Nepal Journal of Science and Technology 11 (2010) 215-222

Thermally Induced Activation Energy of Crystalline Silicon in Alkaline Solution

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Abstract

Etching of crystalline silicon by potassium hydroxide (KOH) etchant with temperature variation has been studied. Results presented here are temperature dependent ER (etch rate) along the crystallographic orientations. Etching and activation energy are found to be consistently favorable with the thermal agitation for a given crystal plane. Study demonstrates that the contribution of microscopic activation energy effectively controls the etching process. Such a strong anisotropy in ER on KOH allows us a precious control of lateral dimensions of the silicon microstructure as well as surface growth of the crystal during micro device fabrication.

Key words: anisotropy, activation energy, etch rate, lattice parameter, micromachining.

Introduction

Micro-electro mechanical systems (MEMS) provide an opportunity for integration of mechanical systems with electronics to develop high-performance devices. MEMS devices are the output of either an etching/ micromachining process from larger structure or are built up atom by atom through material deposition processes. Maintaining dimensional control by micromachining and consistent mechanical properties is considerably difficult because feature sizes are in the micrometer range. Silicon MEMS accept these challenges and now have given a major drive in annual growth rate of sensor industry. However, the need for flexibility in device and performance improvement has motivated the development of new concepts and techniques for design of micromachining. The micromechanical parts are fabricated by selective etching of the silicon substrate in order to leave behind the desired geometries. Wet chemical etching is one where the material is immersed in a chemical solution. Unfortunately, there are some complications since a mask is used at various stages in the removal process to prevent selectively those portions of the material from being etched. These materials include SiO_2, Si_3N_4 etc. Secondly, some single crystal material such as silicon exhibit anisotropic etching in certain chemicals. The classic example of this is the (111) crystal plane sidewalls that appears while etching a silicon wafer of (100) orientation in a chemical such as KOH. The result is a pyramid shaped projections instead of a hole with round sidewall with an isotropic etchant.

Wet etching technology will give good results if one can find the combination of etchant and masking material. Anisotropic etching process allows the etching to stop on certain crystal planes in the substrate and cannot be vertical to the surface when etching holes or cavities. Moreover, complex shapes such as levers, gears and pinwheels have been produced through lithographic patterning coupled with etching methods. A variety of electrochemical silicon etching techniques is under development.

Etching technologies in thin film processes play an important role in the semiconductor industry. Wet chemical etching techniques are used extensively in semiconductor processing because of their low cost, high throughput, and excellent selectivity. Important progress in the fabrication of micro-electrical structure

with integrated circuit has been achieved by many researchers using wet etching. Etchants based on hydrofluoric acid (HF) and water is widely used in treating silicon and silicon dioxide. Though detailed kinetic and electrochemical measurements have not been made, KOH solutions are extensively used for the etching of single crystal silicon (*Rohrer 2001)*. Fabrication of UMOS transistors on silicon (111) wafers for high power and high current densities has been achieved by applying KOH anisotropic wet etching to the silicon substrate (*Mitani et al. 1992)*. Other applications of KOH wet etching include the fabrication of VMOSFETs, radio frequency amplifiers, power supplies, and microcomputers (*Mayer et al. 1990)*. Using its selective and anisotropic etching properties, KOH wet etching has also been applied to yield such devices as field emission devices (*Ammar & Rodgers 1980)*, optical waveguides (*Stone & Berlin 1980)* pressure sensors and ink nozzles (*Tsang at al. 1975)*. KOH wet etching is one of the anisotropic orientation dependent technique (*Bassous &Baran 1978)*. Etching of (100) oriented silicon using aqueous KOH creates V-shaped grooves with (111) planes at an angle of 54.74° from the (100) surface. KOH solution can also be used to produce mesa structures (*Mitani et al. 1992)*. There are several models proposed for the silicon etching mechanism in aqueous KOH (*Herr & Baltes 1992)*. Bean and Runyan (*Bassous et al. 1977)* found that the slow etch rate in the (111) direction is a consequence of the diamond lattice structure because the (111) plane is a double layer bound together by more atomic bonds than that of other planes. (*Glembocki et al.1992)* proposed an electrochemical reaction mechanism that exists in the rate determining step for KOH etching (*Bassous &Baran 1978)*. A compromise model was proposed by Seidel *et al* (*Bassous et al. 1977)* assuming that electrochemical reaction dominate during etching and that anisotropic etching was caused by the orientation-dependent number of dangling bonds available per surface area. The (100) silicon surface etches faster than the (111) because the free surface of (100) silicon is attacked by one OH per silicon atom, whereas the (111) silicon surface is attacked by two OH per silicon atoms. Although the mechanisms are not clear, it is known that electrochemical reactions play an important role in this process. The etching of single crystal silicon in aqueous KOH is of both technological and fundamental importance (*Tsang at al. 1975)*. As reported, results of KOH anisotropic-etch depends, on reaction temperature and KOH concentration. But, here in this paper attempt is being focused on approach of activation energy. The measured etch rate of primary crystal planes, the etching activation energy are proposed to be calculated from Arrhenius plot. Based on experimental values presented here, a model is proposed, which determines the factors that are statistically significant in a given etching process. And, there is interaction between temperature and activation energy, which can be quantified, and it is incorporated with the proposed model.

Methodology

To start with, 30 % by weight KOH solution was prepared in de-ionized water and filtered. Silicon wafers were cut into chips by a diamond cutter. Experiments have been carried out with p-type mirror polished silicon chips inside the etchant in a beaker kept in a water bath. The entire setup was kept inside an electric oven equipped with an auto-heating system. After 30 minutes the chips were taken out and rinsed with deionized water. Samples prepared in this way, were ready for taking etch depth measurements and microscopic observation by AFM. Images were taken in low voltage contact mode.

Before performing the AFM measurement, it was ascertained with the help of spirit level and AFM software, scanner plane and AFM head plane were made parallel inside the dust free environment. During each etched measurement 0.1 µm was taken as scan size. Finally, images were recorded in contact mode AFM. Etch rate, surface roughness (curve for height vs topographical distance), activation/cohesive energy of etched surfaces is chosen as the parameter for analysis.

The silicon wafer of thermally bonded silicon on insulator (SOI) with (100) orientation was used in this study. The thickness of the top silicon buried SiO_2 layer and bottom silicon were 2 and 450 mm respectively. The wafers were of p-type silicon with a resistivity of 4 – 631022 &!-cm for the top silicon and 12–15 &!-cm for the bottom silicon. Only the top silicon layer was etched by the KOH solution. First, the SOI wafers were prepared with standard RCA cleaning, which consist of two consecutive cleaning solutions (standard clean1, i.e. SC1 clean). RCASC1 Cleaning including H_2O-H_2O_2-NH_4OH with volume ratio

typically 5:1:1 was adopted in many steps during fabrication since it removes organic contaminants and particles physically attached to a wafer surface. A 450 Å thick layer of Si_3N_4, which acts as a KOH etching mask, was deposited on each wafer using low pressure chemical vapor deposition (LPCVD). Oxide can be used as an etch mask for short period in the KOH solution, but for long periods, nitride is a better etch mask as it etches more slowly. The SOI wafer was then cut into (10mm×10mm) pieces. With the dice pieces held on a vacuum chuck, positive photoresist, OCG 825, was used to pattern the Si_3N_4 for the KOH etching mask. The nitride was etched with CF4 plasma and then the exposed portion of the top silicon on each SOI wafer was etched in KOH solution of varying temperature and concentration. To assure the sample free of particulate and other airborne contaminants, the experiments were conducted in a dust free room.

Results and Discussion

Etch rate experiment

In this study, 2D moving surface at ambient condition is taken for understanding of wet chemical etching of silicon. Choosing‘d’ as the space parameter for their characterization. This can be achieved by consideration on

$$\frac{1}{d_{hkl}^{2}} = \frac{h^{2} + k^{2} + l^{2}}{a^{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where‘d’ is inter-planer distance, ‘a’ is lattice parameter and (*hkl*) are Miller indices. As a result, inter-planer distance for (100) is: 5.43 ^{0}A and for (110) is: 3.84 ^{0}A. In addition, silicon has diamond lattice, which consists of two interpenetrating fcc lattices displaced along the body diagonal of the cube cell by one quarter the length of its diagonal. In (111) plane silicon atoms are tetrahedrally bonded. So, inter-planar distance would be distance between the apex of the tetrahedron to the base, so that distance between two consecutive planes along (111) is [(a/4)”3]= 2.35 ^{0}A. It is clear from this mathematics that the largest‘d’ spacing occurs for the planes with the lowest indices Miller indices. Hence, this theory specifies the inter-planer spacing characterizes the lattice. Thus, number of planes (A) etched out per second is identified by

$$A = \frac{Etch.rate.per \min}{60 \times Interplana\, r.dist}$$

Duration for removal of single plane is just its reciprocal. Data achieved in this way are given in table1 below. Predicting the reaction rate in this way is one of the major objectives of the analysis of reaction kinematics. The results can have direct impact on the surface growth of the crystal.

Table 1. Data for etching silicon at 30 % KOH by weight

Plane (100)				Plane (110)				Plane (111)			
Temp (^{0} C)	ER (ìm/min)	A	B (^{0}C)	Temp (ìm/min)	ER	A (^{0}C)	B (ìm/min)	Temp	ER	A	B
20	0.024	00.736	1.357	20	0.035	1.519	0.6583	70	0.0052	0.368	2.7137
40	0.108	03.314	0.301	40	0.160	6.944	0.1440	75	0.0342	2.423	0.4125
60	0.410	12.582	0.079	60	0.620	26.908	0.0371	80	0.0722	5.117	0.1954
80	1.300	39.895	0.025	80	2.000	86.801	0.0115	85	0.1672	5.131	0.1948
100	3.800	116.61	0.008	100	5.800	251.72	0.0039	90	0.3982	2.22	0.0818

Where, A and B belong to number of planes removed per second and time taken for removal of single plane respectively.

From this table, non-uniform ER of silicon along different crystallographic orientations is achieved in KOH etchant. Results are displayed in graphical form in Fig. 2 and Fig. 3. Our experimental results in Fig. 2 shows that it is the plane (111) of silicon which etches far slower compared to other two crystallographic planes: (100) and (110). ER along (110) and (100) with temperatures are plotted in Fig. 3 (a), by which one can compare their rates. It is obvious from both Fig. 3 (a) & (b) that the ER is a function of temperature i.e. etches rate increases with temperature. In (111) plane, ER rises little sharper beyond 80^{0}C where as (110) and (100) plane ER stipend before 80^{0}C. Overall comparison shows that exposed (111) plane etched slowly where as (110) plane etched rapidly and (100) plane etched in between (111) and (110) planes. It is clear from the graph that theoretical and experimental results follow similar trends in respective crystallographic directions. From these results, we can conclude that properties of single silicon crystal are highly anisotropic. Hence,

single crystalline silicon has different mechanical properties (*Wang et al. 1999)* with respect to their orientations.

Anisotropic KOH etching of silicon

Dimensional control of a micromechanical structure has close correlation with its performance. Etching techniques allow control of the dimension. Wet chemical etching has been found favorable for etching silicon in micromechanical applications (*Mayer et al. 1990)*. When working with micromachining we need to both add and remove material in a controlled way. Adding material on a silicon wafer can be done by chemical vapor deposition (CVD) for epitaxial growth. Removal of the material is done almost by chemical etching, where a material is removed atom by atom. This can be done either in a liquid (wet etching) or in plasma (dry etching). Still the most simple and versatile anisotropic wet chemical etching for silicon is KOH etching. Etch anisotropy is given by, $E_A = 1 - (ER_L/ER_V)$, where ER_L and ER_V are the lateral and vertical etch rates. A process is said to be purely anisotropic ($E_A=1$) if lateral etch rate is zero. On contrast, if $E_A=0$, lateral and vertical etch rates are identical and etching is said to be isotropic. But in practice, both have nonzero values which indicate there should be anisotropy while working on crystal surface. A simple model of anisotropic etching is shown in Fig.1 below.

Fig.1. Showing anisotropic etch of silicon

Final shape of the etched wafer depends highly on relative etching speed along crystallographic planes. The (111) plane is comparatively inert to alkaline etchants, while the relative etching speed of planes depends on nature of etchant, temperature, concentration, additives etc.

The non-uniform etching rate of silicon along crystallographic orientations is now achieved in KOH etchant. Our experimental result in Fig. 2 shows that it is the plane (111) in silicon which etch slow compared to other crystallographic orientations (100) and (110). Crystal plane have its own inclination with respect to others. Micromachining technology is based on the angular dependence of etch rate with different planes. The angular dependence can be identified by using inner product of Miller indices of the crystal planes 'X' and 'Y' as

$$\vec{X} . \vec{Y} = |X|.|Y| \cos\theta$$

For example, the angle between (111) and (100) is

$$\theta = \cos^{-1}\left\{\frac{(111).(001)}{|(111)| \times |(001)|}\right\} = \cos^{-1}\left(\frac{1}{\sqrt{3} \times 1}\right) = 54.74^{0}$$

Similarly, angle between (111) and (110) is 35.26^0; between (110) and (100) is 45^0. In (110) plane which follows one of the <100> directions, the side walls of the etched pattern form a slope of 45^0 because the etch rate in <100> is higher than in <110> direction. High anisotropic effect of KOH solution results in pyramidal etch stop with sidewall of 54.74^0 as shown in Fig. 1. The graphical nature of such plane is displayed herewith.

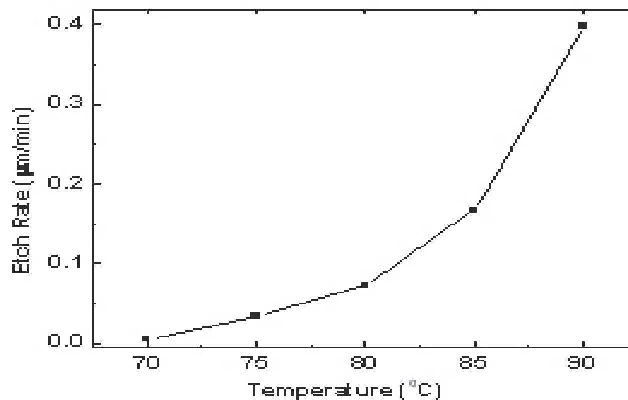

Fig. 2. Variation of silicon (111) etch rate with temperature

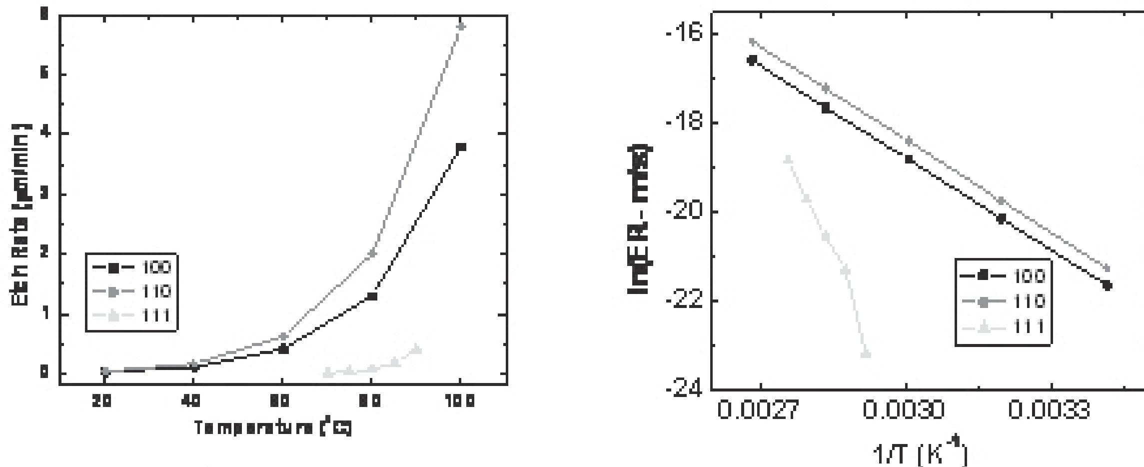

Fig. 3. Etch rates and Arrhenius plot of experimental data of primary crystal planes

Etch rate and activation energy

The microscopic activation energies and ER are explained by the sum of two terms. One corresponds to the average of the microscopic activation energies and other accounts for the existence of fluctuation in the fraction of particles at a fixed temperature (*Bassous et al. 1977)*. Etch rate it depends on p_i and T. In order to understand this, we define *ER* in terms of probability, p_i as:

$$ER = \frac{\Delta Z_{CM}}{\Delta t} = \frac{1}{\Delta t}\sum_i (\Delta Z_{CM})_{i.}\, p_i \quad \text{...... … (1)}$$

Where, ΔZ_{CM} is the distance traveled by the center of mass of the surface, p_i is the removal probability of the surface atom *i*, and is given by Maxwell Boltzmann distribution law

$$p_i = p_{0i} e^{-.\frac{E_{ai}}{k_B T}} \quad \text{…………..(2)}$$

Where T is the temperature, k_B is the Boltzmann constant, E_{ai} is the microscopic activation energy for removal of sites *i* and p_{oi} is a prefactor. Hence, macroscopic parameter, ER, and microscopic measurement, activation energy, both are correlated with temperature. We can take advantage of such approach as to determine activation energies of orientation of silicon atoms lying on different planes as mentioned below in this work.

In order to define etch rate with the distance traveled by the moving surface we have to define centre of mass (CM) of the removal plane. When the etching process has reached the steady state, ER is simply the ratio of the distance traveled by center of mass (CM) of the surface Z_{CM} to the period of time elapsed (t). i.e. ER = Z_{CM}/t. During a modeling, Z_{CM} can be determined as the sum of all individual shifts $(Z_{CM})_i$ of the surface following each successful event (SE), i.e. the sum over all successful particle removal is occurring during t, ER = Z_{CM}/t. Although $(Z_{CM})_i$ is typically positive, occasionally it may be negative if the removal of site *i* involves a reduction in the total number of surface sites. In particular, certain site- types of this formula for wet chemical etching, typically contribute to the motion of the CM with a negative shift on an average. Alternatively, we may consider the sum over all events independently, whether the event is a successful removal or not. Note that the positive/negative shift of the CM of the surface due to the removal of atom i, $(Z_{CM})_i$, may be calculated independently of whether the atom is removed or not. Equation suggests that the etch rate is composed of two factors: one purely geometrical (the CM-shifts) and the other one purely numerical (the number of removed particles). The etch rate is proportional to the average number of surface atoms removed from the surface per unit time. Here, proportionality constant (Z) is precisely a measure of the average shifts in the CM of the surface per removed atom. Z is an exclusively geometrical feature of the etch rate. In particular, it is independent of temperature. Although Z may take different values for different surface orientations, Z does not depend on temperature for a specified orientation. In this way, the temperature dependence of ER is the same. This is

an important observation because the appearance of negative CM-shifts may be accepted as the interpretation of the relative importance (weight) of the different particle types for the calculation of an average. Actually, the interpretation becomes meaningless if some of the weights are negative. However, the use of '*i*' is free of these artifacts and allows unambiguous interpretation, as shown in this study (*Ammar &.Rodgers 1980*]. There are two alternate ways to determine the rate of removal of particles '*i*' during such simulation: (i) as in the case of the etch rate, of the removal of particles which can be determined during the simulation using only successful events. Note that the averages of the number of surface atoms N are not constant. (ii) The rate of removal of particles can be written in terms of a sum over the different types of surface sites. The rate of removal of particles may also be expressed in terms of the average fraction of particles removed per unit time.

The quantitative characterization of the activation energy can be extracted from the proposed simulation of the crystallographic plane with temperature by simply using ER measurement that typically follows Arrhenius law is displaced in Fig. 3 (b) which is in the line of results reported in literature (*Bassous & Baran 1978)*. For a given etch reaction the etch rate is related to its temperature as

$$ER = Ae^{-\cdot\frac{E_a}{RT}}$$

Where R is ideal gas constant (8.314 J/mol-K), T is temperature, E_a is activation energy and A is a constant called frequency factor, which is related to the fraction of collision between reactants having the proper orientation to form activated complex. Here, plot log of (ER) versus 1/T, determines the activation energy of the reaction from the slope. With these experimental results given in Fig. 3(b), E_a, in 30% KOH by weight is now determined: as for (111): 0.79 eV, for (110): 0.53 eV, for (100): 0.55 eV are in line as reported in literature (*Fan et al. 1988)*. These quantitative data justify that why ER is slow in (111) and very fast in (110) i.e., energy needed to remove a single atom is entirely different along concerned planes. Hence, the plane, which has higher activation energy, has slow ER and vice versa. This is because silicon (111) is closely packed; only very few atoms have enough energy to cross the barrier to reach metastable state. Thus, energy requires displacing an atom from its regular site i.e., breakdown of original bonds and move to an energy crest before descending into a metastable position is associated with microscopic activation energy (*Sekioto et al. 1992)*. This choice conforms that macroscopic observations, especially ER, are sound evidence for the behavior of microscopic activation energies to crystallographic orientations.

Thus, anisotropic etching of silicon with KOH is a well-known method of forming grooves in the silicon surface. Etching of (100) silicon on silicon on insulator (SOI) wafers is carried out over a wide range of reaction temperatures. Results presented here are temperature dependent ER along the crystallographic orientations in silicon. Based on this work, temperature is a crucial factor, which control ER. ER is slowest for the (111) face and fastest in the face of (110) silicon. As reported in results, activation energy is seems to be different along different planes. This is because phonons belong to longitudinal and transverse vibration that affects activation energy and ultimately resulted into anisotropic behaviour of ER of silicon crystal. Way of using statistical modeling is quite consistent with observed and graphical analysis of the results in corporate with the activation energy. These results widen the way to control the microstructure during designing and fabrication of micro-devices and provide enough space for building block of silicon nanotechnology nowadays.

Acknowledgements

Thanks for J. Akhtar, Scientist CEERI, Pilani, for the cooperation of sample preparation. Thanks for Prof. P. Sen at School of Physical Sciences, JNU for the permission of doing this Experiment. Thanks for University Grants Commission, Kathmandu, for financial support.

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