each test the dip of 30 seconds in 5% HF was carried out on the samples to remove a thin layer of native grown oxide. With same step equal initial conditions were established for each etch start. The thinning of silicon large samples was first done in four different aqueous KOH solutions (concentrations 20, 27, 35, 42 wt%). The etch rate and the surface quality were recorded every 30 minutes and the sample was then reinserted. After completing the trials, evaluations were made and the results were compared. Primarily from optical observations it has been concluded that samples etched in 35% KOH were superior concerning smoothness. Based on these results and on the fact that anisotropy is the highest at concentrations around 35 wt% /7/, we have chosen the concentration of 35 wt% to further investigate the impact of temperature and bath agitation on surface quality and etch rate. To sustain a sufficient mixing of the solution and between the sample and the solution, stirring of the solution was provided by N_2 gas bubbling through a single nozzle at rate 200 sccm/min. The samples were exposed to the etch solution at 50°,60°,70°,80° and 85°C. The temperature of the bath was held within 1°C what is hardly sufficient due to the high sensitivity of the etch rate on the temperature. Schematic drawing of the experimental setup is presented in Fig.1. The thickness of thinned samples was measured with a micrometer, visual control was provided by optical microscope Olympus and the surface roughness was determined with surface profiler Tencor Alphastep 200. The influence of organic additives on silicon surface roughness (IPA and n-propanol) was also observed by optical microscope and by SEM.

Finally, test patterns of square geometry defined by LPCVD Si_3N_4 mask were exposed to the etchant. The square windows (1x1mm) were defined by wet etching into 74nm thick Si_3N_4 via thermally cured SiO_2 spin-on-glass mask. Some difficulties appeared when photolithography was accomplished on the chemically polished back side due to very rough initial surface (5-10μm). The wafers were mounted in a polypropylene holder to protect one side from etching. The problem of mask pattern misorientation from [110] wafer primary flat was pronounced as well as the effect of insufficient exchange of etching species between the sample and the solution at deep groove etching. The quality of the silicon diaphragm surface was investigated by transmitted light optical microscope Olympus, SEM and by cleaved cross sectioned diaphragm sample observation . Thickness of diaphragm was measured by determining the difference of the focal planes between the wafer surface and the bottom of the groove as well as on cleaved samples mentioned above.

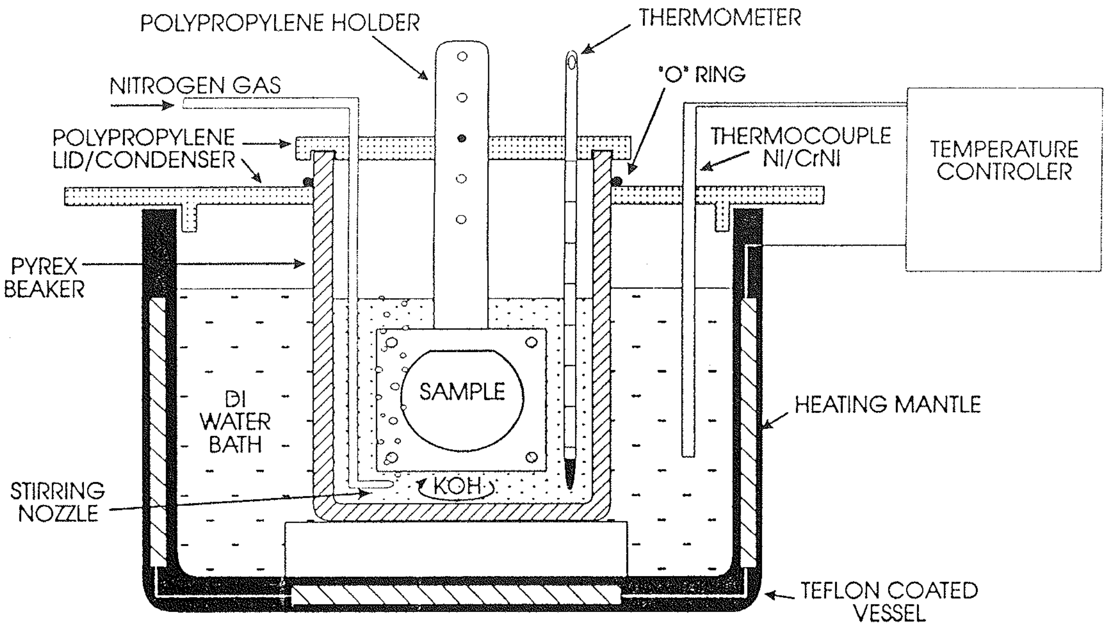

Fig. 1: Schematic diagram of system designed for anisotropic etching of silicon structures

RESULTS & DISCUSSION

The results of thinning large area silicon samples are presented first from the point of surface quality and etch rate. The effect of different KOH concentrations on the etch rate of (100) plane at temperature 80°C is shown in Fig.2. The results from Fig.2 are in good agreement with the work of Seidel et al. /4/.

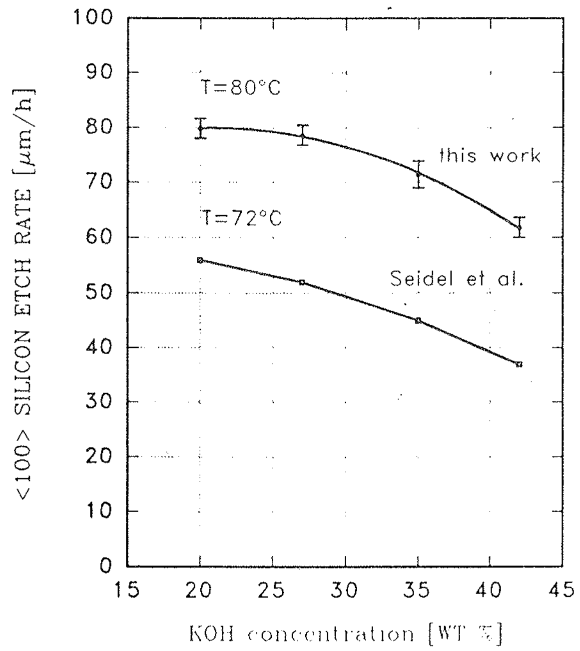

Fig. 2: *Dependence of (100) etch rate vs KOH concentration at 80°C without stirring the solution*

The highest etch rate obtained among selected concentrations was at 20 wt% KOH, but we observed that at this concentration the surface smoothness was spoiled by formation of micropyramides. This tendency decreases with increasing KOH concentration (Fig.5) and increases with etching time for mentioned concentrations . Due to the initially rough surface the cellular surface appears as can be seen from Figures 5,6. At high concentration (42 wt%) KOH the inside cell surface became rougher than at 35 wt% KOH (Fig.5) as was observed under incident light inspection although no micropyramides were formed. The dependence of the thickness of removed silicon versus etch time at four different temperature of KOH 35 wt% is presented in Fig.3. It is obvious from the diagram that the etch rate of the stirred solution was higher than that of unstirred for up to 10%, what is in agreement with Seidel /4/, but not with the work of Palik et al./5/ who noticed negligible effect of stirring on the etch rate. The slope of the lines represents directly the (100) etch rate. The activation energy of 0.593 eV for (100) orientation and 35wt% KOH was determined from Arrhenius plot in Fig.4 with etch rates at five different temperatures. Thus it is very important to maintain the temperature of the bath very constant to avoid etch rate variations, particularly in the case when we rely only on the etch time recording to control the thickness of removed silicon.

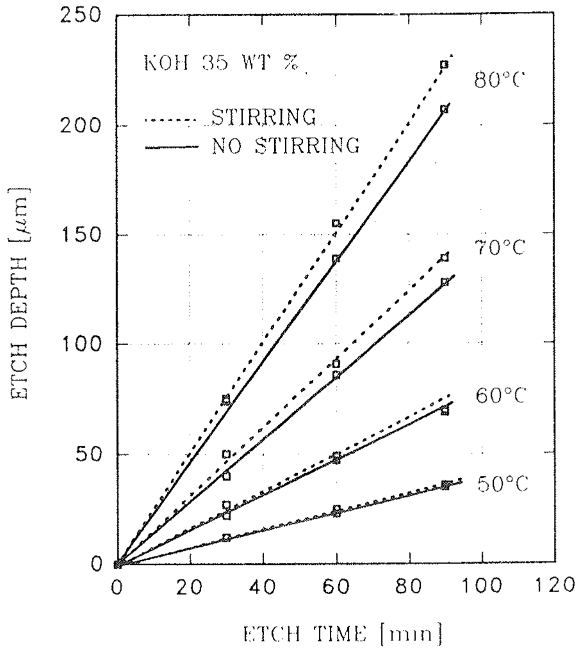

Fig. 3: *Etched depths vs etching time at different temperatures without stirring (full lines) and pronounced stirring effect (dashed lines)*

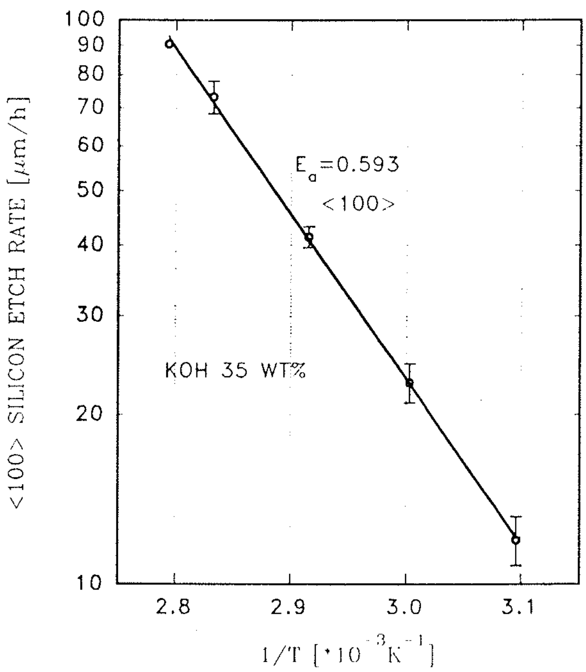

Fig. 4: *Temperature dependence of [100] oriented etch rate for 35wt% KOH solution*

In Fig.6 we present the micrographs of initial chemically polished (100) surfaces out from different bath temperatures after 90 min of etching with stirring of the solu-

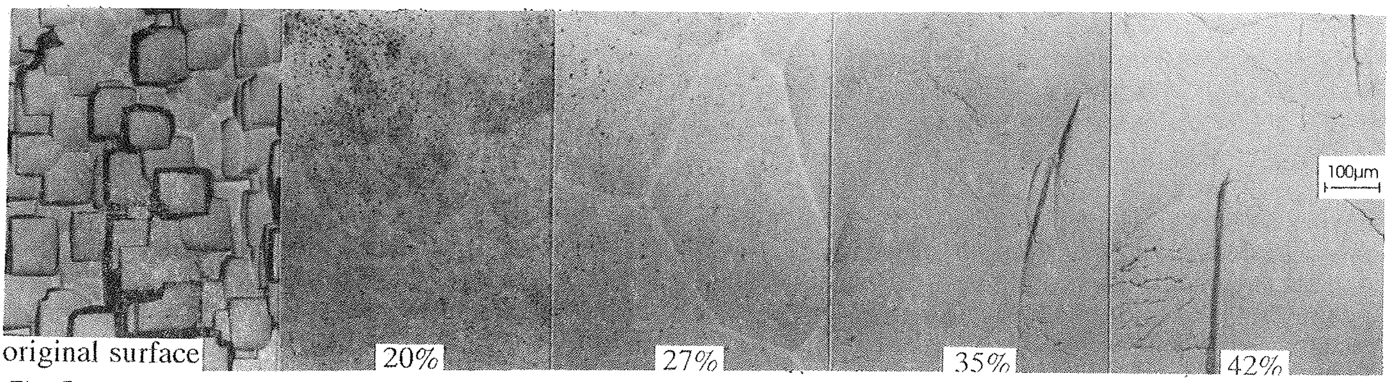

Fig. 5: *Optical micrographs of initial chemically polished surface after 90 minutes in the following KOH concentrations at 80°C. Tendency for the formation of micropyramides is seen for the concentrations below 30 wt%*

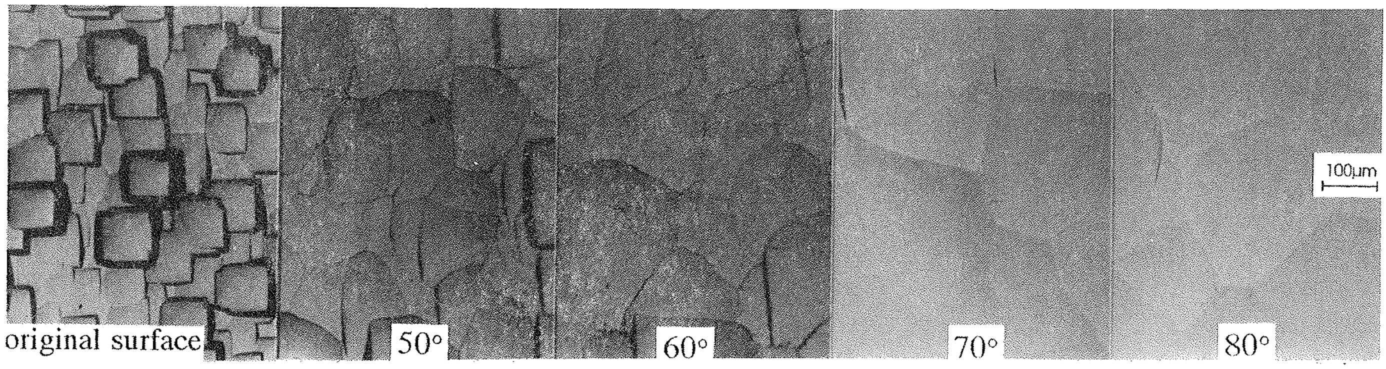

Fig. 6: *Samples etched at different temperatures after 90 minutes in 35 wt% KOH with stirring*

tion. The area of the cells on the surface increases with etch time as well as with temperature. Within cells roughness increases when the solution is not stirred while this is improved with stirring the solution and heating it up to 80°C (Fig.6). It was observed that smoothness is strongly dependent on the thickness of the removed silicon i.e. the cell area is increasing with time and the boundaries are not so much pronounced, meaning that cells at different initial heights of (100) planes are approaching one another /5/.

Initial mechanically polished surfaces exhibit minor changes in roughness at mentioned conditions and were thus difficult to evaluate by means of optical microscope or SEM. The evaluation was done by profilometer Tencor after 90 min of etching at 80°C with stirring and without stirring. The roughness of initial mechanically

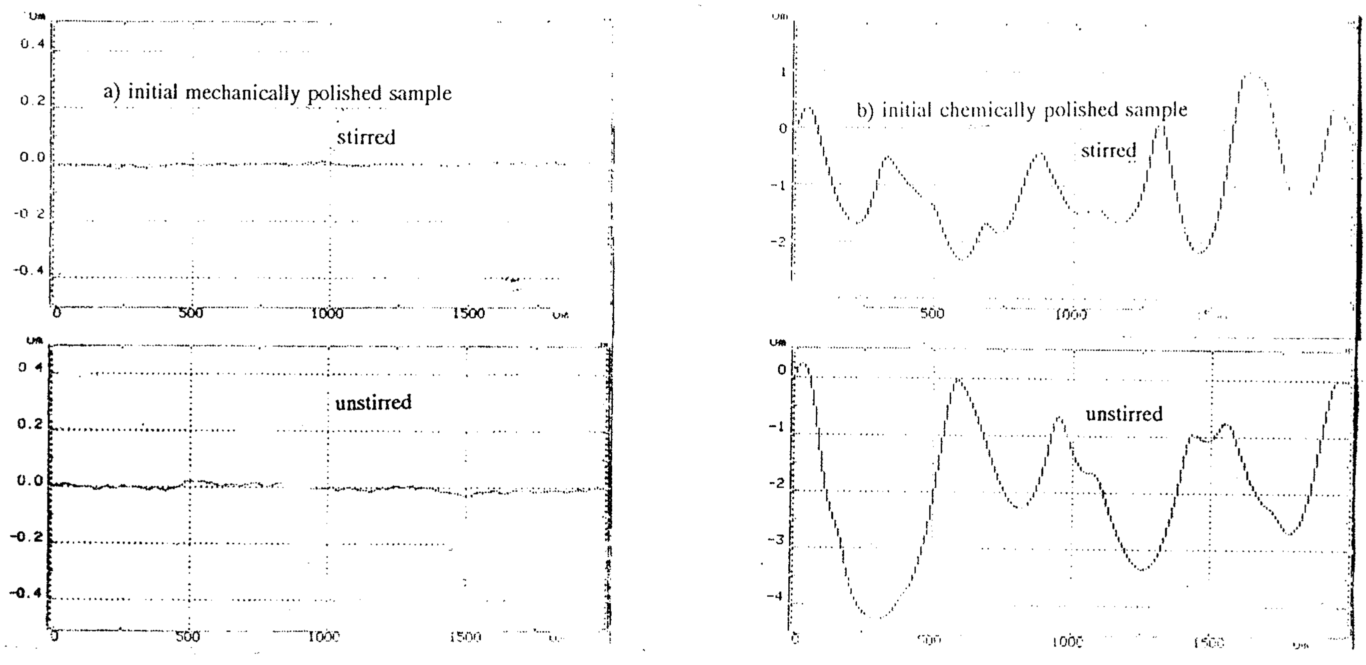

Fig. 7: *Tencor surface profiling scan showing the effect of stirring the 35 wt% KOH, 80°C: a) initial mechanically polished sample, b) initial chemically polished sample*

polished surface remained within few hundred Ångstroms (Fig.7a), while the initial chemically etched surface after 90 minutes still showed roughness of approximately 3 µm (Fig.7b).

Alcohol as an additive does not participate in the reaction when added to the binary KOH-H_2O mixture /4/. The alcohol plays more the role of a moderator and chelating agent /4/. White residues of etching products were collected within alcohol-rich top layer of ternary mixture. Etching in ternary mixtures of KOH-H_2O-IPA with ratio 312g KOH : 1000ml H_2O : 250ml IPA /4/ led us to the results presented in Fig.8. From the initial chemically polished surface, first small pyramides were formed until after 120 min all the surface was covered with them and the etch rate of (100) silicon decreased by 30%. In a similar way acted the solution with added n-propanol in ratio 250g KOH : 800g H_2O : 200g n-propanol /6/. The same was observed also on initial mechanically polished side. Because other authors have not reported these appearance, we have suspected that a probable cause

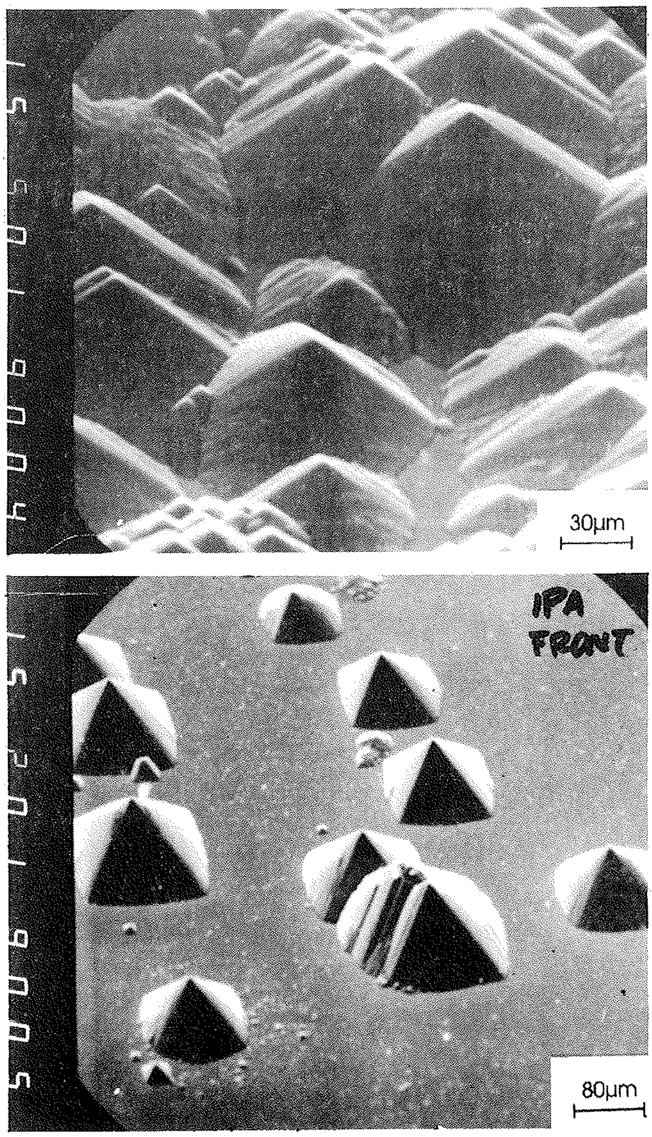

Fig. 8: SEM at 50° specimen tilt, KOH-IPA after 90 minutes at 80°C: a)initial chemically polished sample (500x), b)initial mechanically polished sample (200x)

for miropyramids formation could be our PA grade chemicals.

In our experiments the quantity of added alcohol was also changed and it was found that lower contents (below solubility limit of alcohol in KOH-water solution) improve the roughness but only if KOH concentration in water is at least 35 wt%. Change in anisotropy was noticed as shown on micrograph in Fig.9. In this case (50 ml/l of n-propanol added to the 35wt% KOH) the surface was free of micropyramides. The (110) etch rate has decreased significantly, while (100) etch rate change was negligible. Micrograph in Fig.9 is presenting this influence.

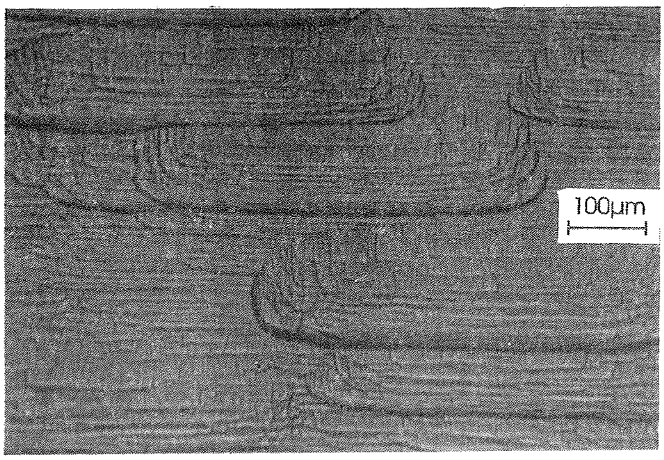

Fig. 9: Micrograph of initial chemically polished sample with addition of n-propanol showing changed anisotropy (lower (110) etch rate)

Based on the results presented above, the work was continued on patterned wafers. The square windows in Si_3N_4 mask were fabricated by lithographic step and inverted pyramidal cavities were subsequently etched down in stirred 35 wt% KOH solution at temperature 80°C. A typical etch rate was 1,2-1,3 µm/min. As one can see in Fig.10 the fast etching (100) plane is bounded by four slow etching (111) convergent self-limiting planes, reaching the surface at an angle of 54,7°.

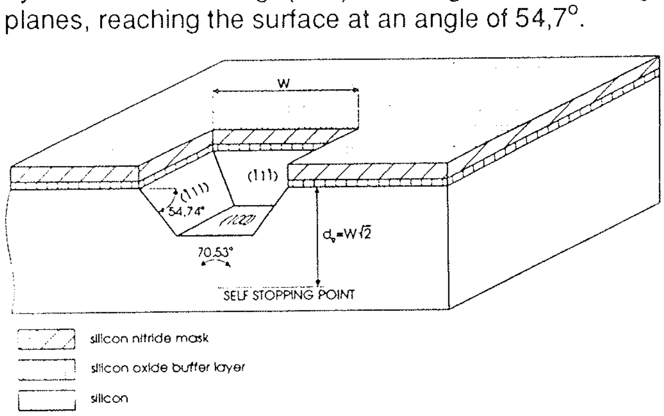

Fig. 10: Anisotropic etching for (100) silicon through a patterned Si_3N_4 mask. A buffer layer is usually used to compensate interface mechanical stresses

When defining the mask pattern on Si_3N_4, essential care must be taken to align the mask parallel to [110] primary flat of the wafer. In the case of misalignment of approximately 3°, the undercutting of mask occurs and the (111) planes are etched in step-like way. As a consequence the edge of the fabricated diaphragm will show saw tooth pattern as shown in Fig.11.

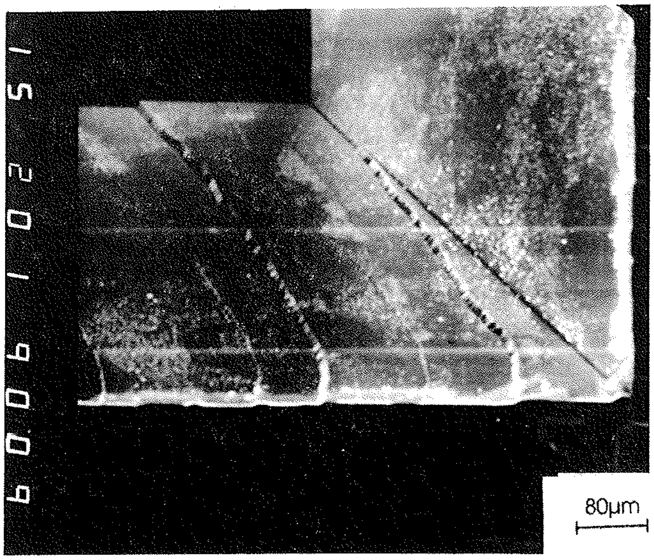

Fig. 11: *SEM, 200x, showing the step like (111) planes due to misorientation of mask to [100] wafer primary flat*

After this severe problem was overcome by more precise mask alignment, the (111) planes were smooth and the etching proceeded down to the depth desired by controlling only the etching time. The diaphragms of thickness 20 μm were easily achieved and we have estimated the variations of the thickness on cleaved cross- sections to 2-3 μm if etching has started from the chemically polished side of the wafer (Fig.12).

In diaphragm etching experiments conducted without or insufficient stirring the peculiar patterns were observed on diaphragm surface across all the wafer as shown in

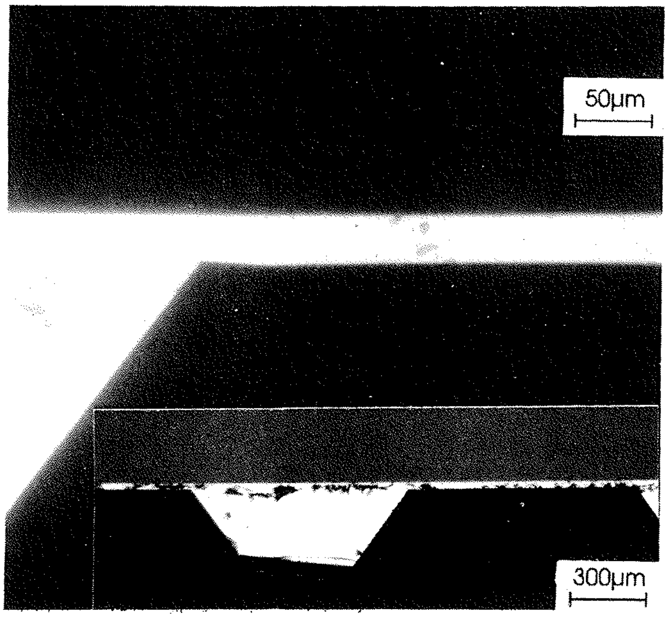

Fig. 12: *Micrograph showing diaphragm cross section at the edge. Thickness variations seen are from 24-27 μm. The inset is showing cleaved cross section of neighbouring devices on the wafer*

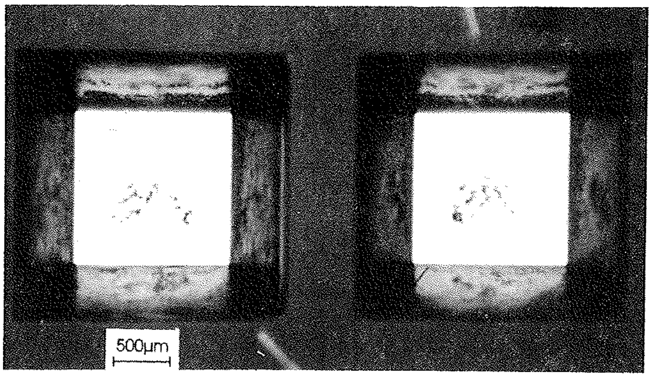

Fig. 13: *Optical micrograph of 20 μm thin diaphragms showing the pattern left on (100) surface due to insufficient stirring of KOH*

Fig.13. This was solved by selecting proper stirring of the solution.

The repeatability of this method was poor and we have not found the reliable method to detect the desired etching endpoint. The method of determining the colour of the transparent light through the diaphragm visually was insufficient for professional use.

It must be mentioned that at the present stage of our work all the results presented apply to the etching of uniformly doped silicon. Research toward optimised electrochemical etching or so called etch-stop methods is in progress. These methods utilize N/P epitaxial wafers and offer more consistent results regarding the surface smoothness and uniform thickness of the diaphragm.

CONCLUSIONS

The observations of initial chemically or mechanically polished (100) silicon surface smoothness and etch rate after long etching in different concentrations of aqueous KOH solution as well as temperatures in the range of 50-85°C were made. A strong temperature dependence of the (100) etch rate was determined with activation energy of .593 eV. The smoothness achieved was optimal between 30-35 wt% KOH solution at 80-82°C according to the evaluation made by optical microscope, SEM and Tencor surface profiler. It was observed that the agitation of bath increases the etch rate and provides smoother surface. At lower concentration (<27 wt%) micropyramides are formed although the etch rate is higher. When adding IPA or n-propanol to low concentration KOH the formation of pyramidal textured surface is even more obvious. Only at higher KOH concentrations and small amounts of alcohol a pyramid free surface was obtained. The square mask patterns on Si_3N_4 should be closely aligned parallel to [110] oriented wafer flat to achieve smooth (111) planes and thus the perfect square diaphragm. The diaphragm fabricated in this way exhibits thickness variations within 2-3 μm .

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