THE MECHANISM OF ANISOTROPIC SILICON ETCHING AND ITS RELEVANCE FOR MICROMACHINING

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ABSTRACT

Several alkaline silicon etchants based on ethylenediamine, KOH, NaOH, and LiOH were characterized experimentally with respect to their dependence on the crystal orientation and on the boron dopant concentration of silicon. Based on these results a model for the electrochemical etch mechanism is proposed explaining the quasi-etch stop behavior and the effects of anisotropy. Finally, suggestions are given as to what etchant composition serves best for a given application.

INTRODUCTION

Anisotropic etching is a key technology for the micromachining of miniature three-dimensional structures in silicon. It is used for the fabrication of a large variety of sensors, such as for pressure, acceleration, vibration, or flow. Two etching systems are of practical interest, one based on ethylenediamine and water, with additives like pyrocatechol and pyrazine, the other consisting of purely inorganic alkaline solutions like KOH, NaOH, or LiOH. Since the effects of the different aniones were found to be minor when solutions of equal molarity are used, the discussion of the inorganic solutions will be limited to KOH.

So far, several papers have been published providing experimental data and models for describing specific aspects of the etching mechanism (1-14). In this work, an attempt is undertaken for giving a consistent model for both etching systems explaining the phenomena of anisotropy and the boron induced quasi etch stop.

EXPERIMENTAL

In this investigation KOH solutions in a concentration range from 10 - 50 %, and an ethylenediamine-based solution (EDP) type S with a composition of 1 l ethylenediamine, 133 ml water, 160 g pyrocatechol, and 6 g pyrazine were used (3). All experiments were carried out in a double-walled thermostated glass vessel with a reflux column and a nitrogen purge.

For measuring the anisotropic behavior, oxidized silicon wafers of p or n type, 1 - 10 Ω cm, with a surface orientation of (100) or (110) were patterned lithographically with a star-shaped mask, exposing blank stripes of silicon with an angular separation of one degree (9). After etching, the depth of the resulting grooves was determined by a Taly-step. The lateral underetching was measured by a linewidth measurement system (Leitz Latimet). The crystal orientation of the sidewalls of the etch grooves was determined by means of laser reflection experiments.

For determination of the boron dopant concentration of the etch rate epitaxial layers with a boron concentration ranging from $1 * 10^{19}$ cm^{-3} to $1.5 * 10^{20}$ cm^{-3} were deposited on (100) and (110) oriented wafers. The same lithography mask as described above was used on a CVD siliconnitride deposited on these wafers and the resulting depth of the grooves was determined after etching.

The etch rates of SiO_2 and Si_3N_4 were determined by ellipsometric measurements.

RESULTS

For all etchants, (111) crystal planes exposed the slowest etch rates being approximately two orders of magnitude smaller than for other principal crystal directions. For an EDP solution type S the temperature dependence of the vertical (100) and (110) etch

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rates, as well as the lateral (111) etch rate as determined on (100) wafers is shown in Fig. 1. Whereas etched (100) and (111) surfaces were found to be quite smooth, (110) surfaces developed grooves bounded by (331) crystal planes.

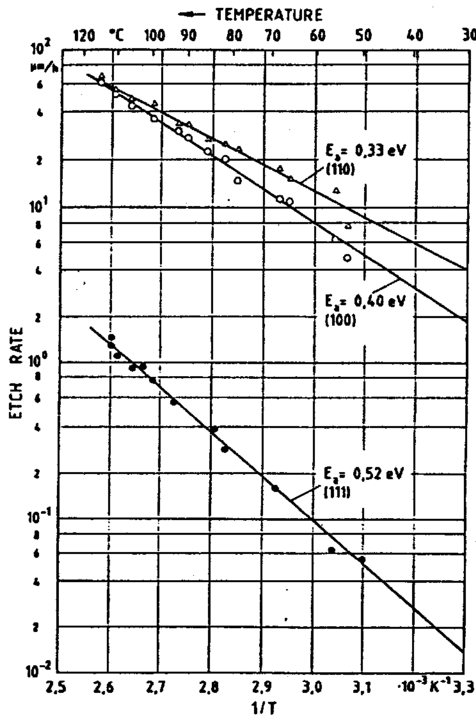


Fig. 1: Arrhenius diagram of the etch rates of the main crystal directions when using an EDP solution type S.

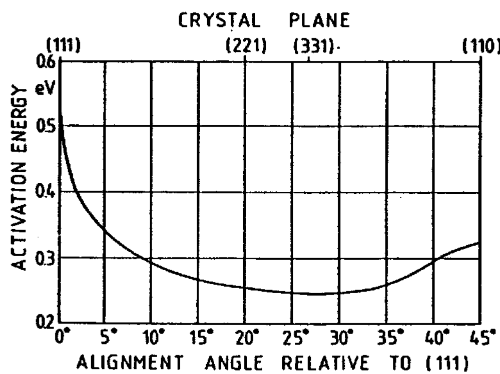


Fig. 2: Activation energy of the lateral etch rates on (100) silicon as a function of the alignment angle. Principle crystal planes corresponding to a certain angle are indicated.

For ethylenediamine-based solutions the laser reflection experiments on laterally underetched (100) and (110) wafers revealed that the etch bordering crystal planes are characterized by the Miller indices (hkk) with h = k. The maximum etch rate is obtained for the (331) crystal orientation (8, 9). The activation energies of the etch rates of different crystal planes were found to be correlated with the etch rates themselves (s. Fig. 2). A maximum of 0.52 eV is obtained for the slowest etching (111) planes, whereas the minimum of 0.25 eV corresponds to (331) with the maximal etch rate.

For KOH solutions, a maximum for the etch rate was observed for a concentration of 15 %. For higher concentrations the etch rate decreases with the fourth power of the water concentration (s. Fig. 3). KOH solutions with a concentration below 20 % were found to be of limited applicability, due to the formation of rough surfaces and a tendency for the development of insoluble white residues on the silicon surfaces. The activation energies for the etch rates of (100) and (110) crystal planes were found to be 0.60 eV. Of special interest is the development of vertical (100) planes on (100) wafers when using KOH with a concentration higher than 30 %.

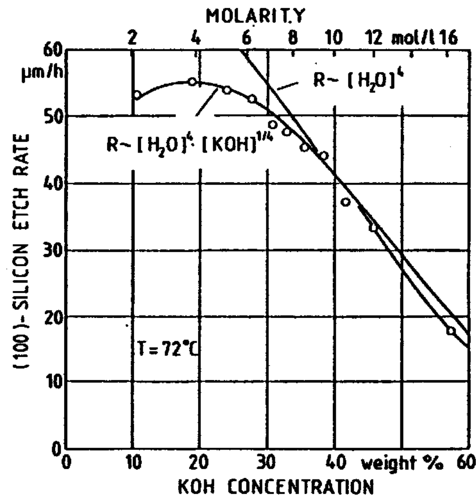


Fig. 3: (100) silicon etch rate as a function of KOH concentration.

Whereas siliconnitride proved to be a perfect masking material, not at all being attacked in alkaline solutions, the etch rate of silicondioxide shows a strong dependence on the composition of the etchant chosen. For EDP solutions this etch rate is about

three orders of magnitude lower than for KOH (s. Fig. 4). The ratio of the (100) silicon etch rate to the SiO_2 etch rate as a function of temperature for EDP type S and for several KOH solutions is shown in Fig. 5.

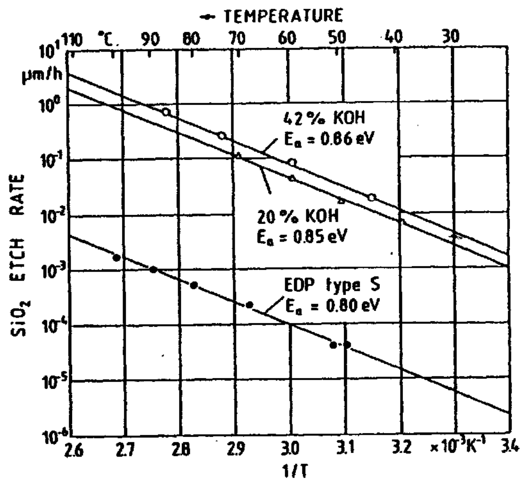


Fig. 4: Arrhenius diagram of the SiO_2 etch rate for EDP type S and KOH.

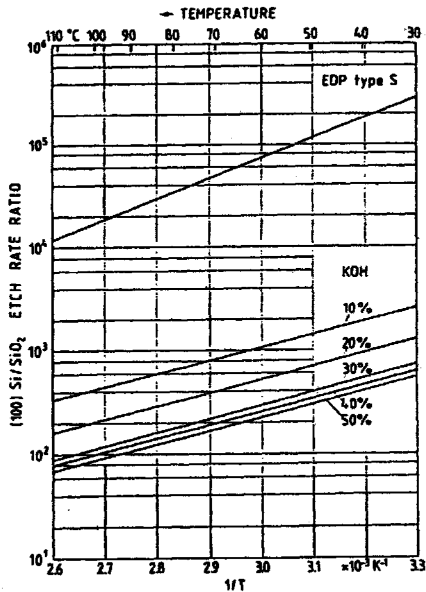


Fig. 5: Ratio of the (100) Si/SiO_2 etch rate as a function of temperature.

For boron concentrations above a critical value C_o of approximately 3 * 10^{19} cm^{-3} a drastic reduction of the etch rate can be observed on both (100) and (110) oriented samples. Fig. 6 shows this effect for an EDP solution type S, where the absolute etch rate was normalized by the etch rate for lowly doped silicon. The drop is inversely proportional to the fourth power of the boron concentration. Based on experimental data, the following semi-empirical formula for the dependence of the etch rate R on the boron concentration C_B is proposed:

$$R = \frac{R_i}{(1 + (C_B/C_o)^a)^{4/a}} \qquad (1)$$

where R_i is the etch rate for lowly doped silicon. The parameter a determines the abruptness of the transition around the critical boron concentration C_o. For EDP solutions an excellent agreement with the experiment is achieved by setting a equal to 4 (s. Fig. 6).

The critical etch rate exhibits a slight temperature dependence with an activation energy of 0.025 eV (s. Fig. 6). This effect was found to be universal for all anisotropic etchants investigated (13). The Arrhenius diagram in Fig. 7 shows the activation energies of the etch rates for various boron concentrations when using an EDP solution type S. For all boron concentrations above the critical value the activation energies are approximately 0.1 eV larger than in the case of lowly doped silicon. This difference is equal to four times the activation energy of the critical boron concentration which can be deduced from the fourth power law in Eq. 1.

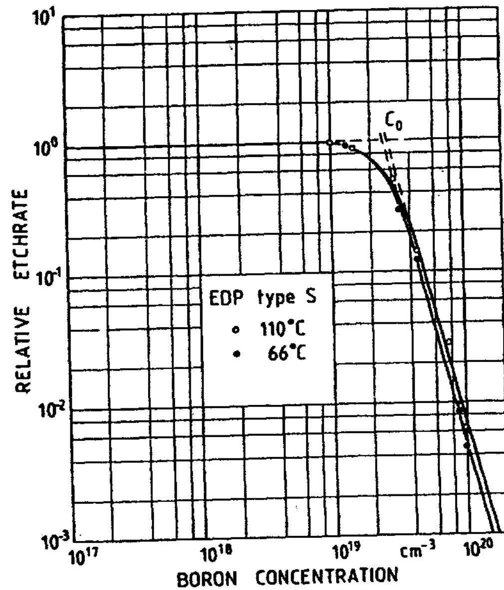


Fig. 6: Relative silicon etch rate as a function of boron dopant concentration for EDP type S.

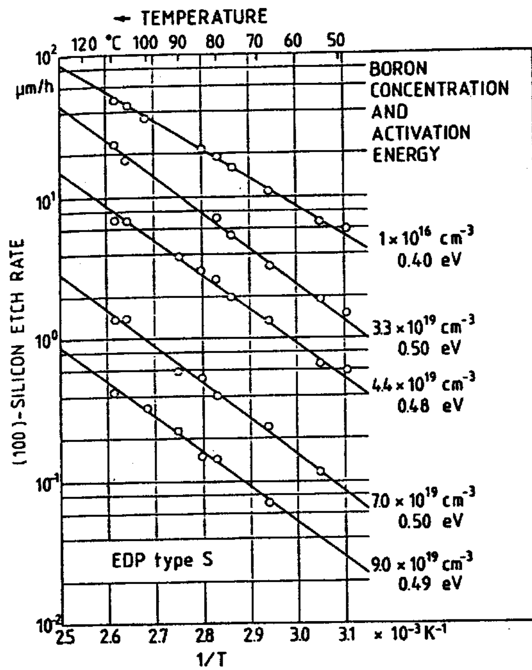


Fig. 7: Arrhenius diagram of the (100)silicon etch rate for various boron dopant concentrations.

When using KOH solutions, the critical boron concentration increases to somewhat higher values (s. Fig. 8). The transition region becomes smoother for higher KOH concentrations. This behavior can be described by Eq. 1 by setting the parameter a equal to 1.

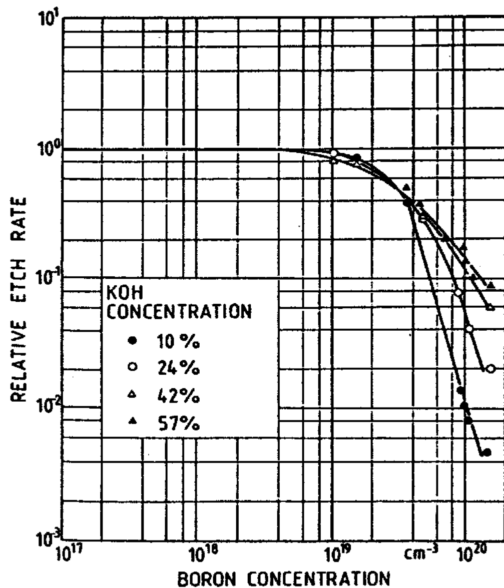
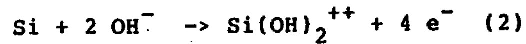


Fig. 8: (100) silicon etch rate as a function of the boron dopant concentration for various KOH solutions.

DISCUSSION

Based on the alkalinity of the solution, the development of hydrogen bubbles during the etching process, the inverse fourth power law for the etch rate in case of highly boron doped silicon and the fourth order dependence of the etch rate on the water concentration in case of high KOH concentrations, the following mechanism is proposed.

The atoms on the silicon surface react with hydroxyle ions with a simultaneous injection of four electrons into the conduction band of silicon:

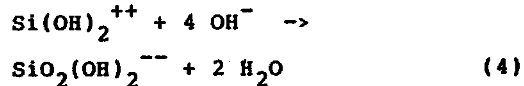


$$Si + 2\ OH^- \rightarrow Si(OH)_2^{++} + 4\ e^- \quad (2)$$

This primary oxidation step is followed by a reduction reaction leading to the development of hydrogen gas:

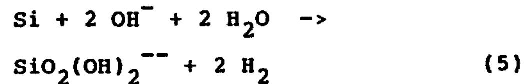
$$4\ H_2O + 4\ e^- \rightarrow 4\ OH^- + 2\ H_2 \quad (3)$$

The positively charged complex of the primary oxidation step (Eq. 2) reacts further to a soluble silicon complex:



$$Si(OH)_2^{++} + 4\ OH^- \rightarrow SiO_2(OH)_2^{--} + 2\ H_2O \quad (4)$$

This ion has been identified as a reaction product by Raman spectroscopy when etching with KOH (7). The overall reaction can be summarized as follows:



$$Si + 2\ OH^- + 2\ H_2O \rightarrow SiO_2(OH)_2^{--} + 2\ H_2 \quad (5)$$

For dopant concentrations below $1 * 10^{19}$ cm^{-3}, an extended space charge layer at the silicon surface provides a sufficiently long lifetime of the injected electrons to be able to react with the water molecules at the semiconductor/-electrolyte interface. At a critical boron concentration of $3 * 10^{19}$ cm^{-3} silicon degenerates (15) and starts to behave like a metal due to the dropping of the Fermi level into the valence band. As a consequence the space charge layer reduces essentially to a surface charge of a few angstrom thickness. Thus, the injected electrons immediately recombine with the holes which are present in a very large concentration making the reduction step in Eq. 3 to the rate limiting reaction. The remaining concentration of free electrons becomes inversely proportional to the concentration of holes and, thus, to the boron dopant concentration. By assuming that four electrons are involved in the electrochemical reaction, the inverse

fourth power law can be explained. The temperature dependence of the critical etch rate C_o is presumably correlated to the temperature dependence of the semiconductor-metal transition, explaining the universality of the observed activation energy of 0.025 eV for all etchants investigated.

Since EDP solutions have a much lower pH of approximately 12.5 as compared to at least 14 for KOH it can be assumed that in the former case the reaction is oxidation limited due to the relatively low concentration of hydroxyle ions. In the case of KOH for concentrations above 20 %, the reaction becomes reduction limited due to the relatively low water concentration. Since a high boron concentration also limits the reduction reaction, the smoother transition region towards a decreasing etch rate for high KOH concentrations can be explained.

The large anisotropic effects with differences in etch rates on the order of 100 : 1 are due to relatively small differences in activation energies resulting from different binding forces of the surface atoms of different crystal planes. The surface atoms of (111) planes are bonded most strongly, having only one dangling bond whereas (100) and (110) have two.

CONCLUSION

For practical applications several recommendations can be deduced from the results given above and from the proposed mechanism.

In applications where the quasi etch stop of highly boron doped silicon is taken advantage of, EDP solutions are clearly preferable. When KOH solutions are preferred for other reasons, the concentration should be chosen as low as possible where 20 % seems to be a practical lower limit because of increasing surface roughness and the likelihood of residue formation. A slight increase of the etch rate ratio between lowly and highly doped silicon can be achieved by lowering the etch temperature.

Due to differences in activation energy, the anisotropic effects generally increase when choosing a lower etch temperature. Since the overall etch rates also decrease considerably, a reasonable compromise has to be found. For KOH solutions a ratio of 400:1 between (110) and (111) has been reported (4). However, even a minute misalignment of 0.5^o would lead to a decrease of this ratio to less than 100. This is the order of magnitude that we found to be practically achievable. The same is true for EDP (s. Fig. 1).

A special effect when using KOH solutions with a concentration higher than 30 % is the formation of vertical (100) crystal planes on (100) wafers. This can be used for etching very high needles, as well as for corner undercutting compensation.

An important consideration lies in the applicability of passivation layers. Si_3N_4 has been found to be a perfect masking material for both systems. SiO_2 is an excellent passivation when using ethylenediamine based etchants. When SiO_2 is to be used as a masking material with a KOH solution, both temperature and concentration of the solution should be chosen as low as possible.

An important consideration is the safe handling of the etchants. Ethylenediamine is suspected to cause cancer and shoud therefore be handled with the greatest care possible. In this respect, KOH is clearly much less dangerous.

Summarizing, the use of ethylenediamine based solutions can strongly be recommended when the necessary safety precautions have been taken. It is superior with respect to SiO_2 passivation layers and the applicability of a boron etch stop. For applications, where anisotropy is the only requirement and the question of passivation can be handled, KOH can also be recommended.

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