THE KINETIC COMPENSATION EFFECT IN ANISOTROPIC ETCHING OF SILICON IN KOH SOLUTION CONTAMINATED WITH METALLIC IMPURITIES

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ABSTRACT

This work accomplishes previous studies in anisotropic etching of silicon in KOH solution and reaction Kinetics Compensation Effect (KCE). It was used p-type [100] Silicon-Cz wafer in KOH with Zinc ions dissolved. Etching rates were measured using a Scanning Laser Microscopy (SLM). For surface analysis it was used Scanning Electron Microscopy (SEM). The reaction Activation Energy (E_a) and Preexponential Factor (R_0) were found and KCE was noted.

1. INTRODUCTION

Silicon anisotropic etching is a key technology for MEMS devices fabrication, as allows three-dimensional structures precision and devices miniaturization such as sensors and actuators, turning then compatible with Integrated Circuits [1,2].

Anisotropic etching is dependent on crystallography, dopants concentration, temperature and electrical potential applied. The aim of this work is to verify how metallic impurities affect anisotropy in KOH solution, besides suggesting a possible control of etching for rate and resulting geometry after adding different metals in solution.

1.1. Kinetics Compensation Effect

Poço et al. [3] correlates silicon etching in KOH with dimethyldichlorosilane (DMDCS) direct synthesis and "Kinetic Compensation Effect" (KCE) or "isokinetic effect", in which both reactions follow Arrhenius law [1,3,4,5,6]:

$$R = R_o \exp(-E_a/KT) \quad (1)$$

This effect most important attribute is that a change in one Arrhenius parameter is compensated by a correspondent change in the other [7]. This behavior is observed in DMDCS direct synthesis at MeCl and silicon reaction, possibly by the anisotropic character of reactions. Therefore, Poço et al. [3,8] suggests that other chemical elements should act like promoters in silicon anisotropic etching.

1.2. Metal selection

Selection of metals was made among those that have an effect as promoting or inhibiting DMDCS synthesis [8], including those that are exposed in Hein et al. (1997) [5] work. In this work it was chosen Zinc, as was the metal with largest anisotropy when used as contaminant in an anisotropic etching in KOH solution [5] and it is also the main promoter in DMDCS direct synthesis [3].

2. EXPERIMENTAL PROCEDURE

The experiments were carried out on a single polish silicon-Cz wafer with 3” diameter. The wafers are boron-doped type, 1–10 Ωcm (100). The samples were soaked in the KOH solution at 27 % wt in the 40–85 °C ± 0,1°C range for one hour each.

The intentional contamination of solution was made with Zn-ion using CH_3COOZn in 100, 300, 780 and 1800 ppm.

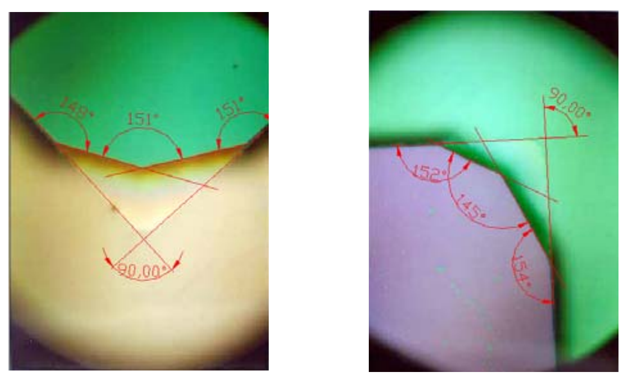
The patterns for anisotropic etching were transferred in the 0,9 μm thermal grow oxide with plateaus sidewalls aligned at <110> or <100> directions. A magnetic stirrer was used for unfastening H_2 bubbles of silicon surface.

The profiles measurements were made with Scanner Laser Microscopy (SLM) and the surface analysis was made with Scanner Electronic Microscopy (SEM).

3. RESULTS AND DISCUSSION

Studies show that an silicon anisotropic etching in KOH 27% is made (without impurities added), in one hour process, using the passivation layer aligned with (110) planes in a (100), a convex corner is formed with its limits aligned with <211> direction [6].

It was observed that Zinc changes etching rates of crystallographic directions, as a result the angle formed by the convex corner was also altered. This effect can be observed in Figure 1.



a) b)

Figure 1 – Convex corners formed in Silicon etching in 27% KOH contaminated with a) Zinc 720ppm and b) Zinc 1800ppm

3.1. Activation Energy (E_a) and preexponential factor (R_0)

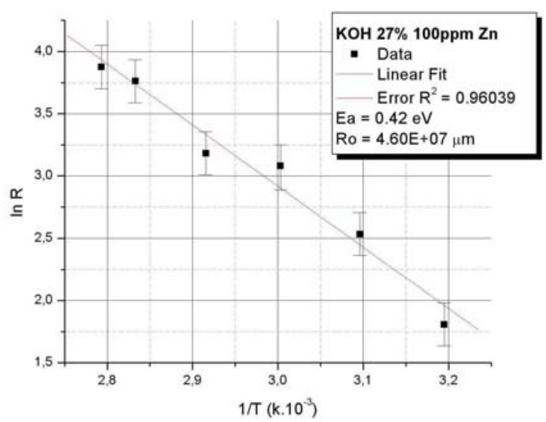
The etching rates vary as Arrhenius law (eq. 1) [9], where the etch rate is referred as R, R_0 the preexponecial factor, E_a the activation, K the Boltzman constant (8,62x10-5 eV/ºK = 1,38x10-23 J/ºK) and T the temperature (K).

Accordingly, with etch rates for different temperatures, E_a e R_0 can be obtained with a linear Arrhenius law analysis [4] from equation (1):

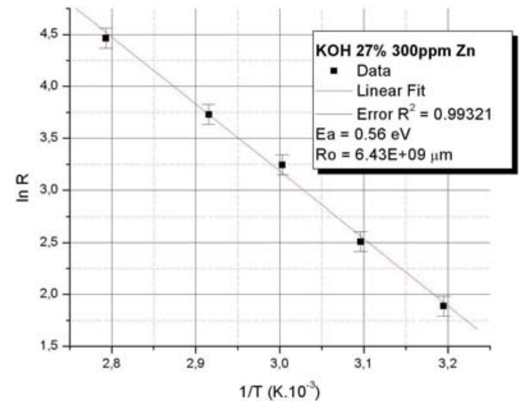
$$y = ln(R)\,,\ b = ln(R_0)\,,\ a = \frac{-E_a}{K} \text{ and } x = \frac{1}{T}$$

A change in E_a e R_o values shows that there is an alteration in KOH and silicon reaction in (100) plan when there is a change in Zinc concentration in KOH solution.

As can be observed in Figure **3**, the possibility made by Poço et al [3] could be noticed as being correct. Thus, silicon etching in KOH follows Cremer-Constable relation, where a change in E_a is compensated by a correspondent change in R_0.



a)



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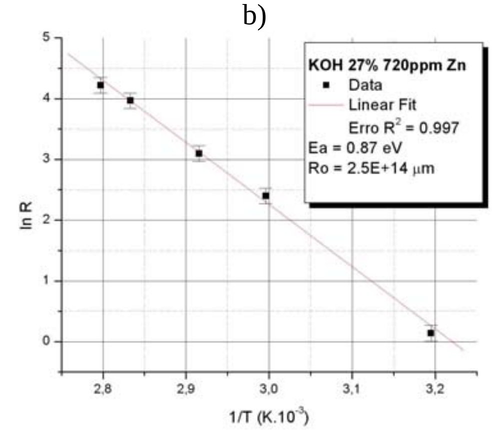

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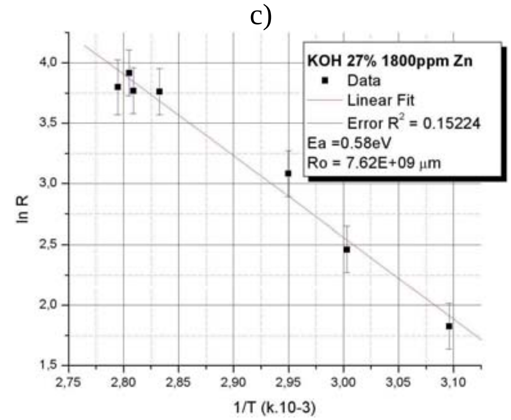

d)

Figure 2 – Arrhenius plot for KOH 27% contaminated with: (a) Zinc 100ppm, (b) Zinc 300ppm, (c) Zinc 780ppm and (d) Zinc 1800ppm.

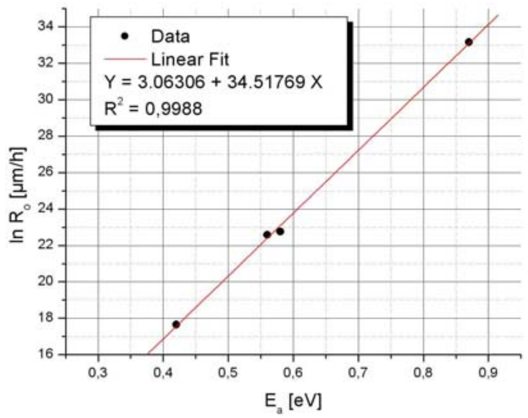

Figure 3 – Cremer-Constable diagram showing kinetic compensation effect for Zinc contamination in KOH and Silicon reaction.

4. CONCLUSION

A variation in Arrhenius parameters was experimentally observed for silicon anisotropic etching in KOH with metallic impurities.

This variation suggests that anisotropy control may be possible. Further studies could be made related with different metals contamination in different proportions aiming a control of etching anisotropy.

The silicon anisotropic etching KCE character could be observed experimentally, providing evidences for the model proposed by Poço et al. [3,8], supporting the relation between silicon anisotropic etching with DMDCS synthesis.

5. ACKNOWLEDGEMENTS

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