THERMAL ACTIVATION OF CRYSTALLINE SILICON IONS IN ALKALINE SOLUTION

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Abstract: Anisotropic wet chemical etching of silicon in alkaline solutions (KOH) is one of the key techniques for the manufacture of microstructure. Fabrication of Micro-electro mechanical system (MEMS) part demand smooth surface finish and angular dependent etch rate. The absolute values of orientation dependent etch rate is found to vary with thermal agitation. In this work, experimental results of etch rate is found with their unusual values of activation energy along different planes. The various sites that an atom can occupy are not equivalent of their energy; some are more favorable to removal than others. In this paper attention is being given to demonstrate thermal activation is the prime factor that influences the behavior of etching mechanism as well as surface morphology. Atomic force microscopy (AFM) has been employed to analyze the morphology of the etched silicon surface at relevant elevated temperature. A systematic variation in morphological growth leads to stabilized surface structure under the influence of associated activation energy.

Keywords: Activation energy; Etching; Anisotropy; Etch rate; MEMS; LPCVD; SOI.

INTRODUCTION:

Microscopic mechanisms responsible for strong anisotropy are still debated. This is due to the existence of significant interaction between the terminating hydroxyl and the terminating species at the next-nearest neighbours, H or OH. MEMS devices are typically made from silicon [1, 2] using conventional semiconductor manufacturing techniques. They can be either etched from larger structure or built up by employing material deposition processes [3]. Silicon micromachining technology has become popular for the fabrication of a number of MEMS devices [2]. Silicon micromachining provides proper dimensional control and consistent mechanical properties and is now established as a mature technology for micro devices. It allows us to control precisely the shape and dimension of microstructure [3-6]. The technology is now being used to fabricate sensors for measuring pressure, force, flow and acceleration using the advantage of batch processing.

Etching silicon strongly depends on orientation of crystal plane and hence anisotropy. Various experimental techniques have been developed to study anisotropic etching of silicon. Etching silicon can be perform with various etchants, such as KOH, TMAH and EDP [4, 6, 7] are few examples. The dissolution of silicon is needed for deep etching and micromachining, shaping and cleaning. Taking out silicon atoms from its surface with time variation for a given temperature and concentration of KOH solution is not same for plane orientation. Its flexibility is exploited to design microstructures with fraction of micron resolution [6, 8] for modern high devices.

For a given temperature and concentration, removal of silicon atom from its planes wouldn't be same with crystal orientation. Combination of removal atoms together forms a moving surface. The moving surface with time variation depends on etchant's temperature [4-7] and etchant's concentration [4, 5] as well as doping level of silicon substrate [8]. A high etching rate is generally desirable in a manufacturing environment. Too high etch rate however may render a process difficult to control because during etching, hydrogen bubbles [3] are formed on silicon surface. Thus, pyramid formations [3, 5, 6] can be related to poor bubble detachment, precluding diffusion to specific point on the surface. However, proposed technique has provided as a tool for shaping of silicon microstructure and as an evaluation of protective surface films on silicon substrate [6, 7, 8]. Due to diverse functional dependence of etch rate (ER), a complete study of this system is extremely complicated. So, accuracy of ER may vary from laboratory to laboratory and level of sophistication of the equipment. In this study, ER of silicon has been measured with the help of atomic force microscope (AFM) and results have been minutely discussed at an atomic level.

EXPERIMENTAL PROCEDURE:

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 V-cm for the top silicon and 12–15 V-cm for the bottom silicon. Only the top silicon layer was etched by the KOH solution. First, the SOI wafers were prepared with Radio Corporation of America (RCA) cleaning which consist of two consecutive cleaning solutions (standard clean1, i.e. SC1 clean). Radio Corporation of America, Standard Clean 1 (RCASC1) Cleaning including H$_2$O-H$_2$O$_2$-NH$_4$OH with volume ratio typically 5:1:1 was adopted in many steps during experimentation since it removes organic contaminants and particles physically attached to a wafer surface. A 450 Å layer of Si$_3$N$_4$, 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 10 mm×10 mm pieces. With the dice pieces held on a vacuum chuck. Positive photoresist-OCG 825 (p-type silicon) was used to pattern the Si$_3$N$_4$ 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. To assure the sample free of particulate and other airborne contaminants, the experiment were conducted in a dust free room. Etch rate (ER) and Activation energy of removal surface is chosen as the parameter for analysis. The chemical used in this experiment are all electronic grades and crystal is 99.6% pure single crystal silicon. The data presented in this paper are average of several samples follows more or less same trend.

RESULTS AND DISCUSSIONS:

During the etching process, the surface of silicon can be both hydrogen and hydroxyl-terminated, depending on the concentration and pH value of the etchant [6]. Even in the case of H dominance, OH groups still terminate a significant fraction of the surface sites [4] that provides the mechanism for further etching. Due to the weakening effect that the OH terminations have on the backbonds [5], the evolution of the etching process is expected to be strongly correlated to the amount of OH coverage. However, this correlation need not be linear for the complete range of surface coverage, since the weakening of backbonds is not the only mechanism involved in the process. The geometrical restrictions to the attachment of OH groups must also be taken into account. In this way, a non-monotonic dependence of the etch rate on coverage is expected for any crystallographic orientation. As the coverage increases, the etching process becomes faster, since more and more OH groups provide larger amounts of weaker bonds, which are more susceptible for thermal breaking. However, as the OH coverage is increased further, the existence of significant OH/OH interactions between the increasing numbers of terminating hydroxyls eventually slows down the etching process. Since the process which destroys hydroxyl (hydrogen) terminations produces hydrogen (hydroxyl) terminations [6], the etch rate should become vanishingly small for the limiting cases of complete hydrogen and complete hydroxyl termina-

tion (complete passivation). Therefore, for any crystallographic orientation, there should be a value of coverage (or concentration) at which the etch rate reaches a maximum. One of the purpose of this work is to show the existence of a maximum in the etch rates as a function of coverage and identification of its reason.

Results are displayed in Fig.1 which clearly tells about ER is other than linear dependence with temperature variation. ER along three primary planes of silicon viz. (111), (110) and (100) with temperature are plotted in the graph so that one can easily compare their ER. From the graph (111) plane etches quite slow compared with other two planes.
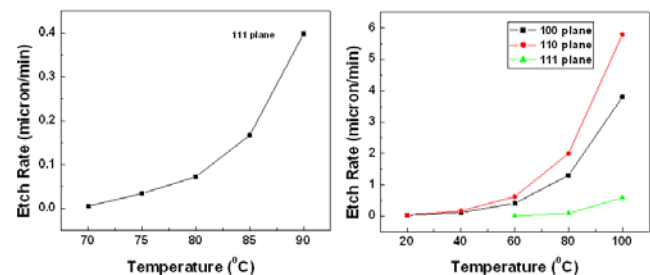

Fig 1: Anisotropic etching of silicon

Based on the results presented here, ER of silicon is highly anisotropic which affect its mechanical properties [2] with respect to orientation. In order to understand basic mechanism of anisotropy in silicon crystal, one should understand activation energy. Activation energy of a reaction is the amount of energy required to start a chemical reaction so that atoms can move from one point to the other. The rate of reaction depends on the temperature at which it runs. ER and surface morphology are macroscopic results [10]. As the moving surface reaches a steady state, ER can be measure with the help of etched depth (ÄZ) with time variation (Ät) as discussed below. As a result, final shape of the etched silicon wafer depends on relative etching speed along the crystallographic planes.

Etch rate (ER) depends on average of the microscopic activation energy and existence of fluctuation in fraction of particles at a fixed temperature i.e. on p_i and T [11] as:

$$ER = \frac{\Delta Z_{c.m.}}{\Delta t} = \frac{1}{\Delta t} \sum_i (\Delta Z_{c.m.})_i \, p_i$$

Where $\Delta Z_{c.m.}$ is distance traveled by the center of mass of the surface, p_i is the removal probability of the surface atom i, is given by $p_i = p_{0i} e^{-E_i / k_B T}$, where T is temperature, k_B is Boltzmann constant, E_i is microscopic activation energy for removal of site i and p_{oi} is a prefactor. So as to understand role of temperature in microscopic energy evolution one should understand reaction mechanism takes place during etching.

The chemical mechanism of etching silicon in KOH solution takes place in two steps [12]. According to Wenspoek, the rate-limiting step for the formation of a solvable silicon complex is the first substitution of terminating hydrogen by a hydroxyl group. After this substitution, the sequence of

further chemical steps is fast. Therefore, it can be expected that OH termination of the neighbouring atoms of initially OH-terminated sites will occur shortly after the initial first substitution, before detachment of the solvable silicon complex. In fact, there is experimental evidence [7] indicating the existence of OH clustering at the initially OH-terminated sites. It is therefore important to establish to what extent the existence of clustering affects the etch rates and the anisotropy of the etching process. In this work we find clustering to the subsequent substitution (H by OH), induced by one initial substitution at a particular target atom, taking place both at the target atom itself (if it is initially terminated by more than one H) and at the first neighbour (if they are H-terminated). Induced substitution occurring at neighbour located further away than the first neighbour is not considered. Their coverage state (either H or OH, for each of the dangling bond) is determined by the nominal value of the surface coverage and is assumed to be uncorrelated to the initial substitution which induces the clustering process. Within this framework, maximal clustering as the complete OH termination of the dangling bonds of the target atom and its entire first neighbour, allowing the second and further neighbour to be partly or totally OH-terminated or H-terminated. Therefore in first step, four electrons are affected in bulk silicon as

$$Si + 4(OH)^- \rightarrow Si(OH)_4 + 4e^-$$
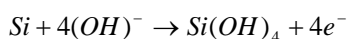
In second step, the electrons are released back into the solution accordingly

$$4e^- + 4H_2O \rightarrow 4(OH)^- + 2H_2$$
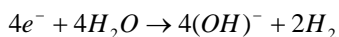
Products in first step $Si(OH)_4$, is supposed to be soluble in water. But actually, $Si(OH)_4$ is decompose into water and silicon-dioxide, as a result of supplied thermal energy and hence there is removal of silicon atom with release of oxygen gas. The probability of removal of particular silicon atom depends on temperature and microscopic activation energy.

Above absolute zero there is gradual increase in the amplitude of atomic vibrations. As the temperature of the system increases, the number of molecules that carryout enough energy to react also increase, this means the molecules move faster and therefore collide frequently. The proportion of collision that can overcome the activation energy for the reaction increases with temperature. Phenomenon for sack out of silicon atom comes into picture if we consider microscopic activation energy; as a result surface morphology is going to be modified. In this view, temperature is a factor for surface roughness. Thus, quantitative estimation of microscopic activation energy will answer these queries.

The quantitative characterization of the activation energy with temperature follows an Arrhenius nature [10] is displaced in Fig. 2. This choice is mathematically guaranteed macroscopic observation, ER, is the result of combination of microscopic activation energies of all atoms [14].
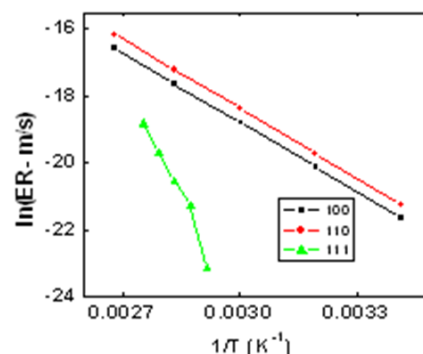

Fig 2: *Arrhenius plot of ER of crystalline silicon*

Based on slope of Arrhenius plot, E_i, is now determined: for (111): 0.79 eV, for (110): 0.53 eV, for (100): 0.55 eV are in the line as reported in the literature [15]. 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 the plane taken. Hence the plane which has higher activation energy has slow ER [16] and vice versa. This is because (111) is closely packed; only few atoms have enough energy to cross the barrier to reach metastable state. Note that energy required to displace an atom from its site i.e., breakdown of the bond and move to an energy crest before descending into a metastable position is associated with activation energy.

Silicon has covalent bond. If it is in excited state, activation energy must overcome the associated covalent energy between silicon molecules. In high temperature silicon etching, activation energy easily dominates covalent energy between silicon molecules so that covalent bonds are going to be broken and hence molecule becomes unstable and starts to leave that particular site. Cohesive energy of a solid is the energy required to disassemble into its constituent parts [17]. Hence, crystal like silicon, cohesive energy is the ground state binding energy. If we go down to atomic structure, cohesive energy is basically based on LCAO (Linear Combination of Atomic Orbital) model [13]. According to this model when a crystal is formed from independent atoms, number of orbital remains same and retains much of their atomic character. However, there are continuous changes in the energies of the orbital with atomic separation with thermal agitation. As the atoms are brought closer together, the orbits begin to interact and hence their bond strength modifies which determines ultimately the crystal property of the silicon.

Each silicon atom has four valence electrons forming strong s-p[3] hybrid as in diamond structure [18] so that energy cost for hybrid s-p[3] is splitting for the removal of the host silicon atom. As we know cohesive energy is a function of nearest neighbor distance [19]. Thus, greater the cohesive energy more will be activation energy [20]. We now arrive at the conclusion that cohesive energy measures the strength of the interatomic forces and hence the stability of the crystallographic plane which answers why ER in (111) is less than the other.

CONCLUSIONS:

Results presented here are temperature dependent ER along crystallographic orientations. This work identify thermal agitation is a crucial factor which control ER, activation and cohesive energy of the crystal plane. ER is slow in (111) face and fast in (110) face. Activation energy and cohesive energy is more in (111) and less in (100). This is possible if interplanar distance is more for (100) and less for (111) plane. Removal of silicon atom should be many particle problems and hence depends on quantum probability laws so that it follows Arrhenius behavior. And hence, strong anisotropy in ER of KOH etching allow us a precious control of lateral dimension of the microstructure bound by the (111) planes [21] to form enough foundation for miniaturized devices.

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