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^{29}Si-Nuclear Magnetic Resonance on the Etching Products of Silicon in Potassium Hydroxide Solutions

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We present results of ^{29}Si-nuclear magnetic resonance experiments on a large number of KOH solutions in which silicon has been dissolved. The goal of the experiments is to clarify the chemical composition of concentrated alkaline solutions after etching of silicon. It is confirmed that the initial etching product of wet-chemical etching of silicon in KOH is a silicate monomer. Increasing the silicon content of the solution gives rise to silicate polymerization products. The often reported aging of etching solutions is due to silica in the etchant.
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Anisotropic wet-chemical etching of silicon in alkaline solutions[1] is a key technology in the manufacturing of sensors and actuators. In this technology, etching through masks is used for fast and reproducible shaping of micromechanical structures.[2] The exact geometry of the structures depends on the etchant, temperature, substrate orientation, electrochemical potential at the substrate surface, substrate doping profiles,[3] mask material and the geometry of mask-substrate junctions,[4,5] ultrasound vibrations,[6,7] etchant additives like isopropanol (IPA) [1] or salts,[8-11] surfactants,[12-16] a complexant,[17] metal impurities in the etchant,[18-20] presence of gases over the etchant,[21] silica (polymers) in the etchant,[22-26] and oxygen precipitates in the substrate.[27]

Although there is still much controversy about the reaction mechanism of silicon etching in alkaline solutions, all mechanisms proposed will now assume that the rate-determining step in the mechanism occurs at the silicon surface, when a hydrogen-terminated silicon becomes a hydroxyl-terminated silicon atom (*e.g.*, Ref. 8, 14, 28-29). The second generally accepted assumption is that water subsequently attacks the back-bonds of that silicon atom, resulting in a silicate monomer that leaves the silicon surface.[8,9,28-30] Disagreement also exists on the thermodynamic conditions that are present during silicon etching in KOH solutions. Estimations of the driving force (*i.e.*, the chemical potential difference between silicon atoms in the solution and in the crystal), based on simple dissolution reaction schemes, lead to relatively high values. This would imply that the etching system is so far from equilibrium, that it can be considered irreversible. In crystal growth it is well known that, if the driving force exceeds a certain critical value, no flat faces will develop on a growing crystal. One may expect a similar behavior for the dissolution of crystals, although this has not been confirmed (in fact, we have found indications that the situation is indeed different for dissolution[31]). Nevertheless, stable and nominally flat {111} faces are always observed during anisotropic etching.

In order to obtain a better understanding of the thermodynamics of silicon etching, we decided to study the chemistry of the etching solutions in detail. In this paper we discuss a ^{29}Si nuclear magnetic resonance (NMR) study of the composition of freshly prepared and aged solutions of different KOH concentration and with different silicon content.

Experimental

Seventeen samples with varying silicon content and KOH concentration were prepared (see Table I). The solutions were prepared by dissolving silicon wafers (boron doped, resistivity 0.01-10 Ω cm) or silicon powder (Merck) at various temperatures. The powder was used to speed up the dissolution process. Evaporation of water was reduced by using either a watch glass or a spiral cooler. Two samples were saturated with isopropylalcohol (IPA). Two others were measured immediately after preparation at 353 K, and thereafter again at room temperature (indicated by an asterisk in Table I). A frequently used temperature for silicon micromachining is 353 K. From a few samples, two spectra were obtained, to monitor the "aging" of the solution.

^{29}Si-NMR is a powerful tool to determine the configuration of silicon atoms in alkaline solutions.[32-38] The chemical shift of ^{29}Si, due to different chemical environments, gives direct information about the Si-O linkages in silicate anions in which silicon atoms are surrounded by other silicon atoms via a bridging oxygen atom. Hence, the species shown in Fig. 1 can easily be discerned. In this paper, the Q^i-notation introduced by Engelhardt *et al.*[33] is used, where i indicates the number of neighboring silicon atoms bound through an oxygen atom. We assign the peaks in the spectra on the basis of data collected by Engelhardt *et al.* (Fig. 1).

All spectra were collected on a Bruker DPX 200 (39.86 MHz for ^{29}Si) and a Bruker AMX 500 (99.45 MHz for ^{29}Si), at room temper-

Table I. Overview of all the samples that were prepared. +IPA indicates that the sample was saturated with IPA and an asterisk indicates that the spectrum of the sample was taken immediately after preparation.

Sample	[Si] (g/L)	[Si] M	wt % KOH	Age (days)
A	2.3	0.08	10	1
B	10.5	0.37	10	1
C	11.2	0.40	10	25, 167
D	30.0	1.07	10	4
E	66.7	2.37	10	5
F	3.8	0.14	25	6
G	9.0	0.32	25	8
H + IPA	9.0	0.32	25	5
I*	9.1	0.32	25	0
J	30.7	1.03	25	7
K	31.2	1.11	25	37, 180
L + IPA	40.0	1.42	25	2
M	49.5	1.76	25	37, 180
N	50.3	1.79	25	7
O*	68.1	2.42	25	0
P	69.5	2.47	25	35, 177
Q	72.0	2.56	25	7
R	78.0	2.78	25	13, 157

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ature or 300 K, except where indicated. All measurements were performed in a glass NMR tube with a 10 mm diam, flushed with hot water and preflushed with the sample solution. A 10 mm broad-band Bruker probe was used. The glass tube was rotated at a frequency of 12 Hz. A reference spectrum was measured with only 25 wt % KOH: no peaks were found, except a broad peak due to the glass of the sample tube. This background signal was subtracted from the spectra presented here.

90°-Pulse (pulse duration 19 μs) excitation was used. Due to the long spin-lattice relaxation time, obtaining a spectrum with a reasonable signal-to-noise ratio takes 4-12 h. Spectra are calibrated with respect to an external tetramethylsilane (TMS) sample. As the spectra were collected without locking, some drift can be observed in the spectra.

Results

10 wt % KOH solutions.—In Fig. 2, an overview of the spectra of the samples of 10 wt % KOH is given (A, B, D, and E). It is clear that when more silicon is dissolved, more peaks appear at higher field in the spectrum, *i.e.*, more silicate polymers are formed in the solution. Going from low to high field, we observe the monomer peak, the end group peak, the cyclotrimer peak, the cyclotetramer peak, the middle group peak, and the branching peak. In A, we observe only monomer species, whereas the relative amount of monomer becomes smaller at solutions that contain more silicon. Peak integration shows that the amount of monomer is small in A (~75 mM), larger in solutions B and D (~230 mM), and again smaller in E (~62 mM). The amount of cyclotrimer is larger in D than in E (relative as well as absolute) due to particle growth. Note that the age of the samples is only a few days. The cyclotetramer and branching peaks broaden into one featureless line at higher silicon concentration (E).

Babic *et al*. performed Raman spectroscopy on solutions similar to ours. They found that in solutions with a silicon concentration lower than 3.4 M, cyclotrimers, cyclotetramers, and cyclo-oligomers are the predominant polymeric species. In solutions with a silicon concentration higher than 3.4 M, the cubic octamer becomes dominant.[24,39-40] This is in agreement with our results. All our samples have a silicon concentration under 3.4 M and we do not observe the cubic octamers, although one might argue that in D and E, the split peak around −95.0 ppm comprises a cubic octamer and a branch peak. In all other spectra, only one peak is observed around −95.0 ppm.

25 wt % KOH solutions.—In Fig. 3, an overview of the spectra of the sample of 25 wt % KOH solutions is given (F, G, J, N, and Q).

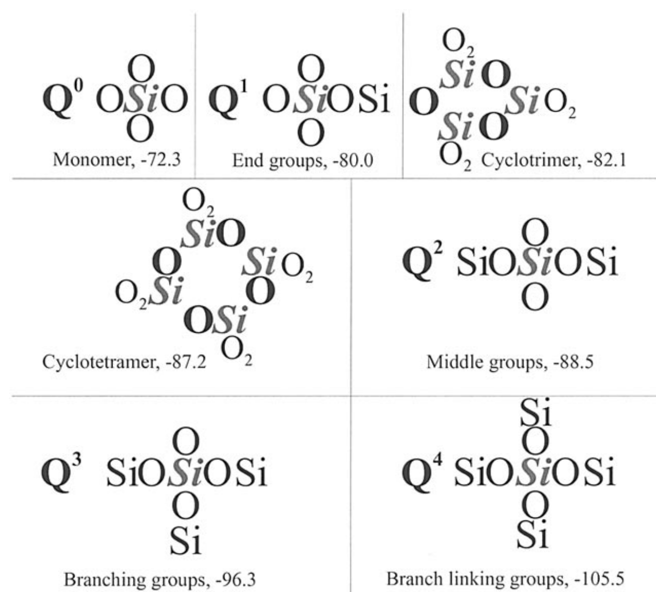

Figure 1. Overview of the species that can be discerned by ^{29}Si-NMR and the Q^i-notation of Engelhardt with assignment of peaks.

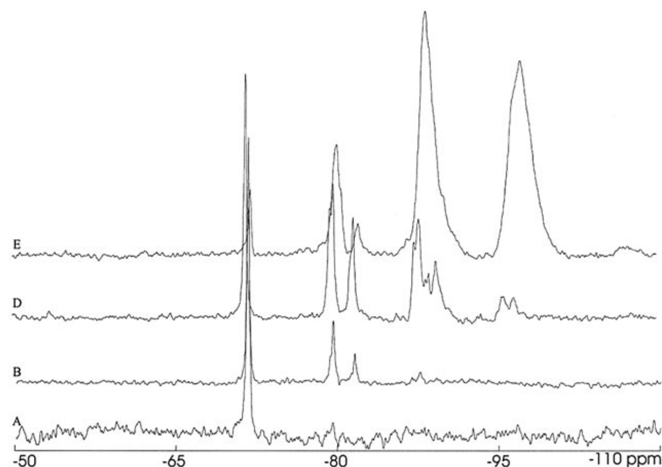

Figure 2. Spectra of samples A, B, D, and *e* (bottom to top) from −50 to −110 ppm. The samples contain an increasing [Si] in a 10 wt % KOH solution.

Again it is clear that the higher the concentration of silicon, the higher the degree of polymerization. In F, we observe only monomer species. The amount of monomer in J, N, and Q is equal (~600 mM). Only in Q do we observe a small branch linking group. Note that the samples are again relatively young. A concentration of 25 wt % KOH is generally preferred for silicon micromachining; because at this concentration the etching rate for the relevant [100] direction is almost the highest.[41]

10 wt % vs. 25 wt % solutions.—Comparing the spectra of Fig. 2 and 3, we observe that the end group peak to middle and branching peak ratio changes significantly. More end groups and less middle and branching groups implies that the silica particles become shorter at a higher etchant concentration. Therefore, we conclude that the degree of polymerization is higher when the KOH concentration in the solution is lower.

IPA samples.—In Fig. 4, the spectra of H and L are shown. These two samples were saturated with IPA during preparation. As expected, we observe that spectrum L, with the higher silicon content, displays more high-field peaks than the spectrum of H. Comparing H to G and L to J and N, which are samples with similar Si concentration, we observe no significant difference. Thus we conclude that IPA has no important influence on the etching products of the dissolution reaction. Apparently, the effect of IPA on etching[1] is due to inhibition or catalyzation of one of the chemical reaction steps in the etchant, or on

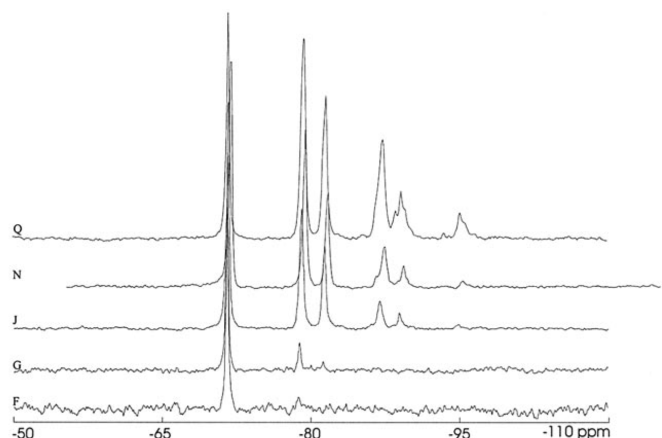

Figure 3. Spectra of samples F, G, J, N, and Q (bottom to top) from −50 to −110 ppm. The samples contain an increasing [Si] in a 25 wt % KOH solution.

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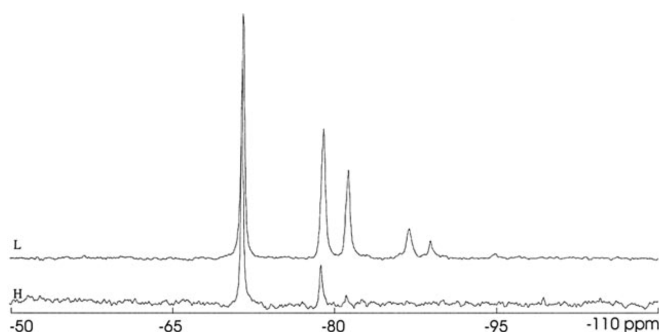

Figure 4. Spectra of samples H and L (bottom to top) from −50 to −110 ppm. The samples contain an increasing [Si] in a 25 wt % KOH solution that was saturated with IPA.

the surface, for example a poisoning effect on surface processes, like atomic step movement.[42,43]

Temperature effects.—Figure 5 displays the spectra of sample I and O at 300 and 353 K. The lower spectrum is measured at 353 K directly after preparation. The upper spectrum is measured at 300 K immediately after cooling. Comparing the two, hardly any difference other than a lower signal-to-noise ratio in the high-temperature spectrum can be observed. The lower S/N ratio was deliberately tolerated, in order to limit the time between the two measurements. It might be argued that in the 300 K spectrum the end group and especially the cyclotrimer peaks are somewhat larger. It is, however, impossible to discern whether this is due to a temperature effect or whether this is simply a matter of noise. Concerning the high and low-temperature spectra of sample O, the same observations can be made. There are no significant differences between the cold spectra of I and O and the spectra of G and Q.

These two samples suggest that cooling a solution to room temperature does not change the composition of the solution. Therefore, we assume that all spectra in this paper represent the situation during etching at elevated temperatures, as far as the composition of silicon species is concerned.

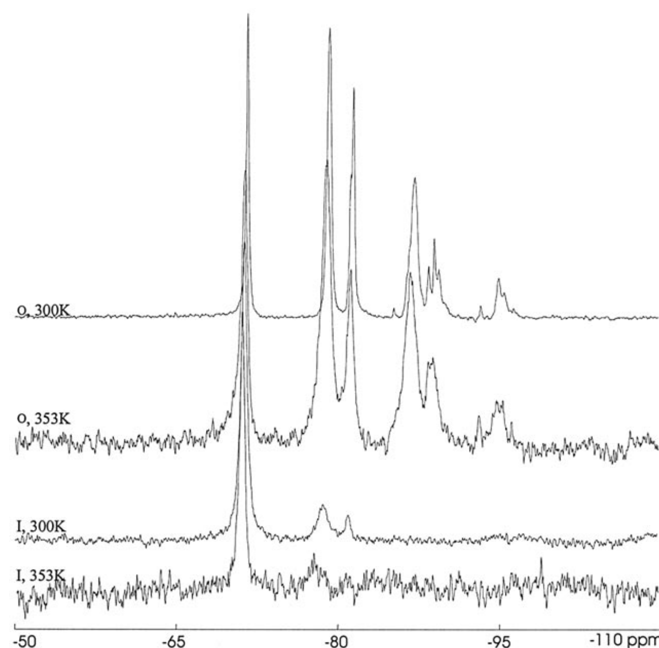

Figure 5. Spectra of samples I and O at 353 and 300 K, respectively, (bottom to top) from −50 to −110 ppm. The samples were measured immediately after preparation.

As indicated in Table I, some samples were left on the shelf for a considerable amount of time to investigate the slower polymerization reactions. From Table I, a number of similar solutions can be followed in time. They are B, C_{25}, C_{167}; J, K_{37}, K_{180}; N, M_{37}, M_{180}; O_{353K}, O_{300K}, and Q, R_{13}, R_{157}. The spectra revealed no significant changes, however. Neither did they in those cases where samples changed in physical appearance, *i.e.*, became turbid or turned slightly gelatinous, not even in the case of solution R, that started to precipitate. In this respect it has to be mentioned, though, that such precipitation is not seen in the spectra, since we performed solution NMR and not solid-state NMR, only the silicon atoms at the surface of solid particles will contribute to the solution spectrum.

From these observations it must be concluded that the so-called "aging of solutions" is an effect that is caused purely by an increase in the amount of polymeric species in the solution. Aging of solutions is the observed increasing irreproducibility of etching results when the etchant is not refreshed after a certain number of etching experiments. The polymeric silicate species act as impurities that reduce the etch rate of silicon, thereby changing the anisotropy of etching. In light of this observation, the term aging seems awkward since it points to a time-induced effect, while we now find that it is an impurity-induced effect; it is probably the amount of dissolved silicon that has an influence on the etching characteristics and not the time that the dissolved silicon has been in the etchant. We roughly estimate that the maximum concentration in the etching vessels in our silicon device facilities is about 30 g/L, indicating that the solutions we prepared in this study represent samples comparable to normal fabrication conditions. This estimation is based on the fact that refreshment of the etchant is generally performed after dissolution of *ca*. 20% of some hundred 3 in. wafers in *ca*. 3 L of etchant.

Discussion

Much research has been performed on the behavior of silicic acid, $Si(OH)_4$, in various aqueous media. Most of this research is aimed at understanding the formation of sols and gels out of silicic acid, a weak acid that exists only in dilute aqueous solutions. When its concentration becomes larger, it polymerizes via condensation of silanol groups. Condensation involves an ionic mechanism, giving rise to silica particles with increasing molecular mass, ultimately leading to sols and gels. Above pH 2 the condensation rate is proportional to the concentration $[OH^-]$. Polymerization leads to particles that have a minimum number of uncondensed −OH groups and a maximum of siloxane (Si-O-Si) bridges and therefore ringlike structures are easily formed.

Above pH 6, silica starts to dissolve and form soluble silicates. When the electrolyte concentration is low and pH is smaller than 10, the monomer silicate polymerizes rapidly, in a matter of minutes, at room temperature. After formation of 1-2 nm sized three-dimensional particles, the concentration of monomer is in equilibrium with these particles and decreases while the size of the particles increases. This process depends strongly on temperature and particle size. Alkali-stabilized sols have shown to polymerize in a few months at 30°C, while at 90°C it takes only a few days. Solubility of particles depends on the creation temperature.[44]

Our results indicate that upon dissolution of silicon, the composition of the KOH solution shifts to higher amounts of polymerized products. The concentration of the primary product of silicon dissolution, the silicate monomer, increases sharply to a certain saturation value, that depends on the KOH concentration, while it decreases again when large amounts of silicon are dissolved. This is shown in Fig. 6, where we have plotted the silicate monomer concentration, obtained by peak integration of the NMR spectra as a function of the total silicon content of the solutions. The latter decrease seems to be caused by the onset of silica precipitation, as evidenced by the increased turbidity of these solutions. The results indicate that the chemistry going on in typical silicon micromachining solutions resembles silica solution chemistry. This is expected from a thermodynamic point of view: silicon in an alkaline solution, or even in pure water, is unstable with respect to the formation of silicon diox-

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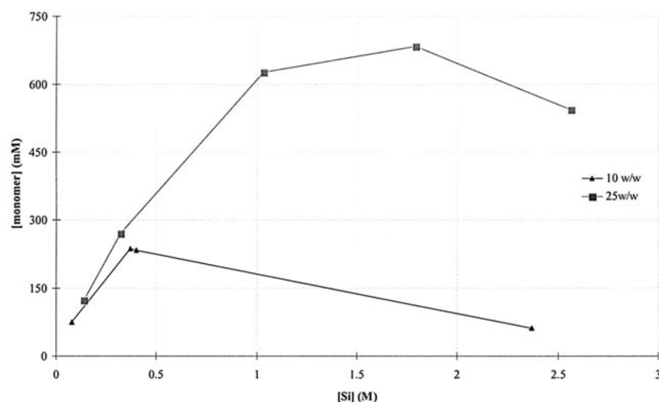

Figure 6. Graph of the silicate monomer *vs*. silicon concentration.

ide. A calculation of the change in Gibbs free energy for this process amounts to −515 kJ per mol of silicon.[45,46] So the Si-KOH system is strongly driven toward the formation of solid SiO_2, and the route through which this occurs obviously involves the polymerisation of silicates in solution.

Referring back to the statements on the driving force in the introduction to this paper, we want to stress here that the polymerization process complicates the quest for an exact value of the driving force for etching of silicon. Because to the best of our knowledge the relevant thermodynamic properties of $Si(OH)_4$ and its polymerization products are not known, it will be impossible to calculate the equilibrium concentration of silicon in concentrated KOH solutions.

Conclusion

We have analyzed the chemical composition of a large number of concentrated alkaline solutions containing various amounts of dissolved silicon using ^{29}Si-NMR. The results indicate that the chemistry of the solutions is comparable to silica solutions. We observed that in 25 wt % KOH solutions the degree of polymerization is lower than that in 10 wt % KOH solutions. Temperature does not seem to have an influence on the concentration of the soluble species present. IPA has no influence on the composition of the solutions, nor has time or temperature. The phenomenon of aging of solutions is an effect of silica polymer concentration. Silica polymers are present in substantial amounts and affect the reproducibility of an etching system.

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