Basic 2
Anisotropic Wet-etching of Silicon: Characterization and Modeling of Changeable Anisotropy

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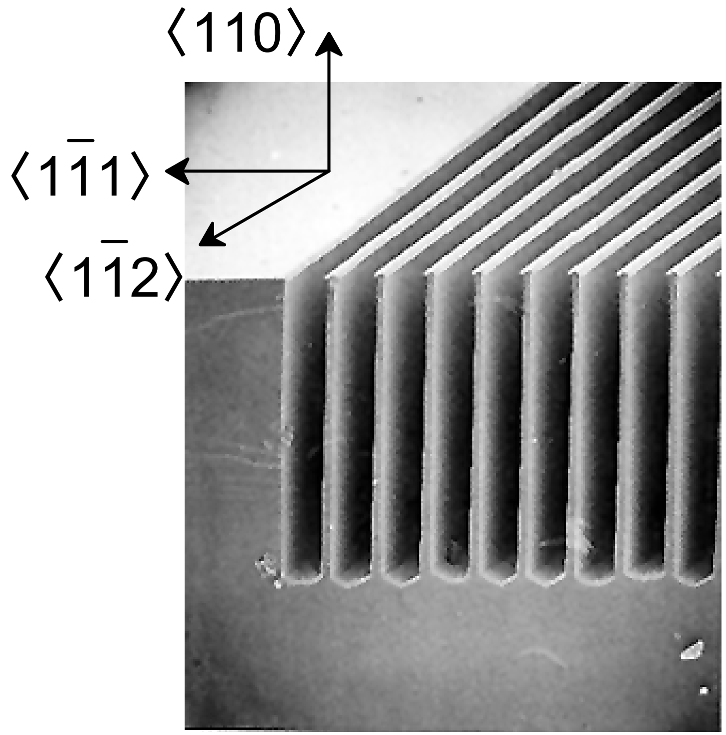
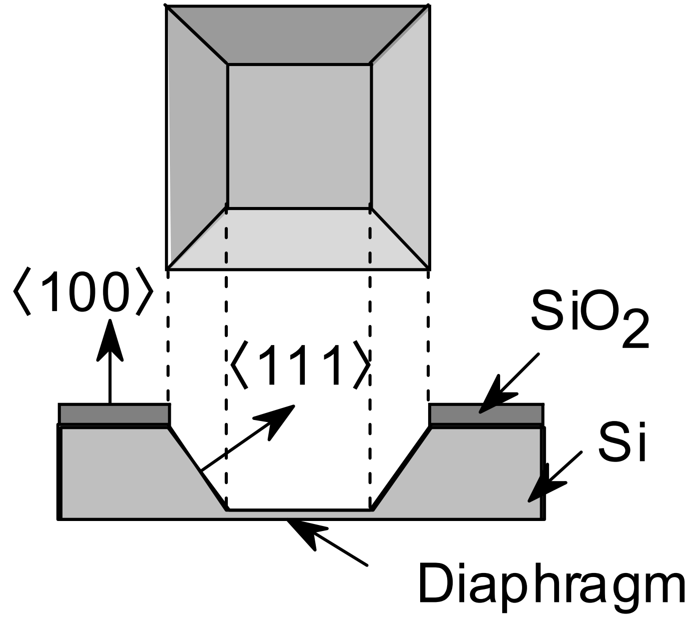
Orientation Dependent Etching (Conventional Products)

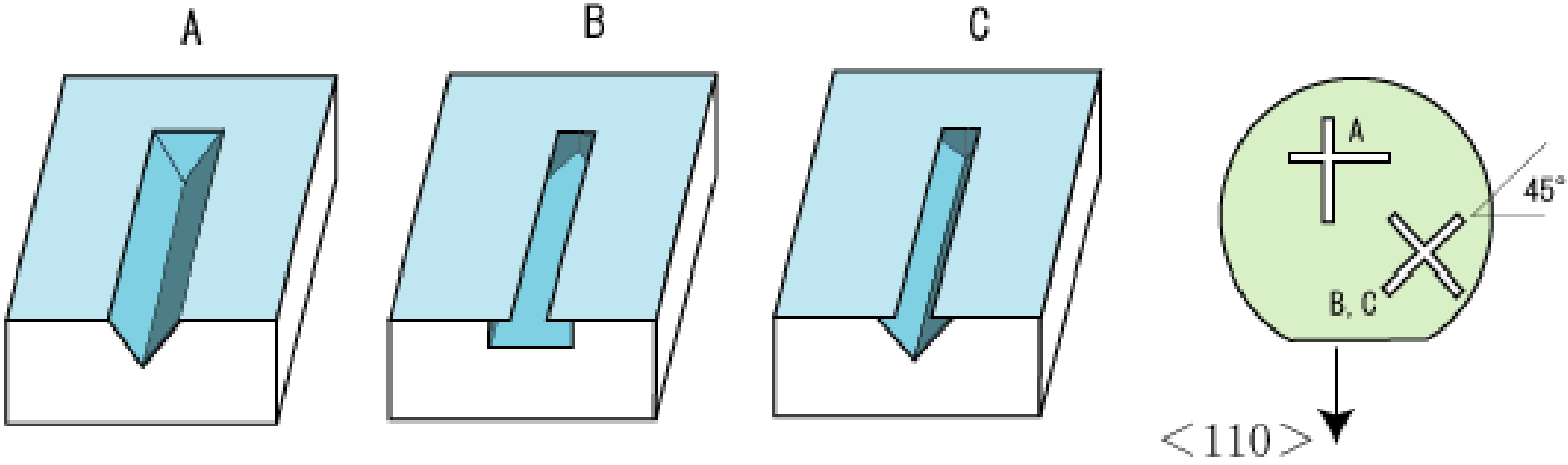




Deep grooves on a (110) wafer

Diaphragm on a (100) wafer

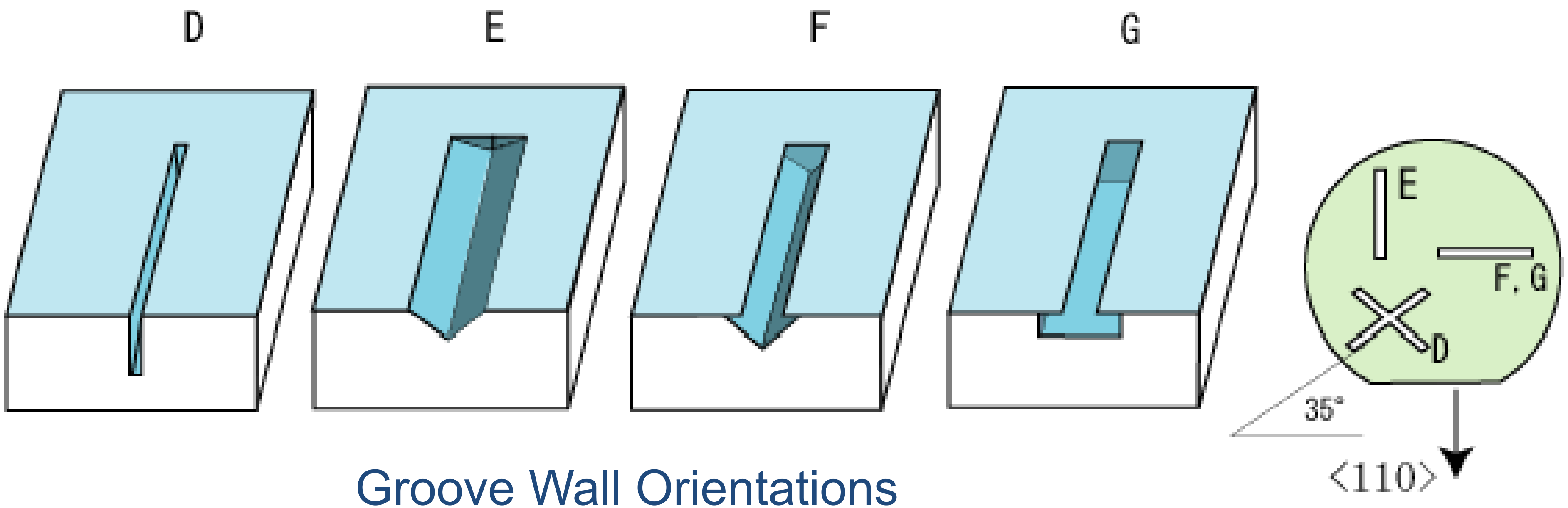
Variation in etching profile on (100) silicon wafer



Groove Wall Orientations

(111)	(100)	(110)
KOH	KOH	KOH/IPA
TMAH	TMAH	TMAH/surfactant
EDP		EDP

Variation in etching profile on (110) silicon wafer



Groove Wall Orientations

(111)	(111)	(100)	(110)
KOH TMAH EDP	KOH TMAH EDP	KOH TMAH	KOH/IPA TMAH/surfactant EDP

Non-conventional 3-D microstructures using KOH anisotropic etching

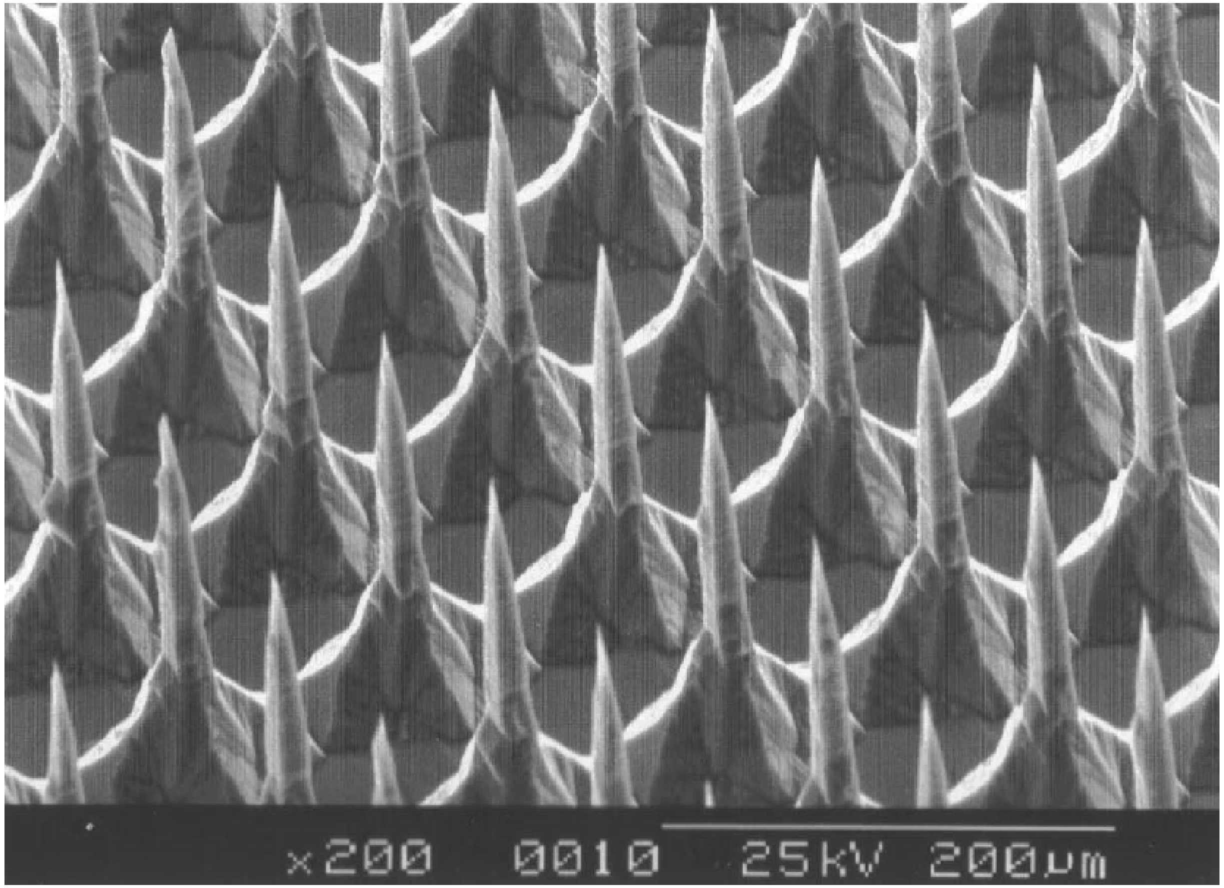
Etching from both sides of a wafer

Two-step etching using two mask layers

K. Sato, et al, Proc. IFToMM Intl. Micromechanism Symp. (Tokyo, 1993.6) 155-160

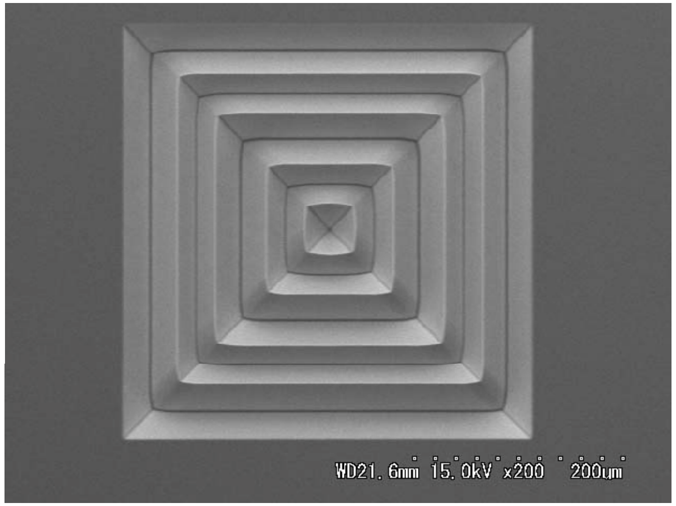
Densely Arrayed Silicon Needles with a Pitch Distance of 200 microns Aiming at Transdermal Drug Delivery

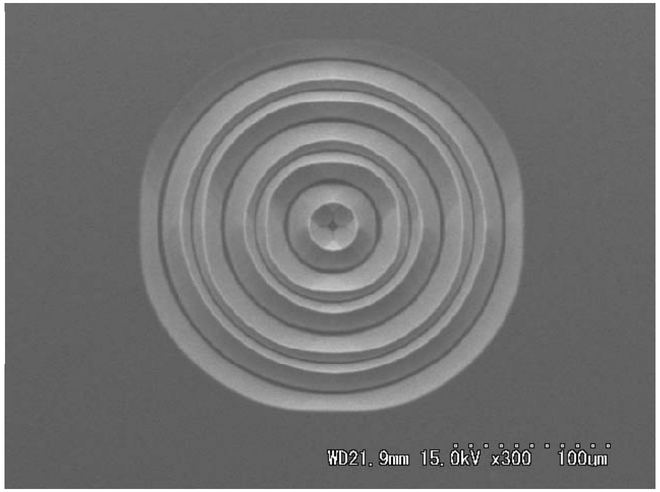
M. Shikida et al.:Proc. MEMS-03 (Kyoto, 2003), 562

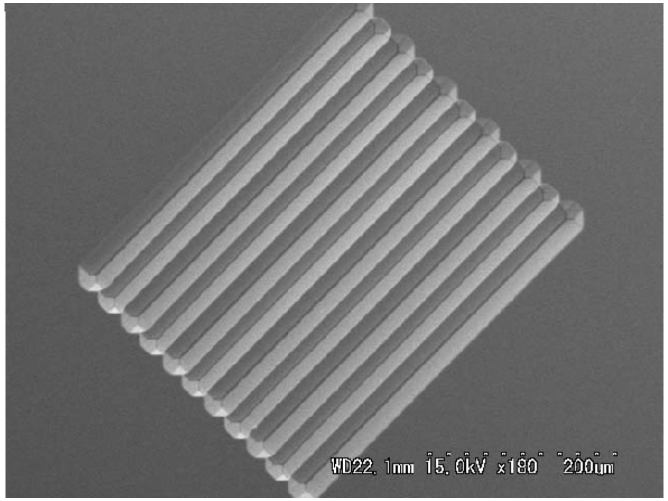


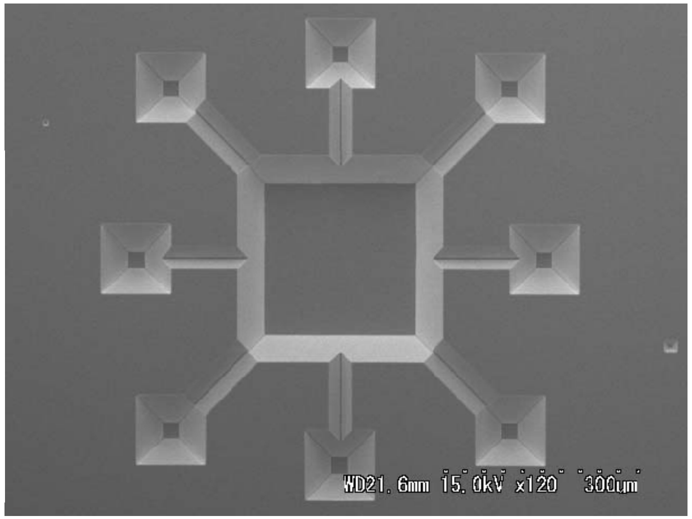
New types of anisotropically etched 3-D structures: Curved, Sharp-cornered, 45-degree-angled V-grooves

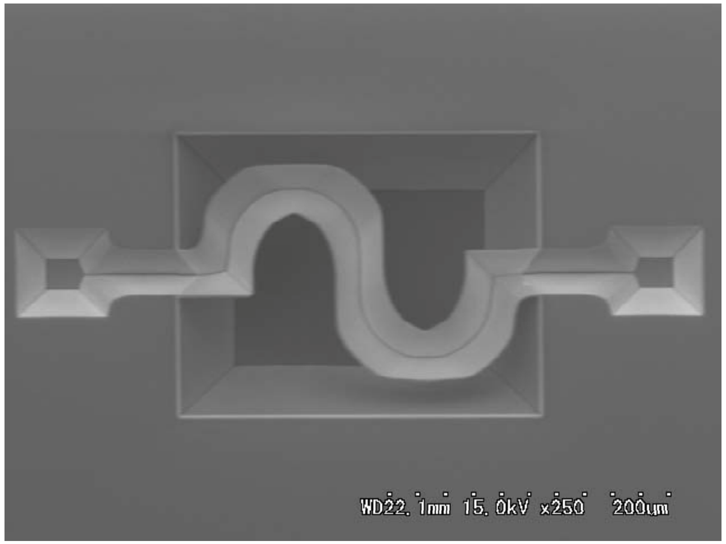
Prem Pal: Jpn. J. Appl. Phys. 49 (2010)056702

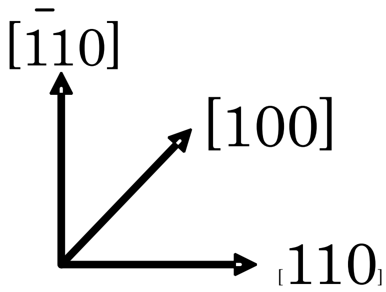












Anisotropic chemical etching of Si from MEMS Point of View

- **Etching Solutions**
  KOH, “TMAH”, “EDP”, N_2H_4, NaOH, CsOH, etc.
- **Chemical reaction**
  $Si + 2OH^- + 2H_2O$
  $\rightarrow \; Si(OH)_4 + H_2 \rightarrow \; SiO_2(OH)_2^{2-} + 2H_2$
- **What are known;**
  Si (111) shows an extremely low etch rate.
  Etch-stop techniques: B-dope, Electro-chemical, etc.
- **Applications**
  Diaphragms, V-grooves, Cantilevers
  ---Limitations in fabricated shapes
  Many mysteries

Sequential reactions of Si etching in alkaline solution

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

This is the results of the following steps.

(R. A. Wind, M.A. Hines, Surface Science 460 (2000) 21-38)

$$=SiH_2 + OH^- + H_2O \rightarrow =SiHOH + H_2 + OH^-$$

$$=SiHOH + OH^- + H_2O \rightarrow =Si(OH)_2 + H_2 + OH^-$$

$$(\equiv Si)_2 = Si(OH)_2 + 2H_2O \rightarrow 2(=Si\text{-}H) + Si(OH)_4$$

$$Si(OH)_4 + 2OH^- \rightarrow =SiO_2(OH)_2^{2-} + 2H_2O$$

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in macroscopic domains

"Dangling-Bond Model" does not tell the truth,
because no dynamics included.

"Step Flow Model" explains anisotropy in the vicinity of Si (111)

*Reversed anisotropy between KOH and TMAH

*Etched shape clearly reflects atomic-step behavior in the vicinity of Si (111)

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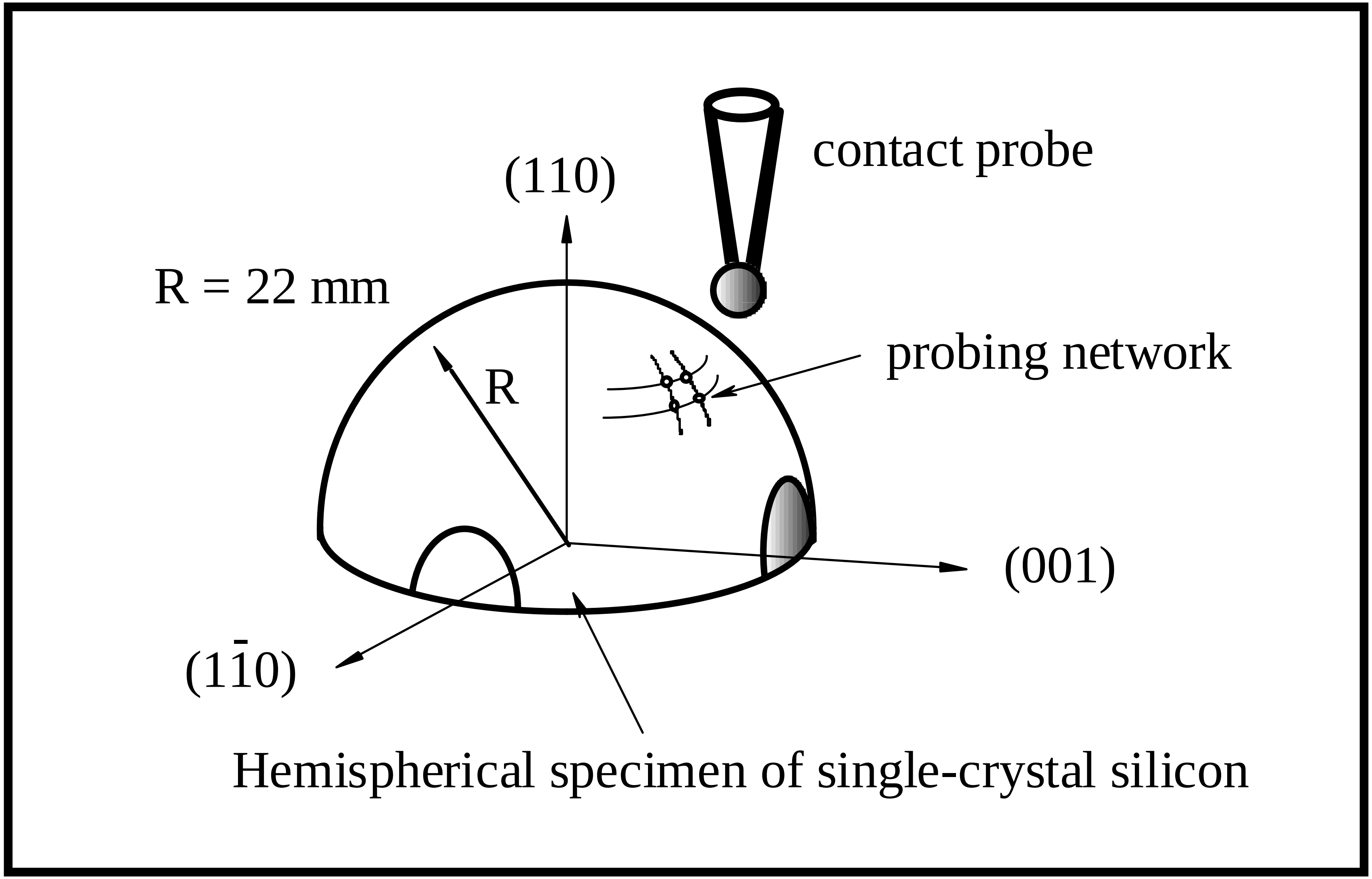
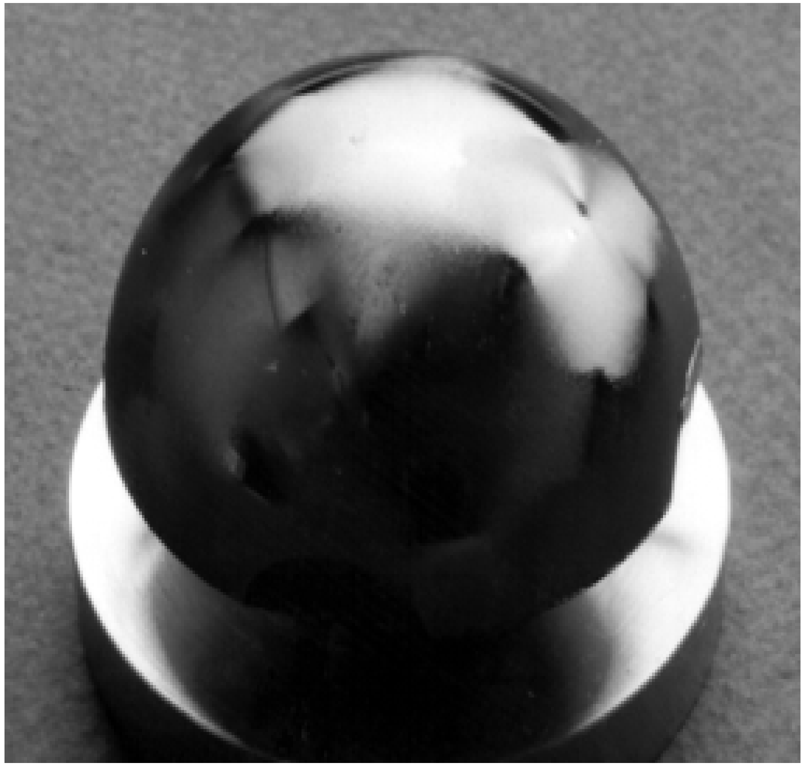
Etching rate measurement

K. Sato et al.: Sensors and Actuators A-64 (1998) 87-93.



Hemispherical specimen

Before

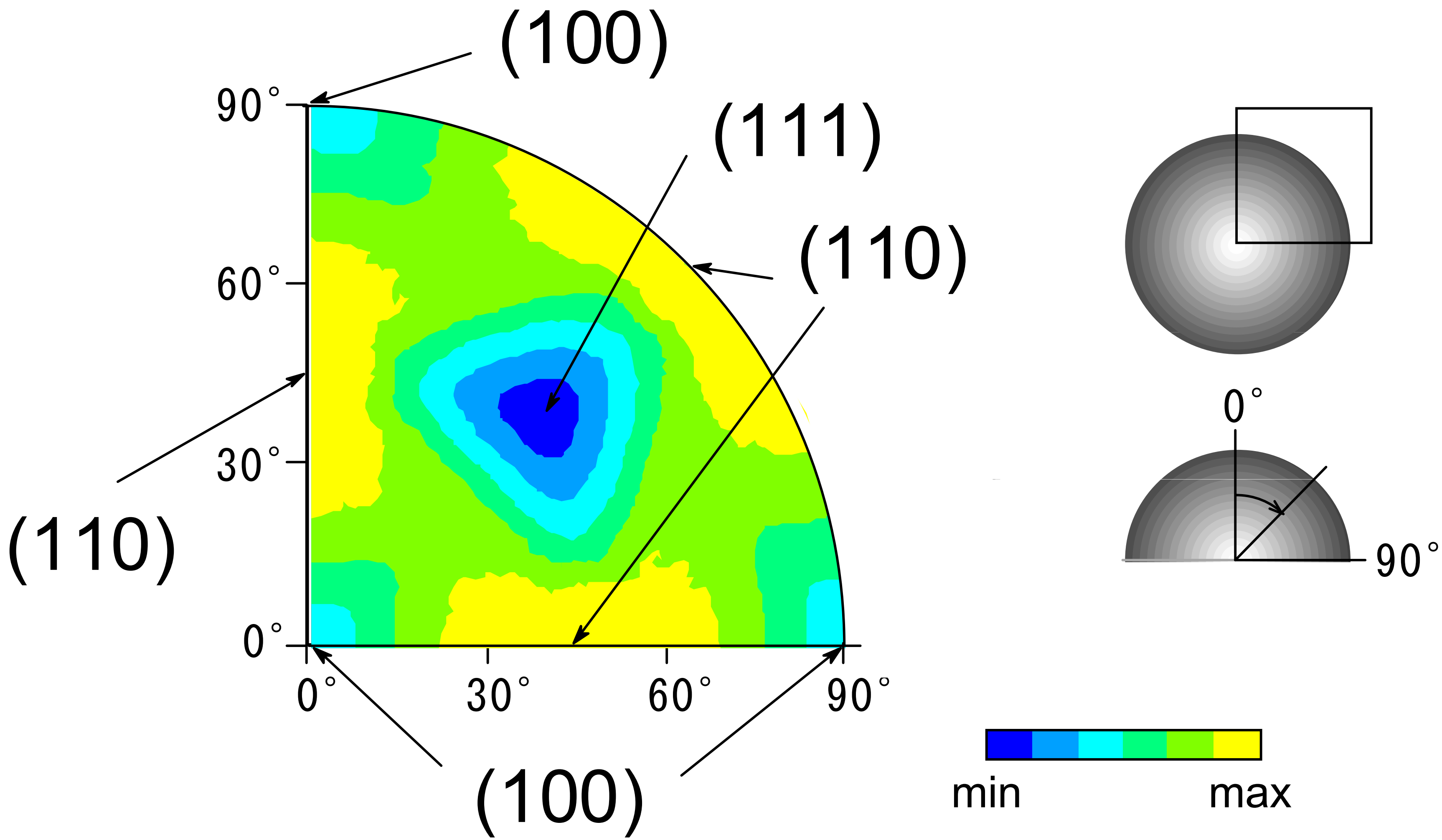


After

- Maximum etching depth: 100 - 150 μm

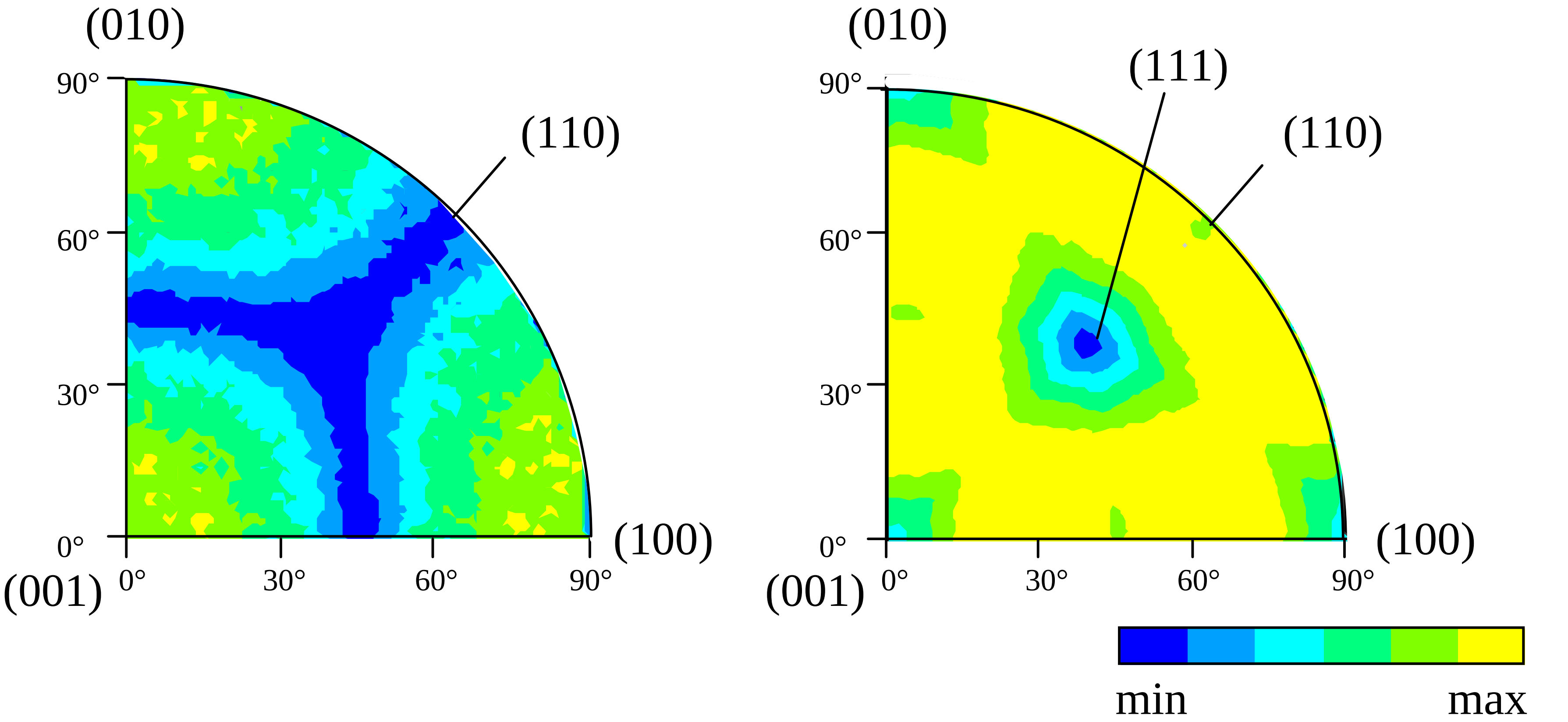
Etching rate contour map for a KOH solution

K. Sato et al.: Sensors and Actuators A-64 (1998) 87-93.



Effects of a surfactant added to TMAH solution

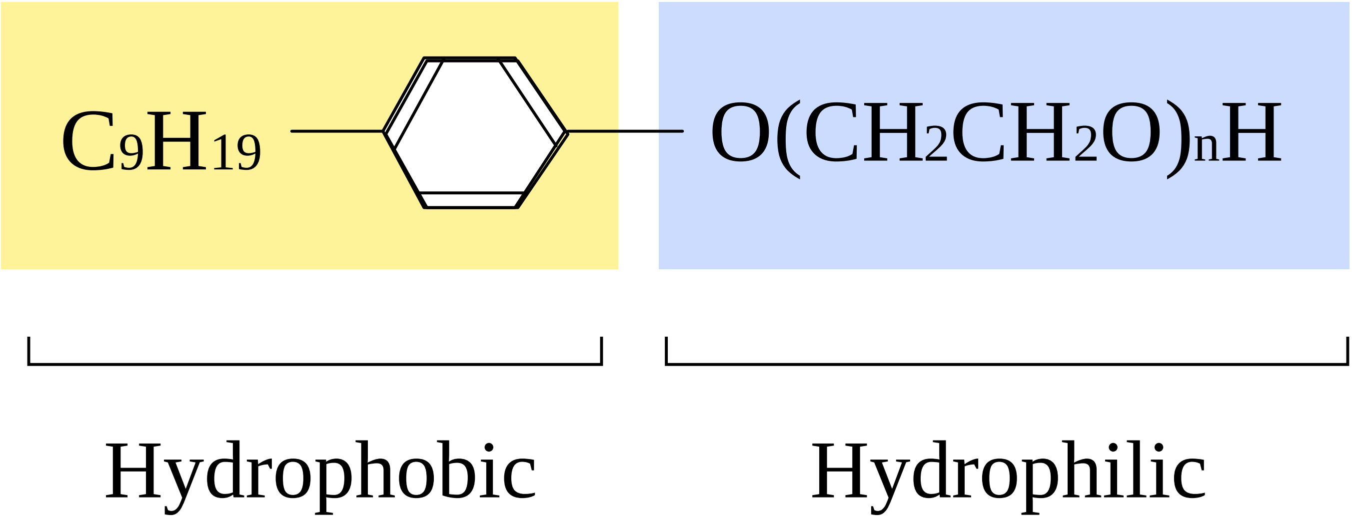
K. Sato et al.: Sensors and Materials 13-5 (2001) 285-291.



25%TMAH + NCW

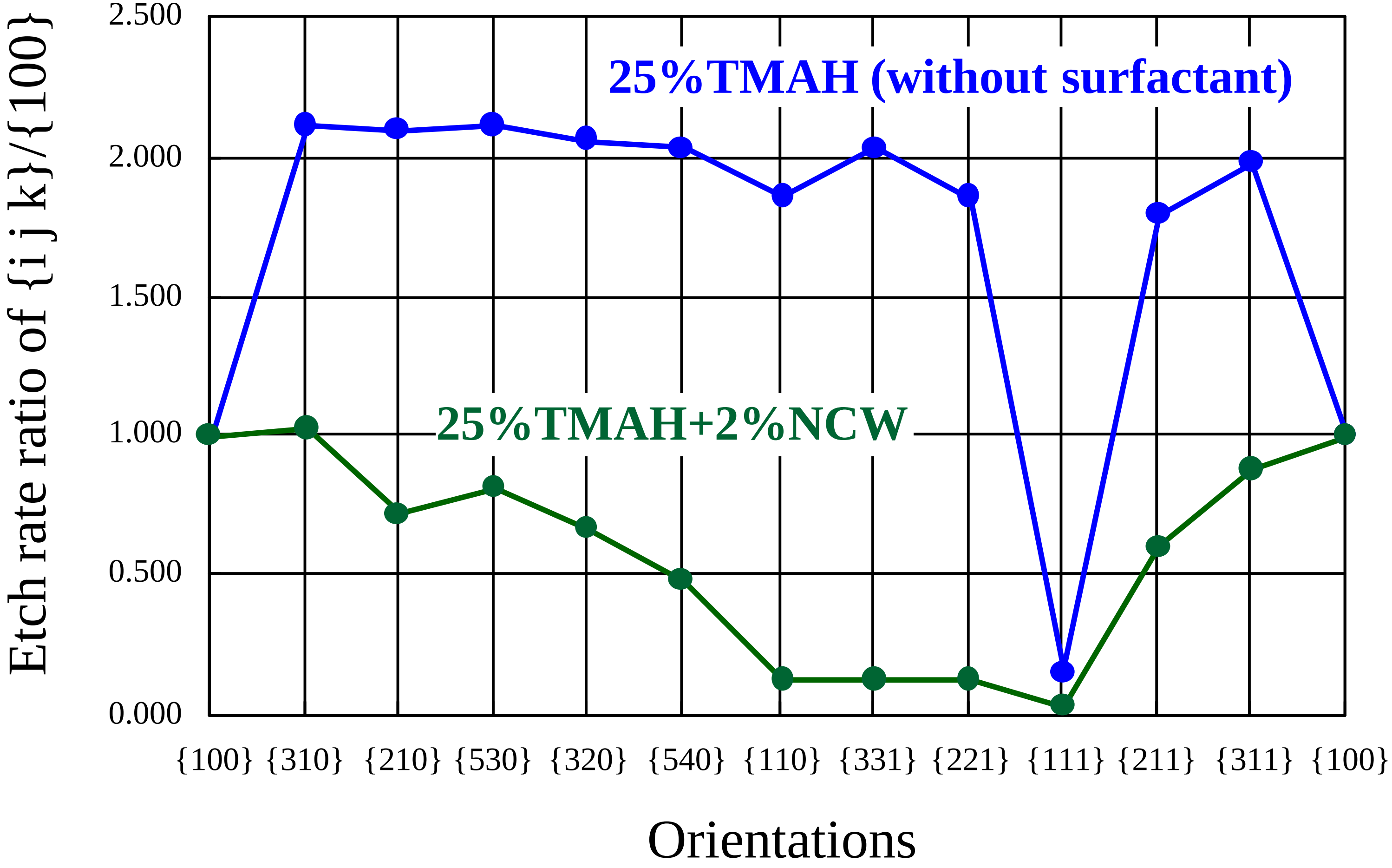
25%TMAH

Poly-oxiethylene-alkyl-phenyl-ether



- Liquid easy to operate with little foaming
- Stable both in acid and alkaline solutions

Orientation-dependent effects of surfactant decreasing etch rates of silicon

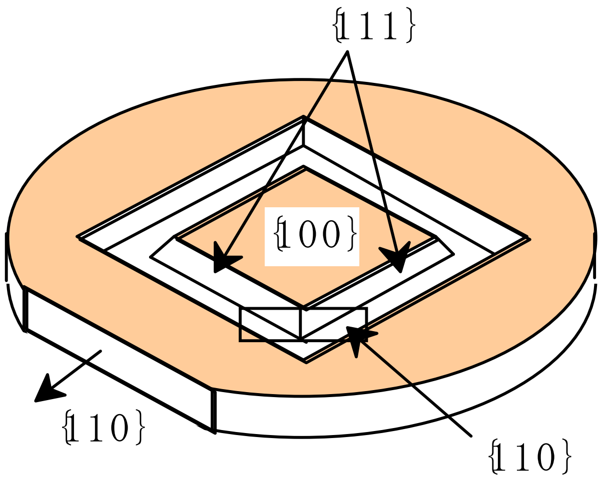


K. Sato, et al., Sensors and Materials 13-5 (2001) 285-291.

Mask-corner undercut suppression

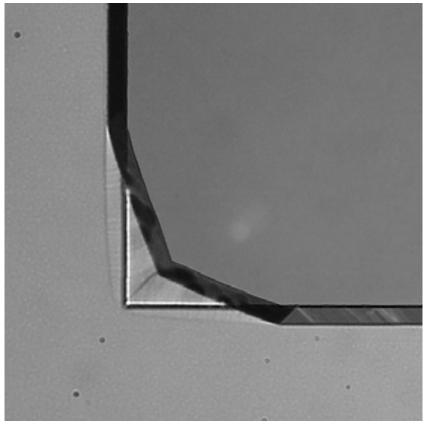
K. Sato, et al., Sensors and Materials 13-5 (2001) 285-291.

Orientations appearing on a vertex:
(111) - (j j 1) - (110)

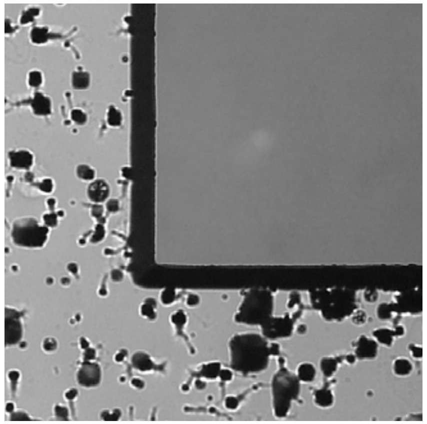


Effects of the surfactant NCW

25 wt.% TMAH, 80 ºC
Etching depth: 50 μm



without NCW

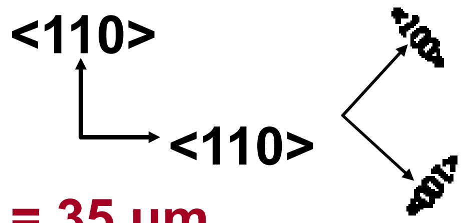


with
2 wt.% NCW

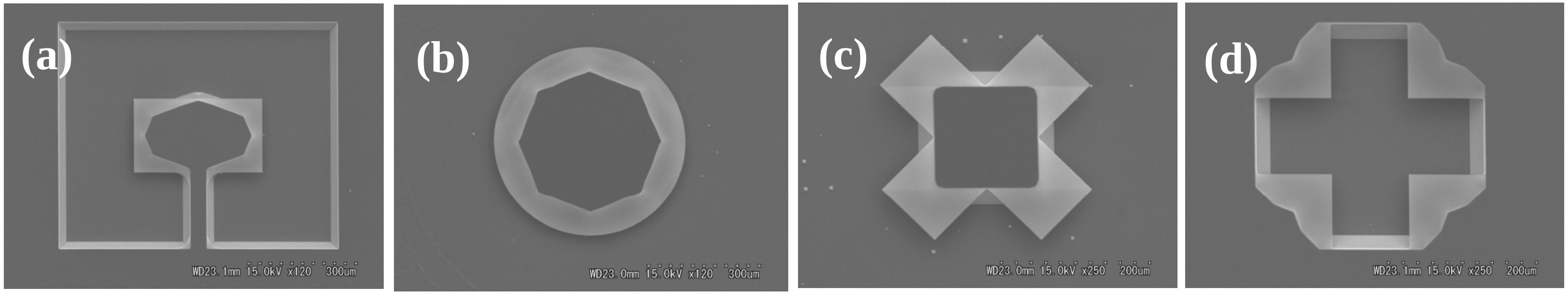
300 μm

Comparison of Structure Shape Etched from Same Mask Apertures

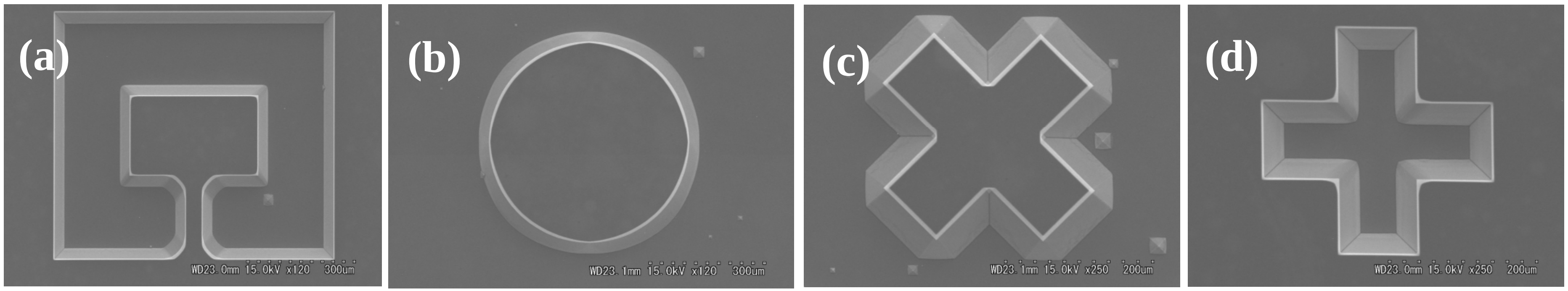
Prem Pal, J. Micromech. Microeng. 17 (2007) 2299–2307



Etch depth = 35 μm



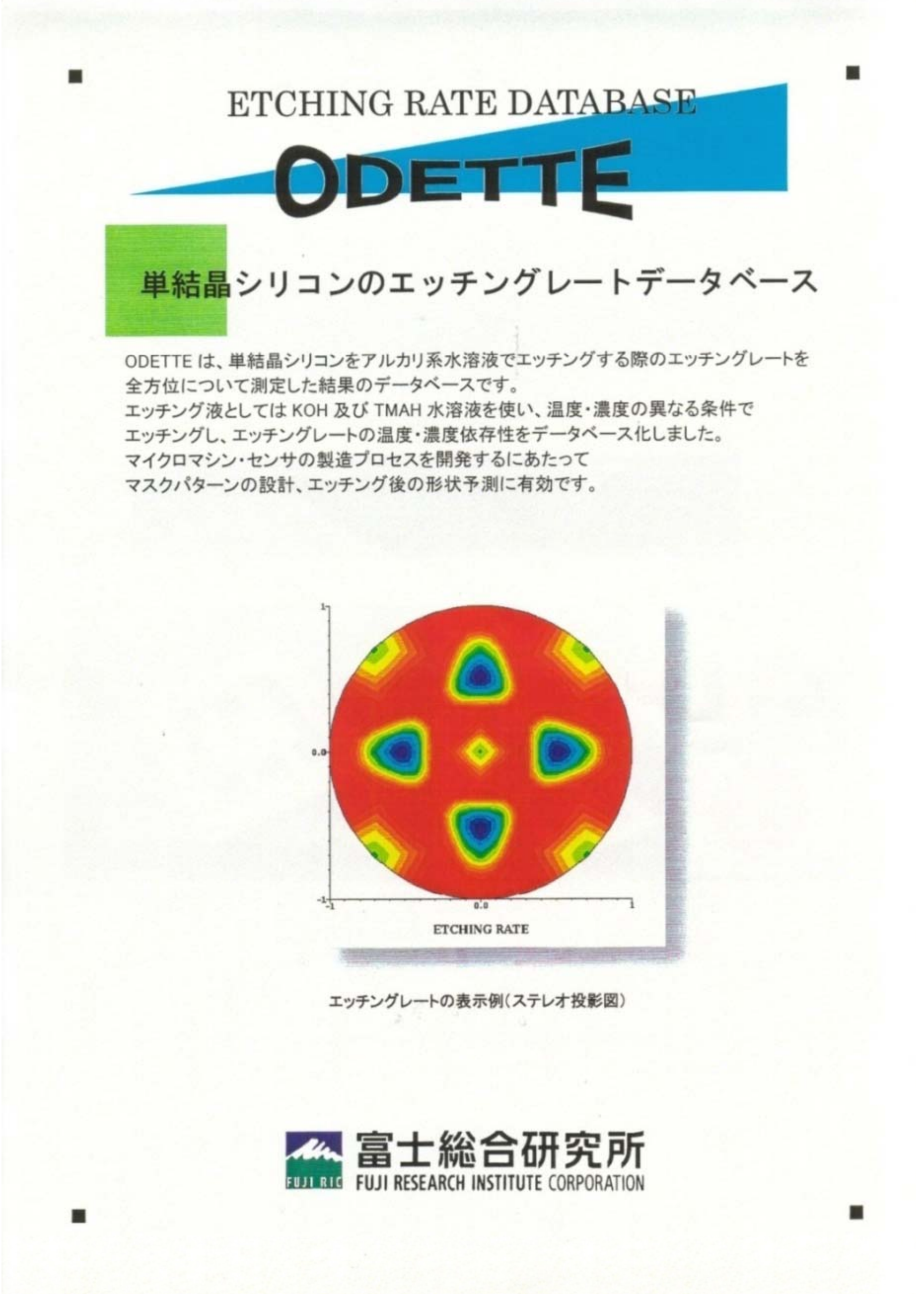
Pure 25 wt% TMAH



25 wt% TMAH + NC-200

T-Shaped cantilever	Circular island	Cross island	Cross aperture

Etching rate database



ETCHING RATE DATABASE

ODETTE

単結晶シリコンのエッチングレートデータベース

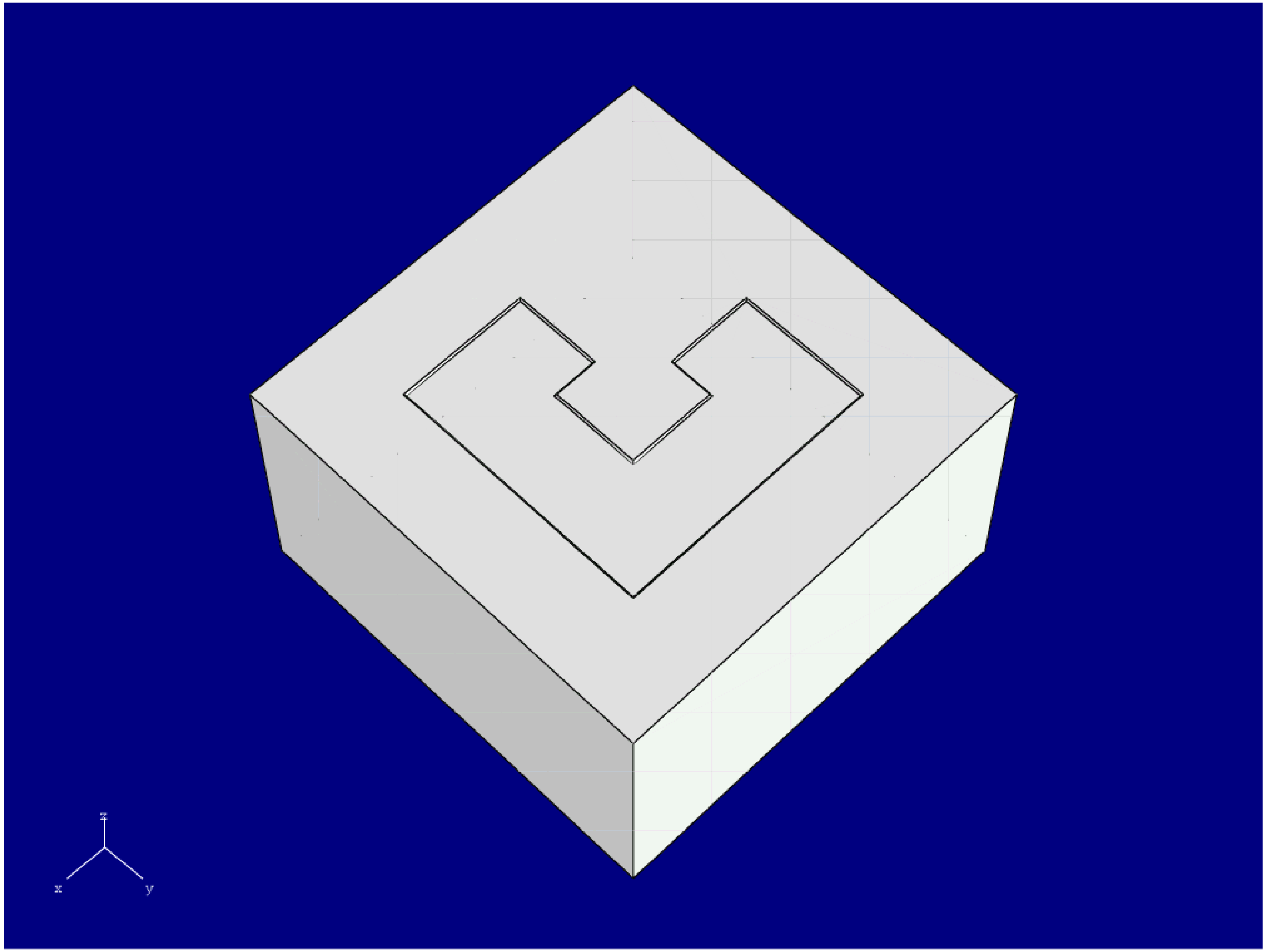
ODETTE は、単結晶シリコンをアルカリ系水溶液でエッチングする際のエッチングレートを
全方位について測定した結果のデータベースです。
エッチング液としては KOH 及び TMAH 水溶液を使い、温度・濃度の異なる条件で
エッチングし、エッチングレートの温度・濃度依存性をデータベース化しました。
マイクロマシン・センサの製造プロセスを開発するにあたって
マスクパターンの設計、エッチング後の形状予測に有効です。

エッチングレートの表示例（ステレオ投影図）

富士総合研究所
FUJI RIC
FUJI RESEARCH INSTITUTE CORPORATION

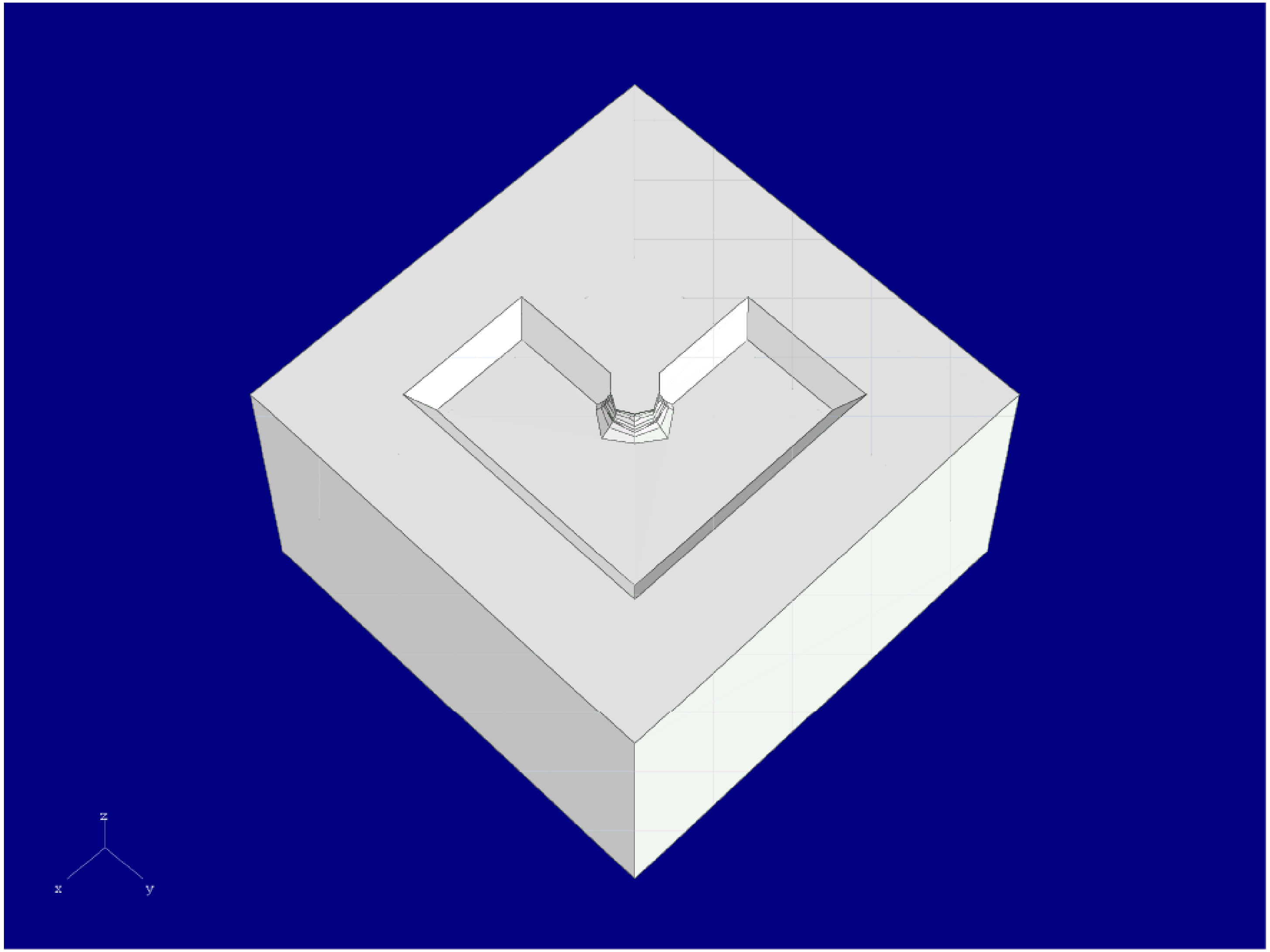
Anisotropic etching simulation system MICROCAD

Simulation results using MICROCAD

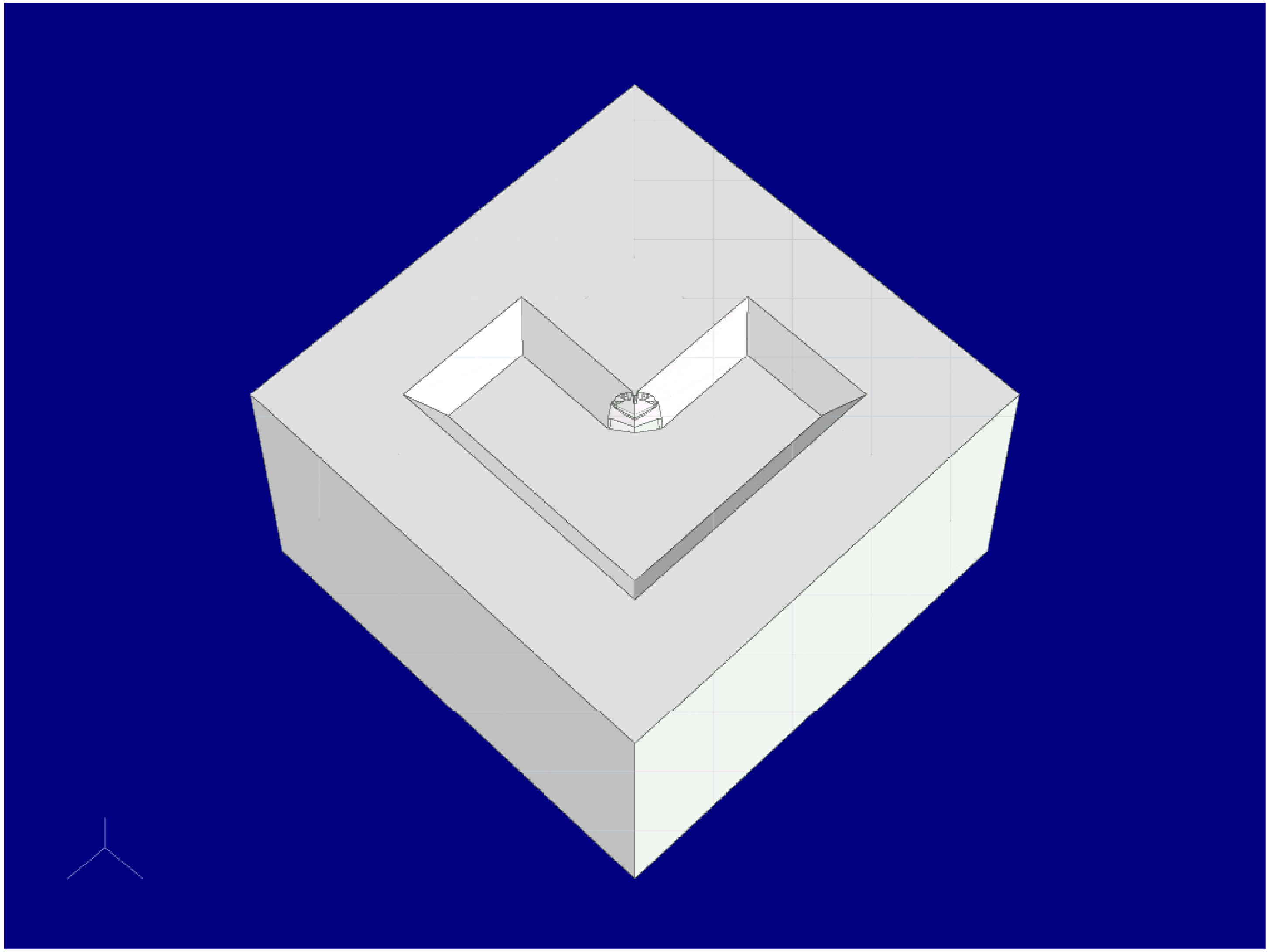


K. Sato, et al., Electronics and Communications in Japan, Part2, 83-4 (2000).

Simulation results using MICROCAD

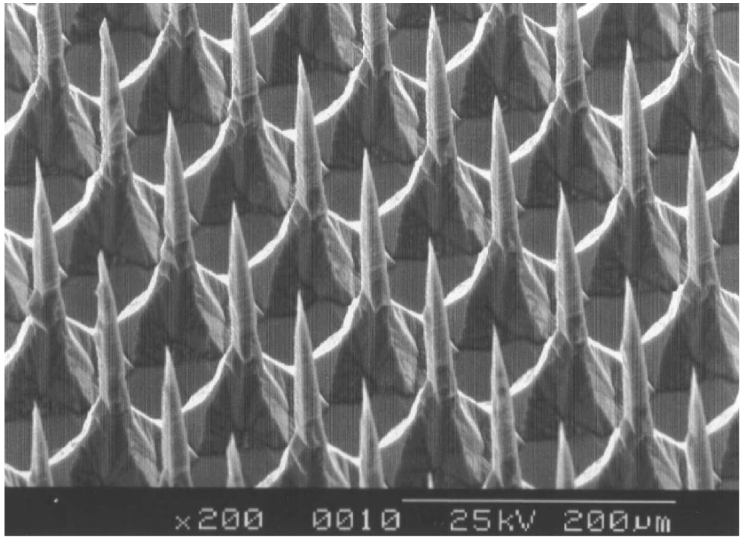


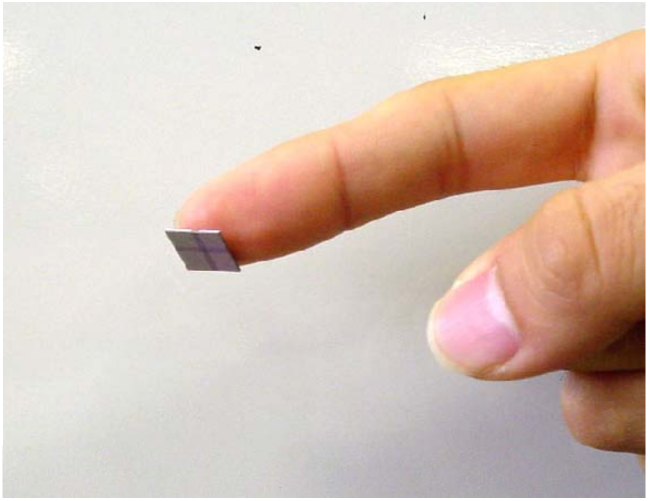
Simulation results using MICROCAD

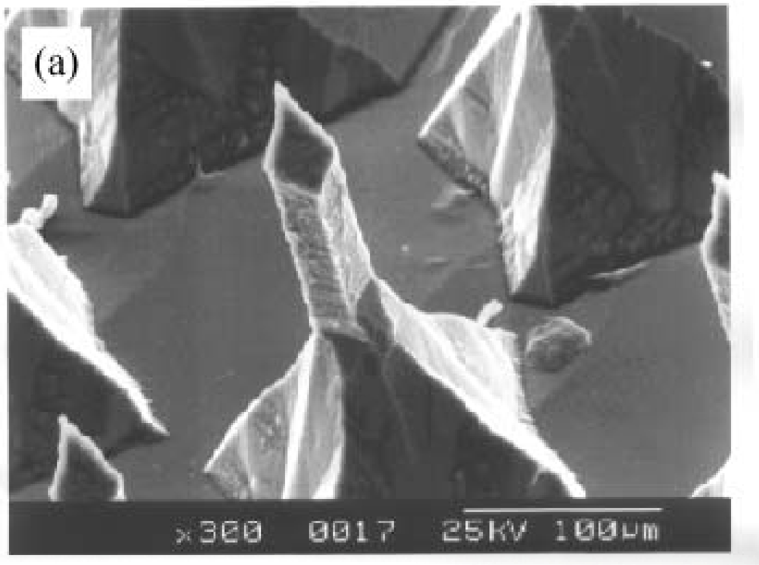


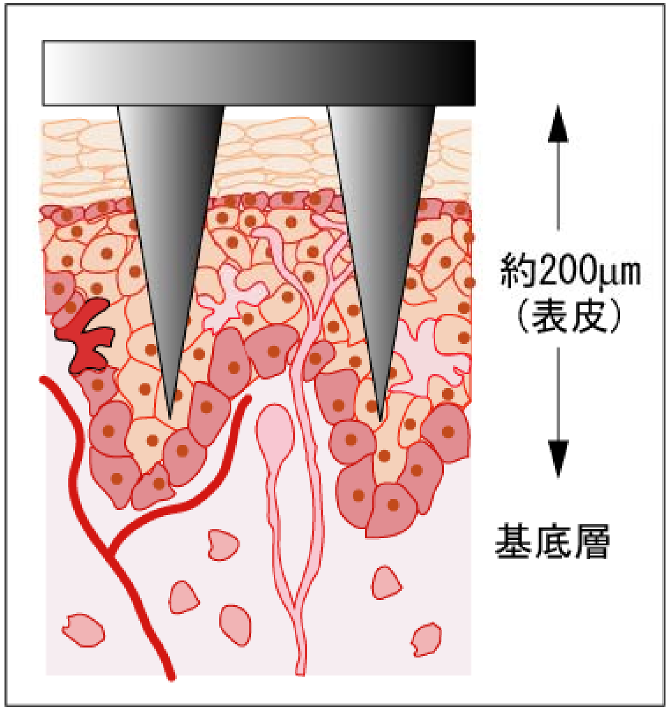
Densely Arrayed Silicon Needles with a Pitch Distance of 200 microns for Transdermal Drug Delivery

M. Shikida et al. Sensors and Actuators A 116 (2004) 264–271



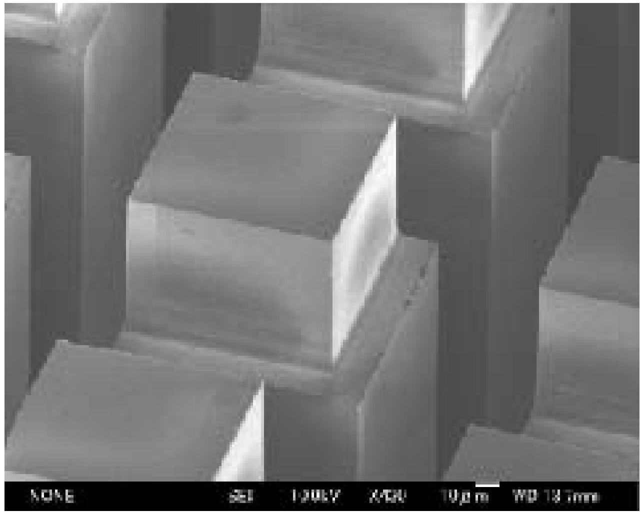




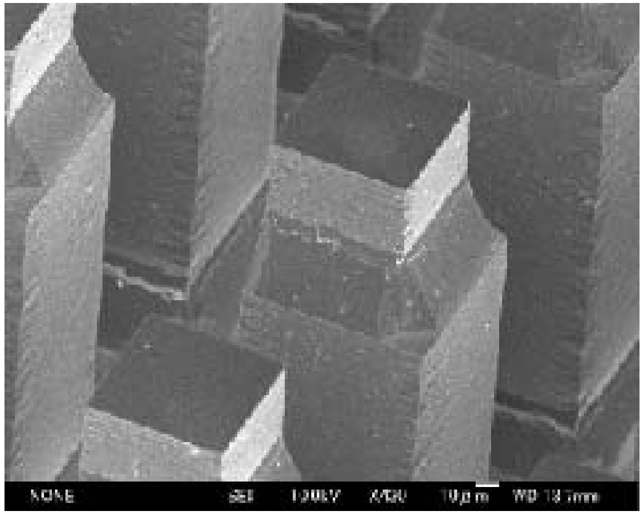


Arrayed Needle Fabrication Process: Combination of mechanical dicing and wet etching

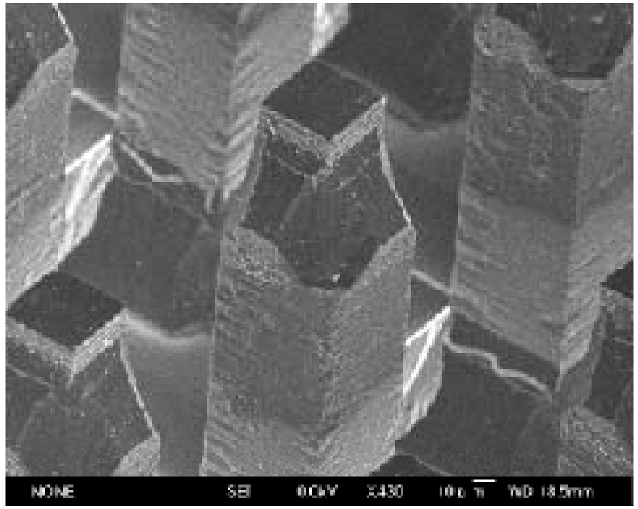
M. Shikida et al. J. Micromech. Microeng. 14 (2004) 1462–1467



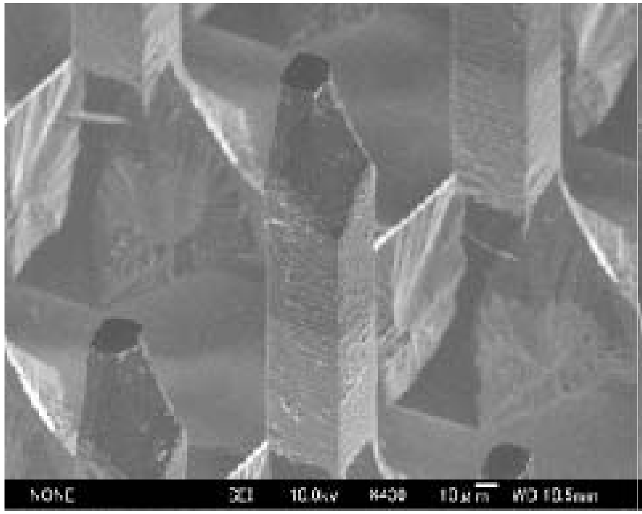
Etching time: (a) 0 min.



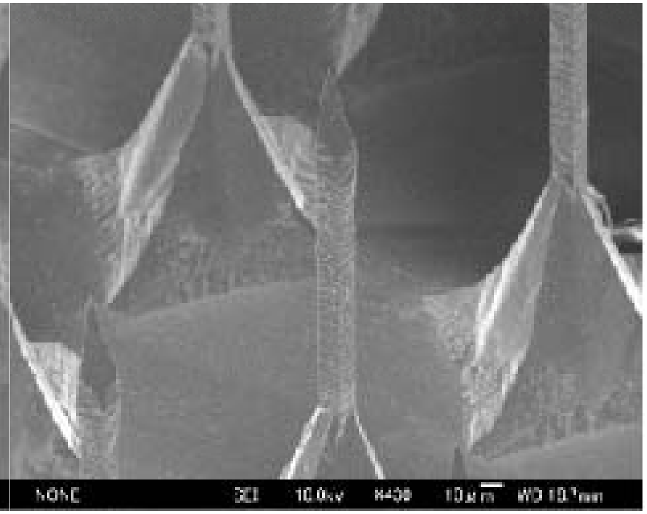
(b) 10 min.



(c) 20 min.



(d) 30 min.

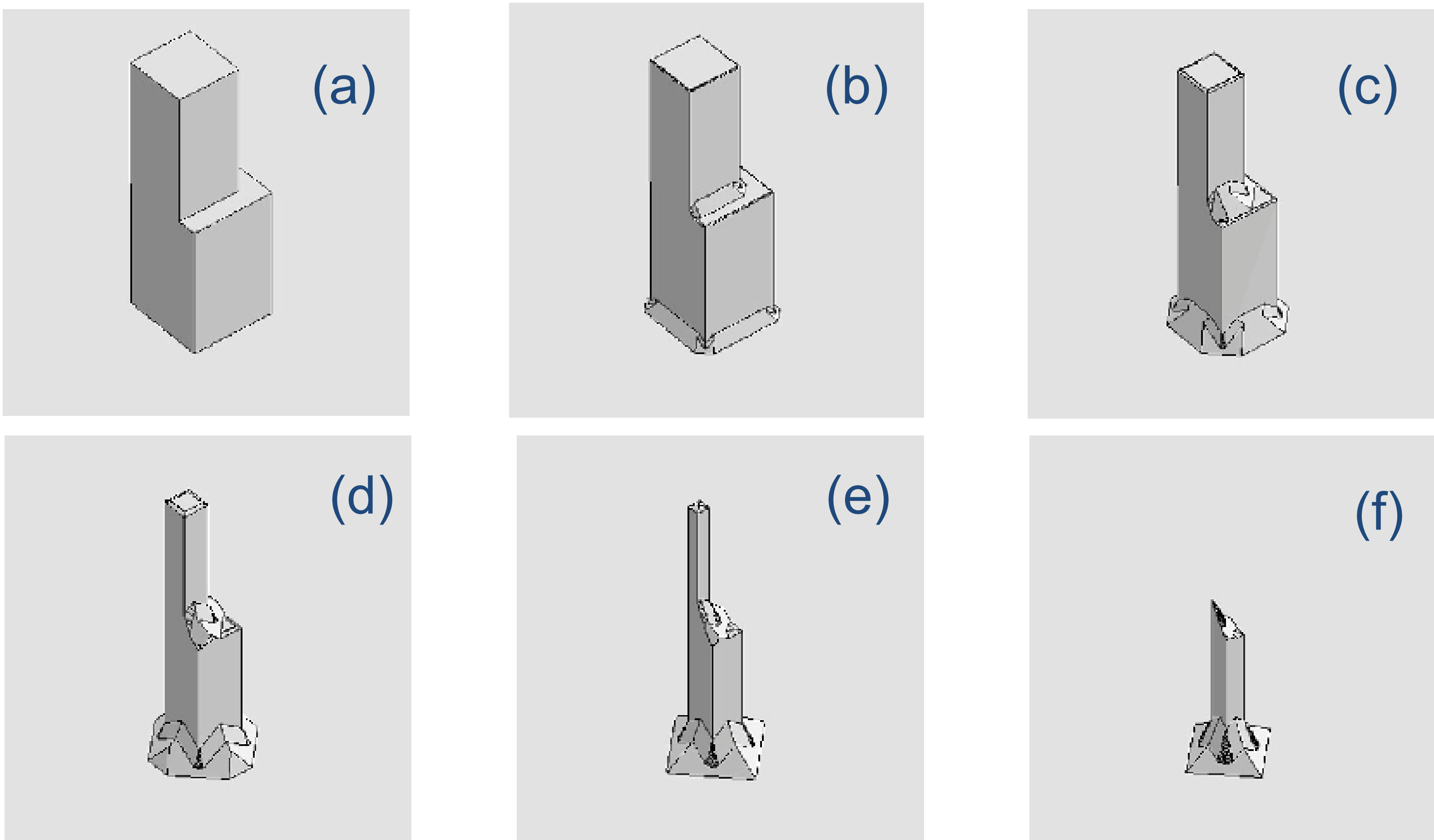


(e) 40 min.

MICROCAD Simulation Results.

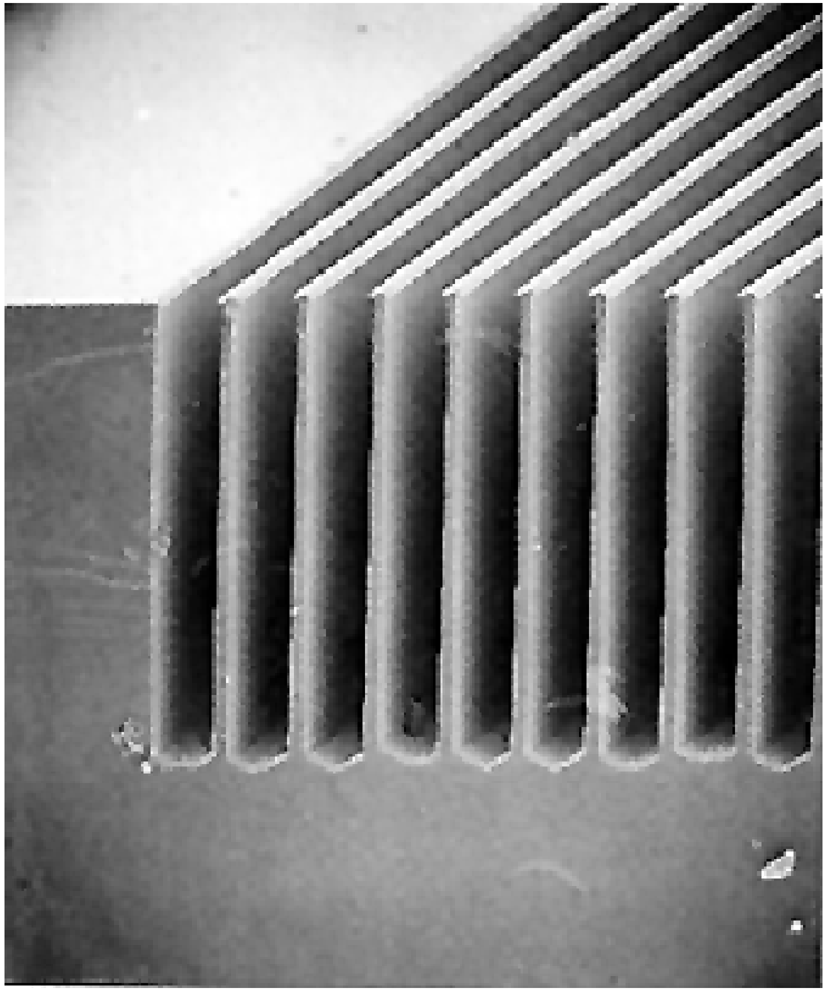
Etching time: (a) 0 min., (b) 5 min., (c) 10 min.,
(d) 15 min., (e) 20 min., (f) 25 min.

Etching conditions: 34.0 wt.% KOH, 80°C



M. Shikida, et al, J. Micromech. Microeng. **14** (2004) 1462–1467

Etched deep grooves on (110) Si using a KOH water solution

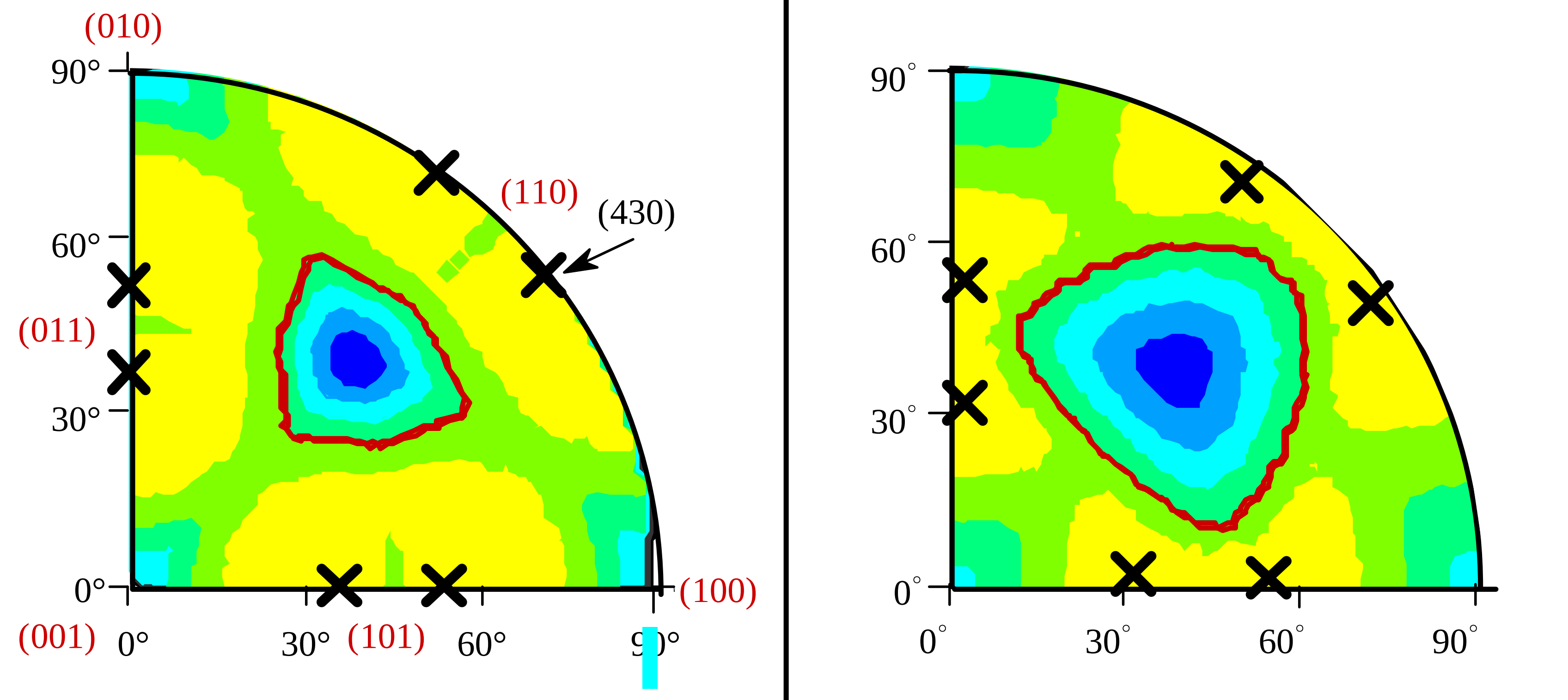


Groove depth:
90 microns

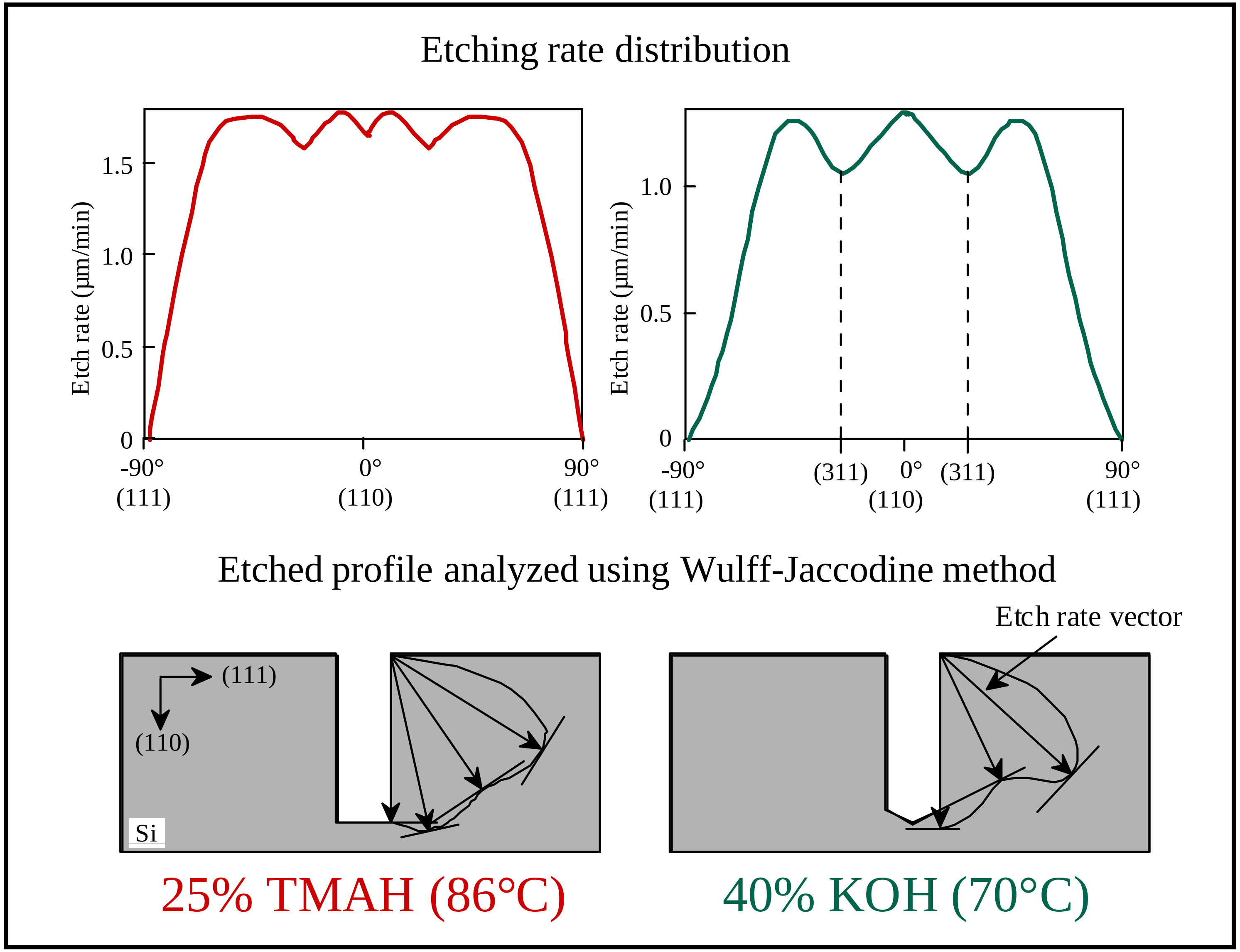
KOH and TMAH show different types of anisotropy

K. Sato, et al.: Sensors and Actuators A-73 (1999) 131-137.

TMAH: 25%, 90°C	KOH: 40%, 90°C



Relation between the etching rate distribution and etched profile



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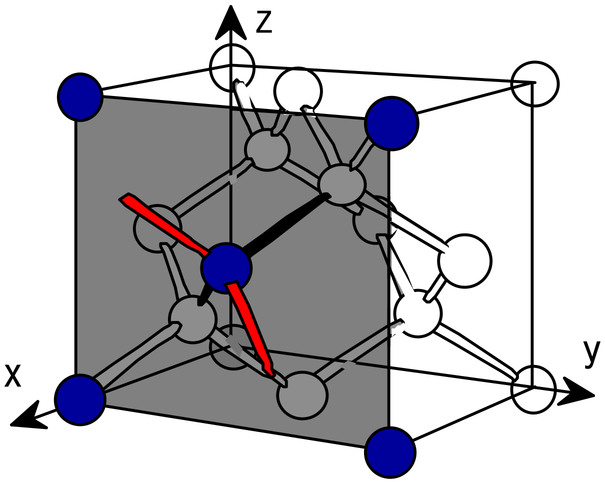
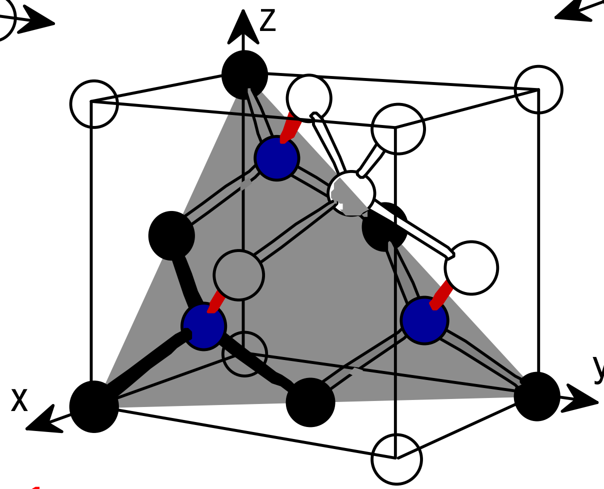
Conventional Explanation of Anisotropy in Etching

Hypothesis: Number of dangling bond appearing on the silicon surface determines the etching rate



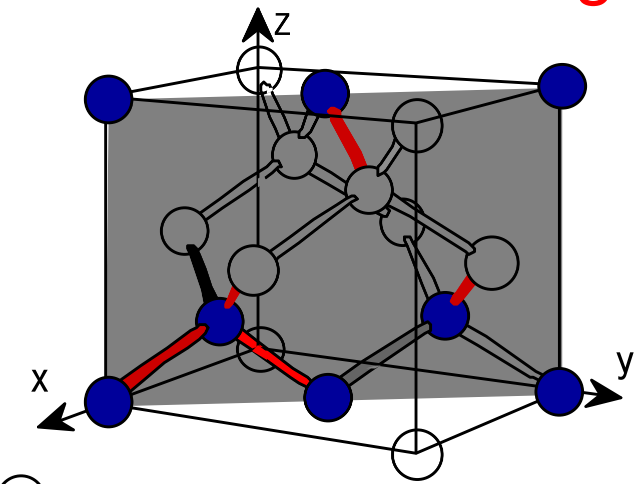
(100)面

Dangling bond : **2**
Back bond : **2**



(111)面

Dangling bond : **1**
Back bond : **3**

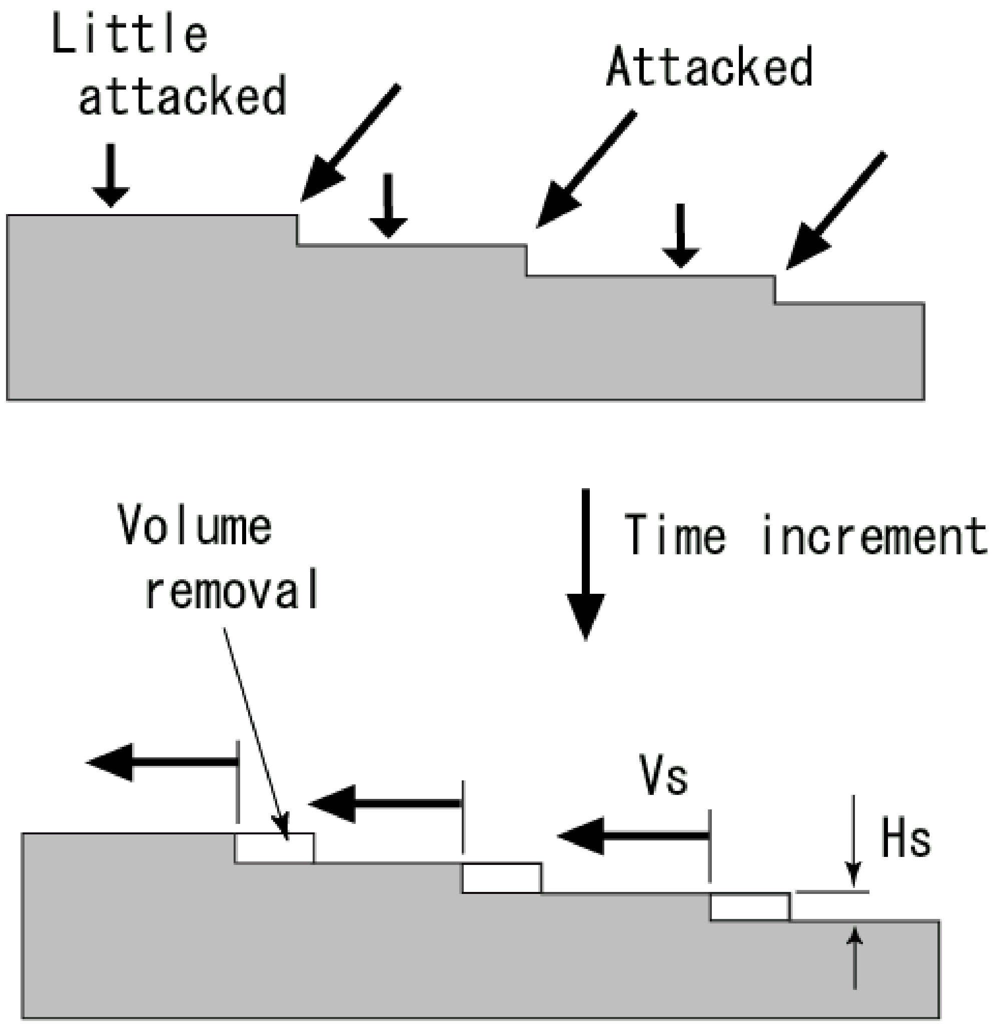


(110)面

Dangling bond : **1 +(2)**
(Exposed back bond : **2**)
Back bond : **3**

Step Flow Model for (111) Silicon

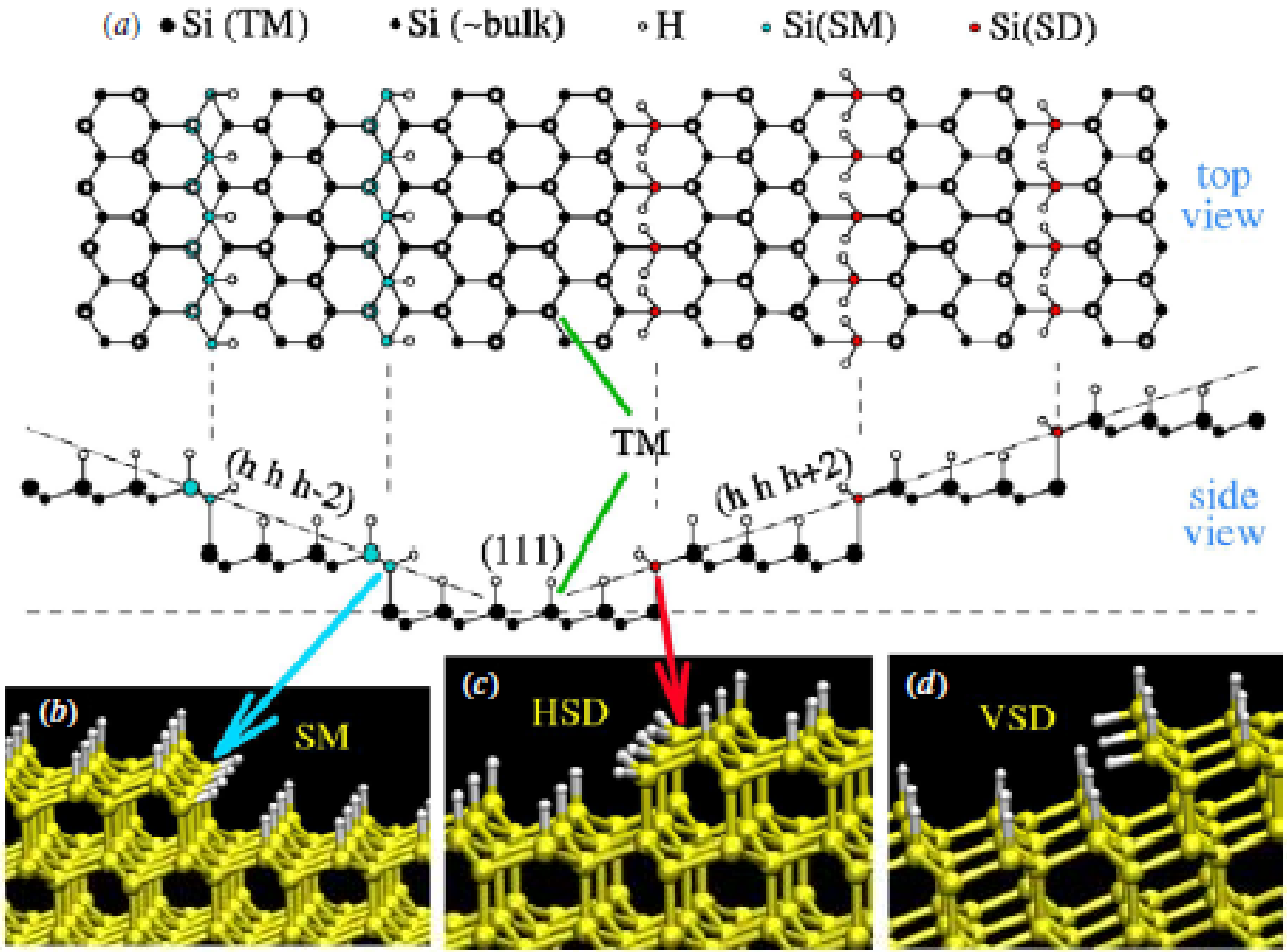
M. Elwenspoek, J. Electrochem. Soc. 140-7 (1993) 2075-80



Volume removal rate:
$R = H_s V_s L_s$

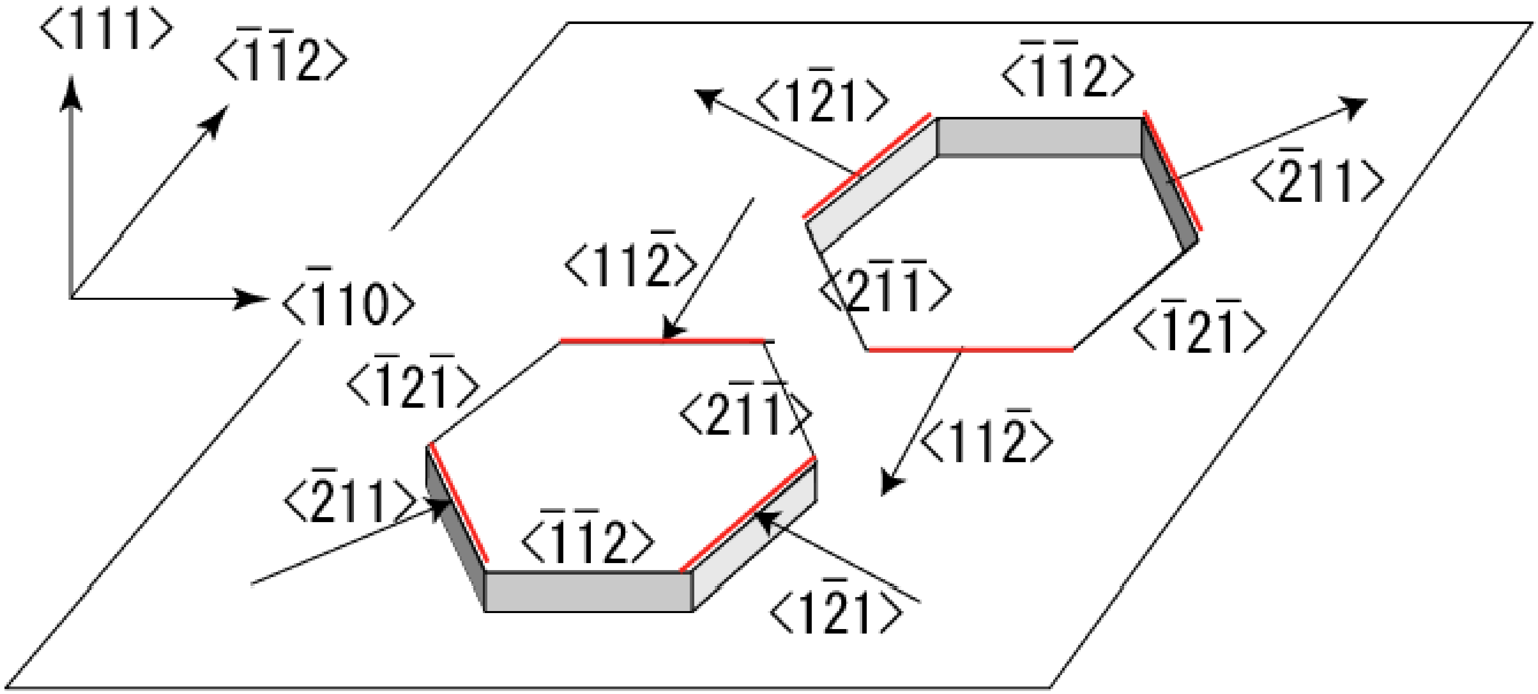
Hs: Step height
Vs: Step velocity
Ls: Length of step per unit area

Two types of stable steps on Si (111) surface (Mono-hydride and Di-hydride steps)



M.A. Gosalvez, et al. J. Micromech. Microeng. 17 (2007) S1–S26

Step movements determine profiles of pits and mesa on (111) silicon surface

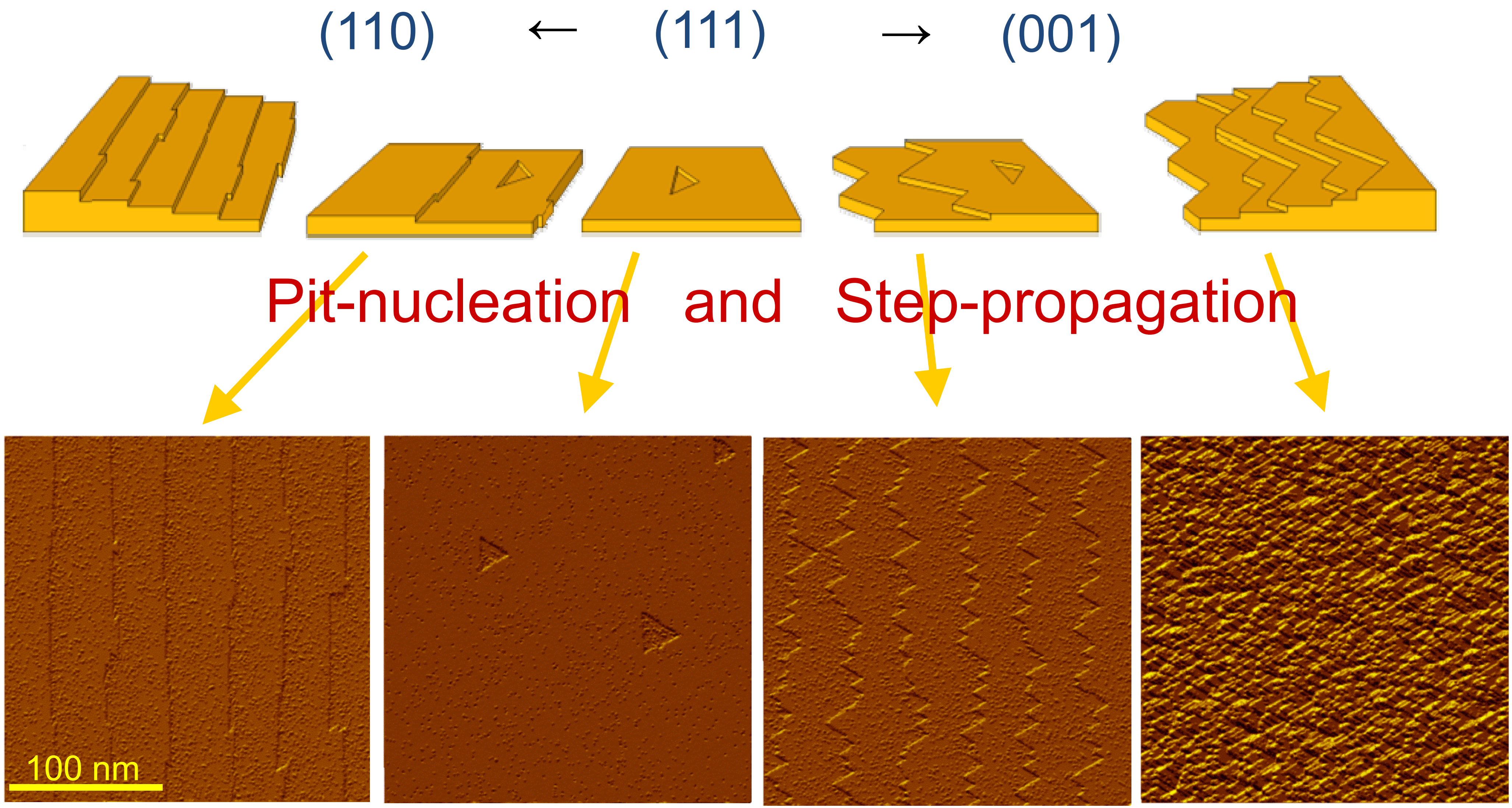


$\langle \bar{1}\bar{1}2 \rangle$, $\langle \bar{1}2\bar{1} \rangle$, $\langle 2\bar{1}\bar{1} \rangle$: (black line)
$[\bar{1}\bar{1}2]$ steps with 1 dangling bond (3 backbonds)

$\langle 11\bar{2} \rangle$, $\langle 1\bar{2}1 \rangle$, $\langle \bar{2}11 \rangle$: (red line)
$[11\bar{2}]$ steps with 2 dangling bonds (2 backbonds)

Atomic level etching simulation in the vicinity of Si (111)

M.A. Gosalvez, et al. J. Micromech**. Microeng. 17 (2007) S1–S26**



Our concern

- Is the atomic scale step flow model applicable to macroscopic etching?

  Etching solutions: KOH, TMAH

  Etching depth: tens of micrometers

- Does the number of dangling bonds determine the activeness of the surfaces or steps?

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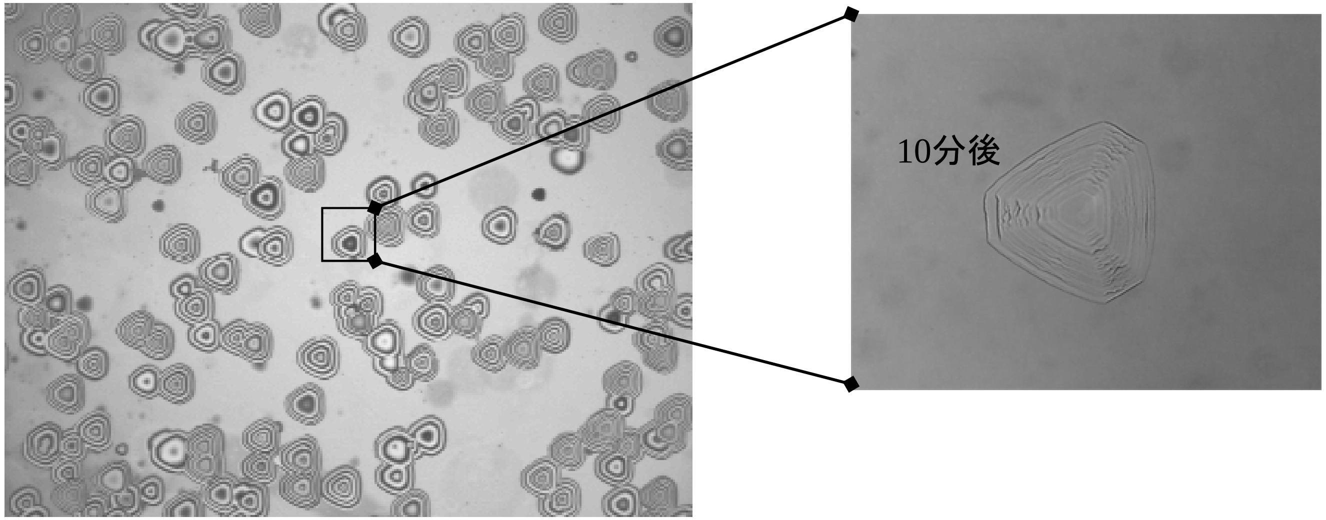
Etch Pit Growth on (111) Silicon.

K. Sato, et al.: Sensors and Materials 15-2 (2003) 93-99.

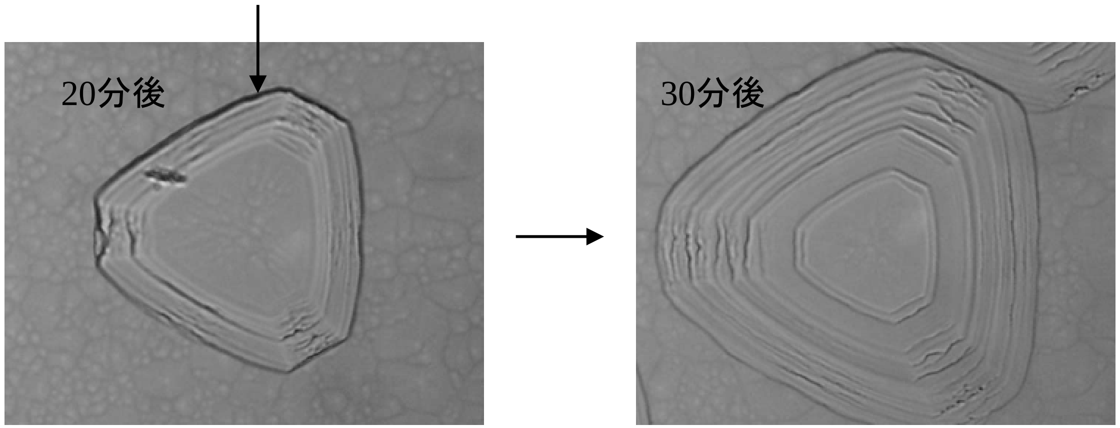
Growth of individual pit traced during TMAH etching.



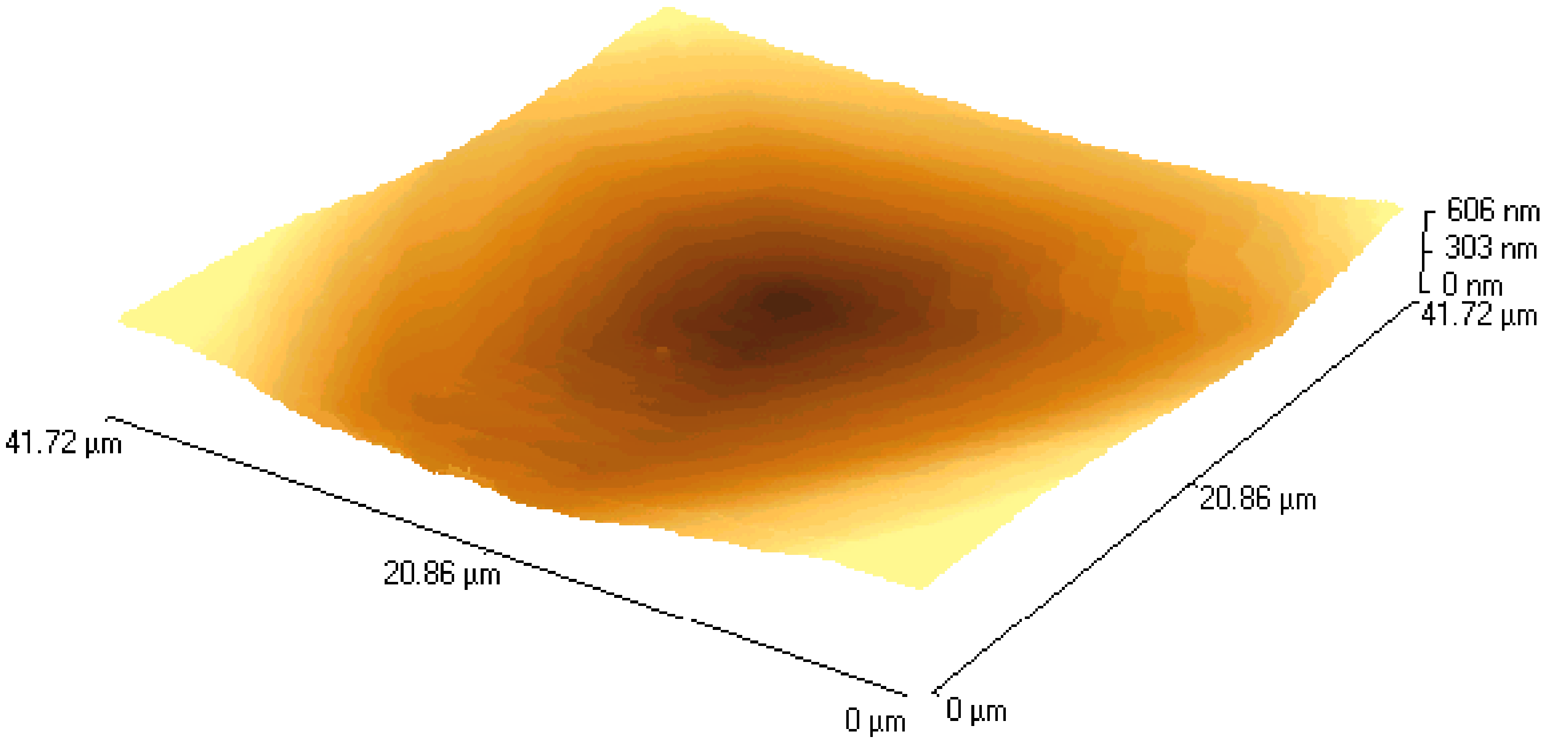
Optical microscope images with time increments

・Wafer preparation… Oxidization for 20 hours (3μm thick oxide) followed by oxide removal using HF.

・etching condition…25%TMAH, 80° 30min



AFM image at the center of a pit etched with TMAH solution



Comparison in the shape of etch pits between KOH and TMAH

K. Sato, et al.: Sensors and Materials 15-2 (2003)

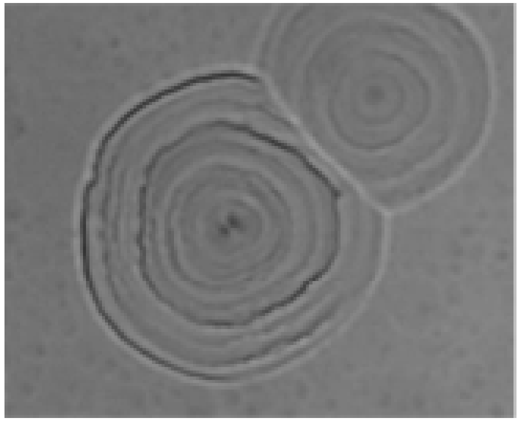
40%KOH 70℃30分

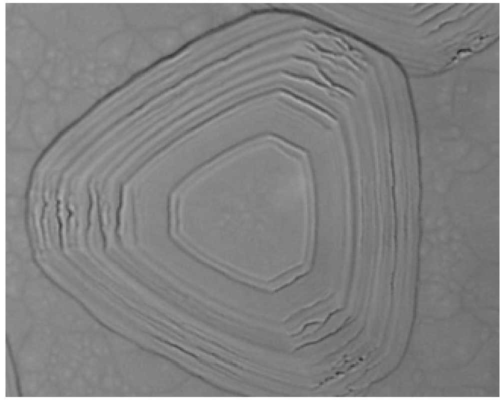
[-1-1 2] ← → [1 1-2]

25%TMAH 80℃30分

[-1-1 2] ← → [1 1-2]

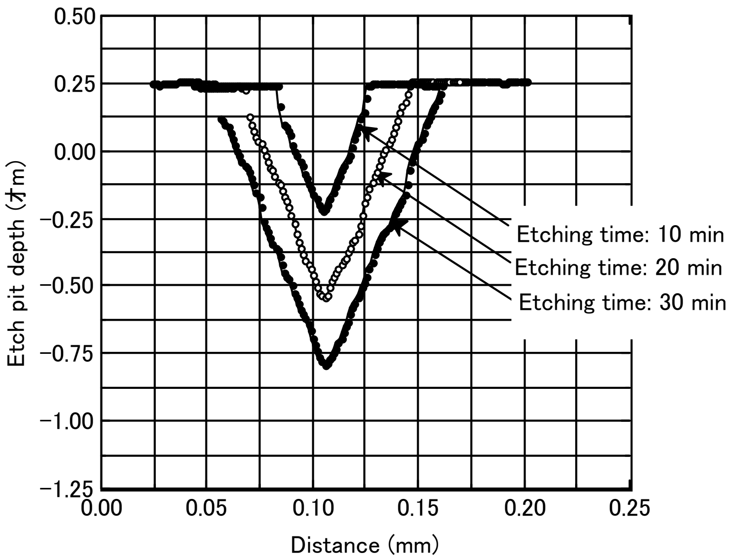
Top View

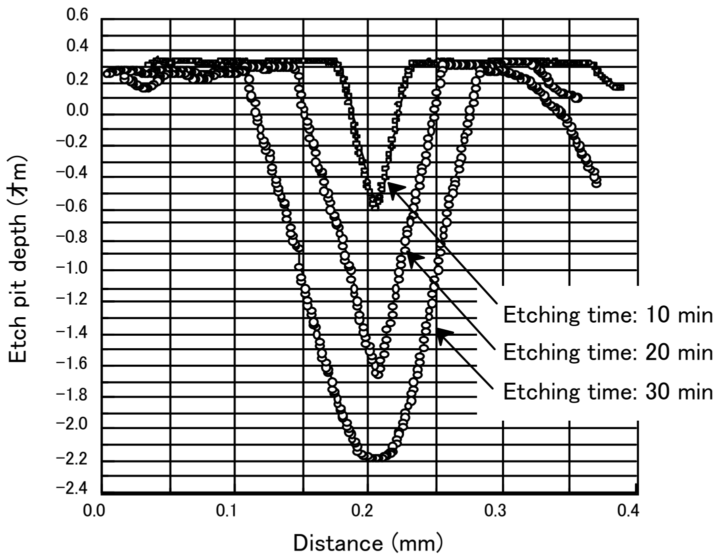




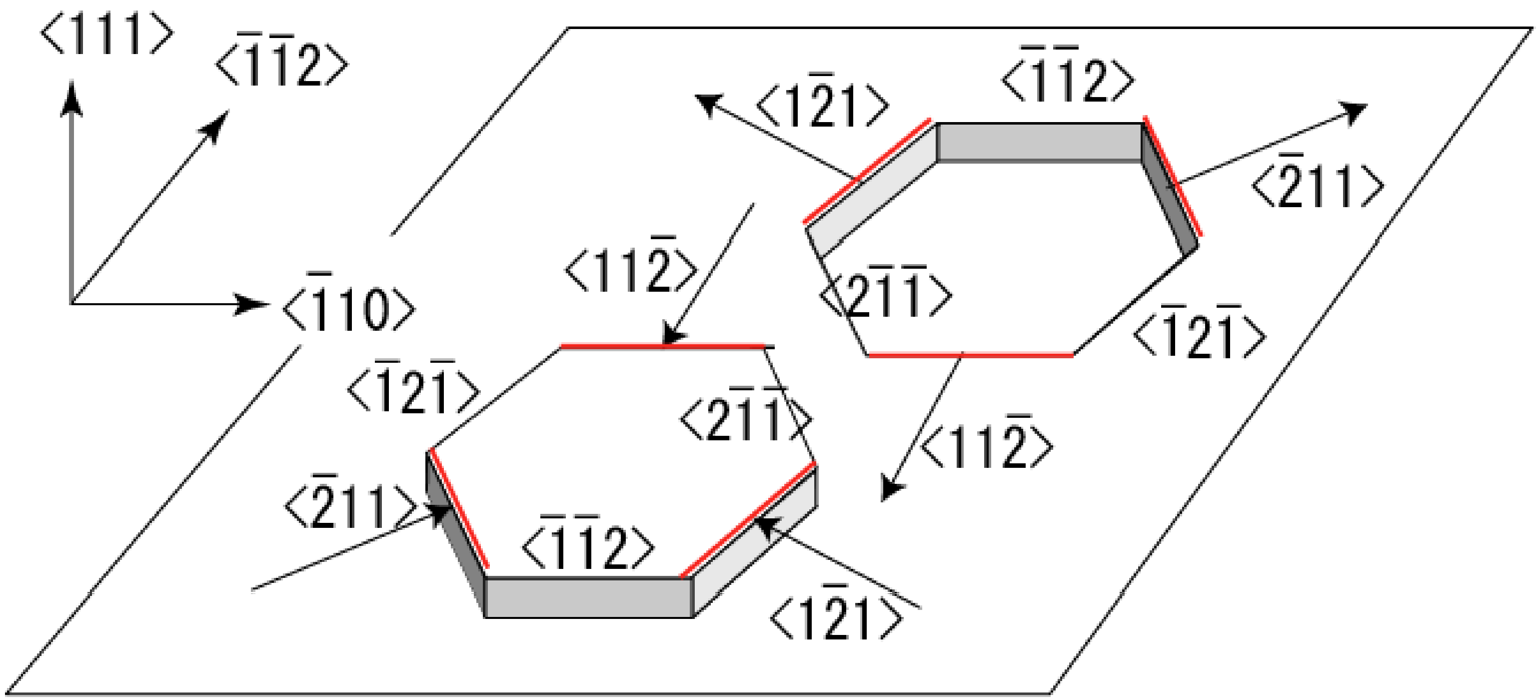
100 μ m

Cross-Section





Step movements determine profiles of pits and mesa on (111) silicon surface



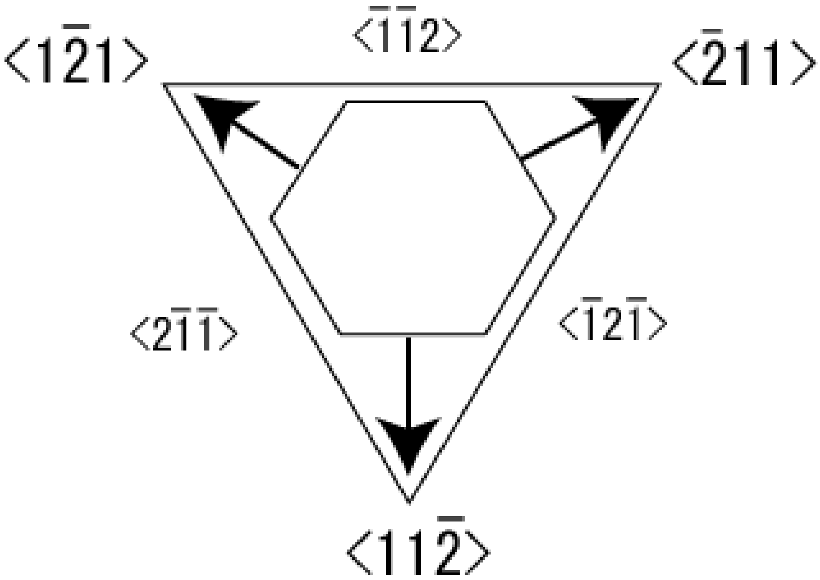
⟨$\bar{1}\bar{1}2$⟩, ⟨$\bar{1}2\bar{1}$⟩, ⟨$2\bar{1}\bar{1}$⟩: black line

[$\bar{1}\bar{1}2$] steps with 1 dangling bond (3 backbonds)

⟨$11\bar{2}$⟩, ⟨$1\bar{2}1$⟩, ⟨$\bar{2}11$⟩: red line

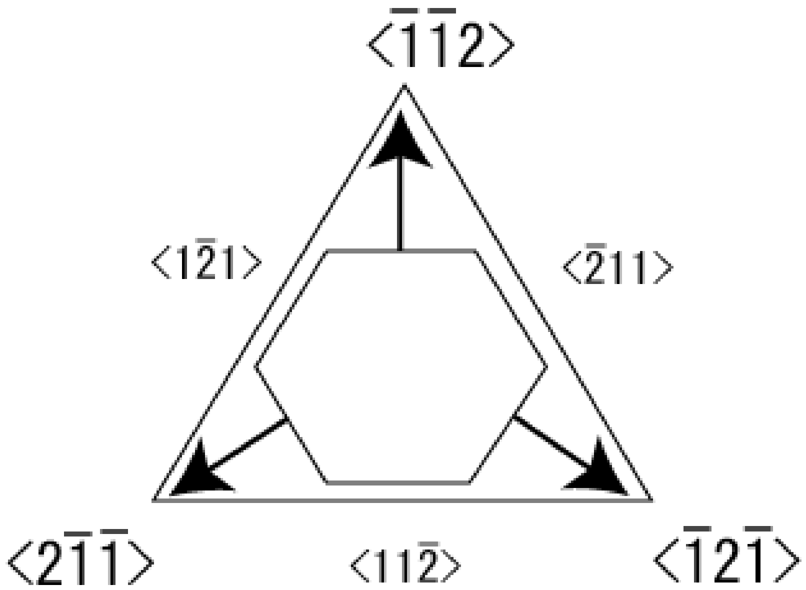
[$11\bar{2}$] steps with 2 dangling bonds (2 backbonds)

Differently oriented etch pit growth governed by the difference in activated step



KOH

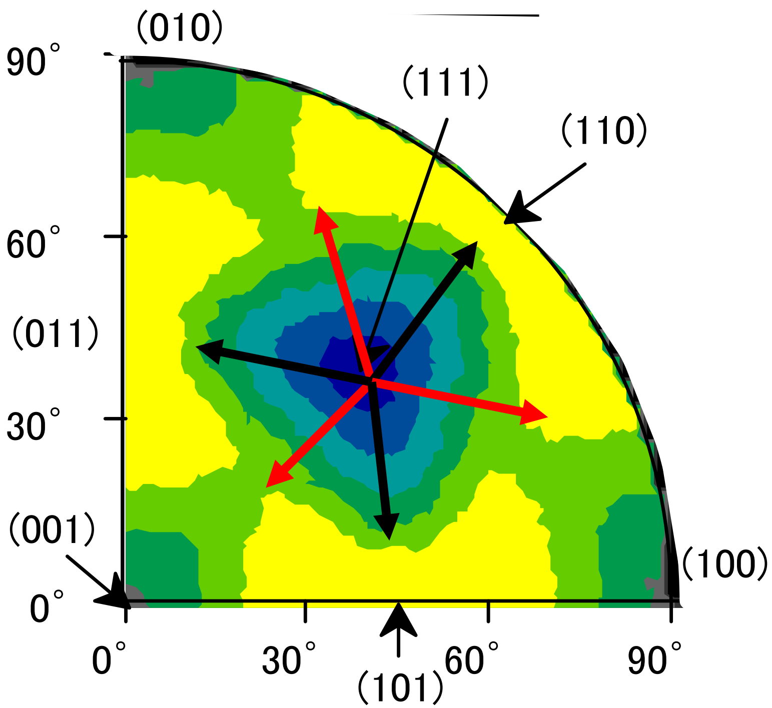
$[11\bar{2}]$ steps activated



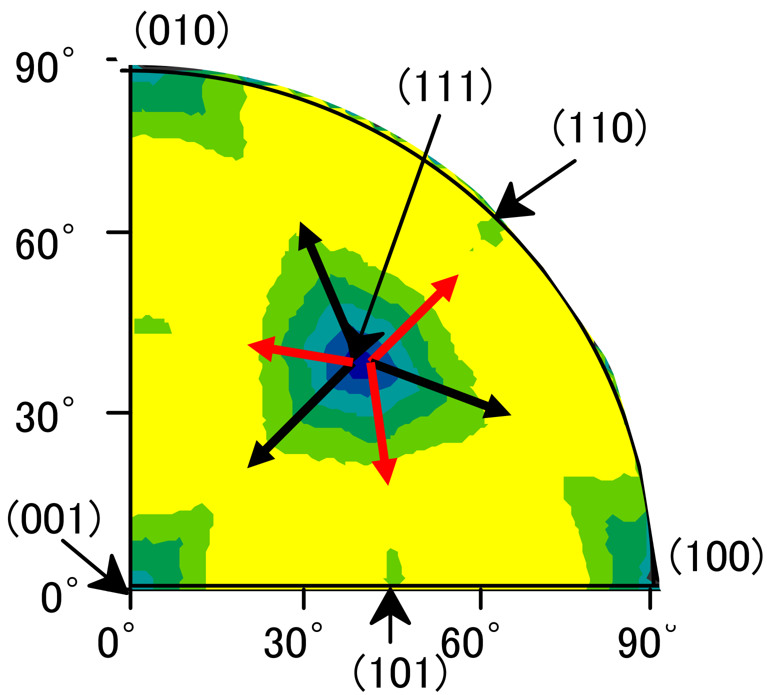
TMAH

$[\bar{1}\bar{1}2]$ steps activated

Difference in Etching Rate Contour Map between KOH and TMAH



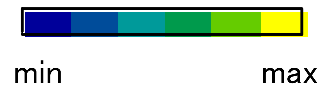
KOH40%70℃



TMAH25%80℃

KOH: Etch rate sharply increases by misorientation toward [1 1-2]

TMAH: Etch rate sharply increases by misorientation toward [-1-1 2]



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in macroscopic domains

"Dangling-Bond Model" does not tell the truth,
because no dynamics included.

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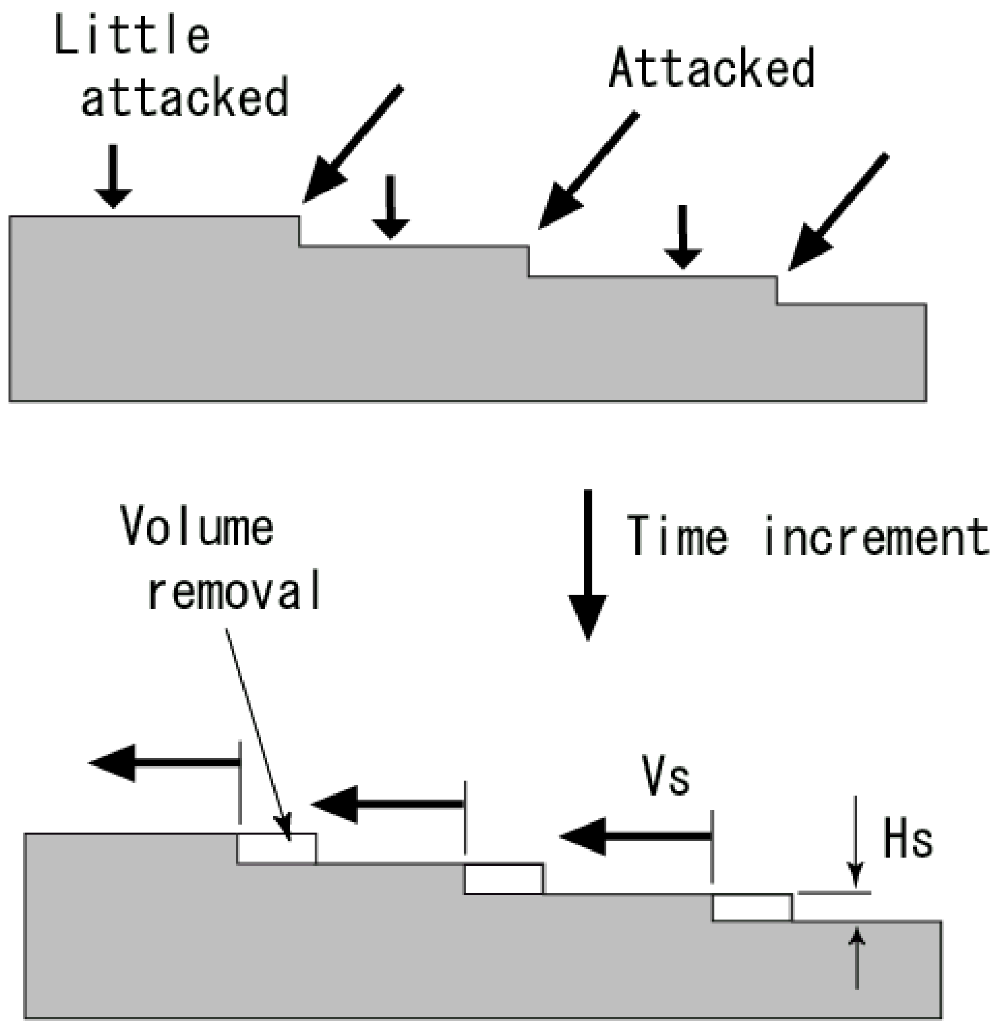
*Reversed anisotropy between KOH and TMAH

*Etched shape clearly reflects atomic-step behavior in the vicinity of Si (111)

Step Flow Model for (111) Silicon

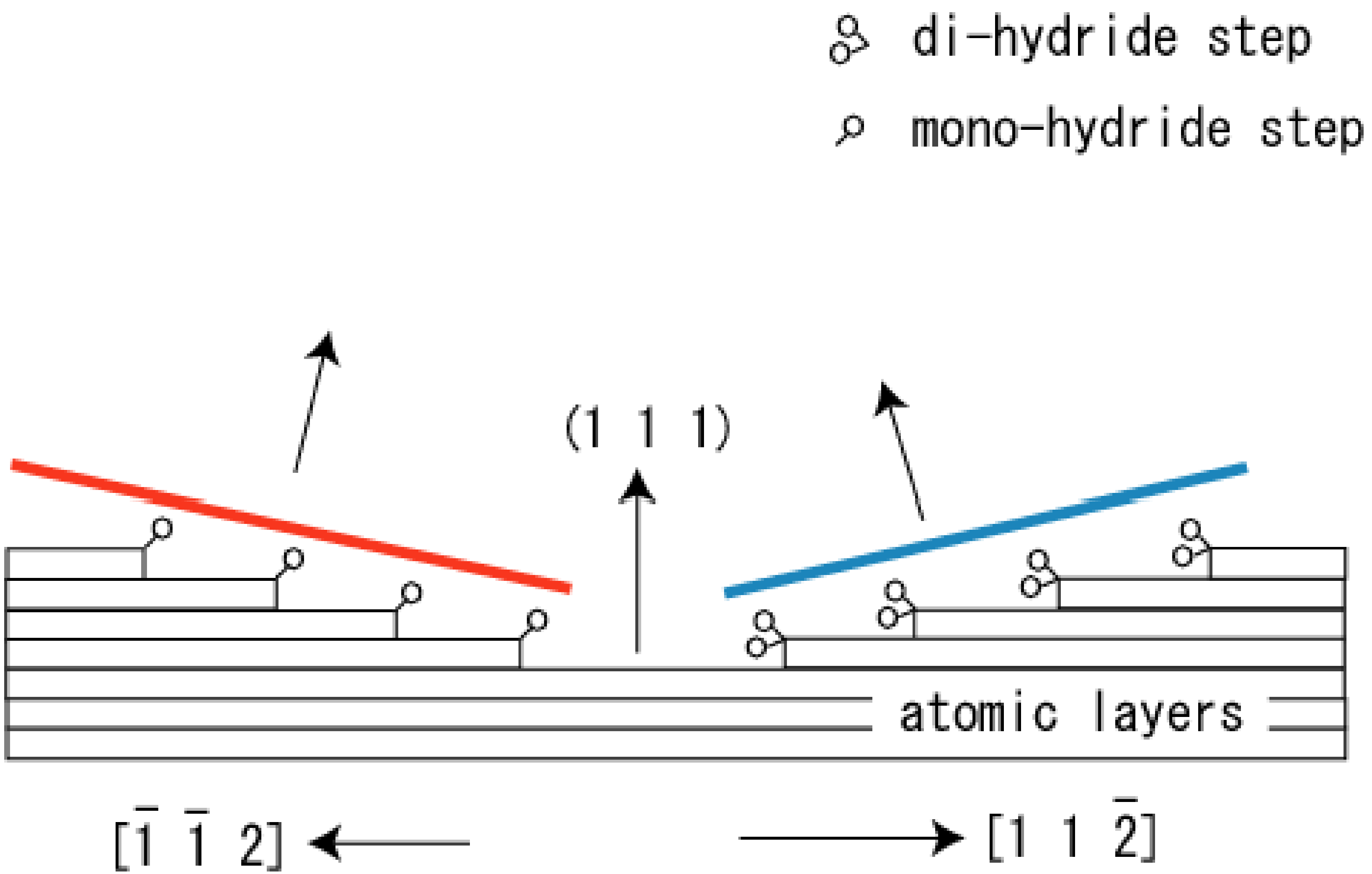
M. Elwenspoek, J. Electrochem. Soc. 140-7 (1993) 2075-80



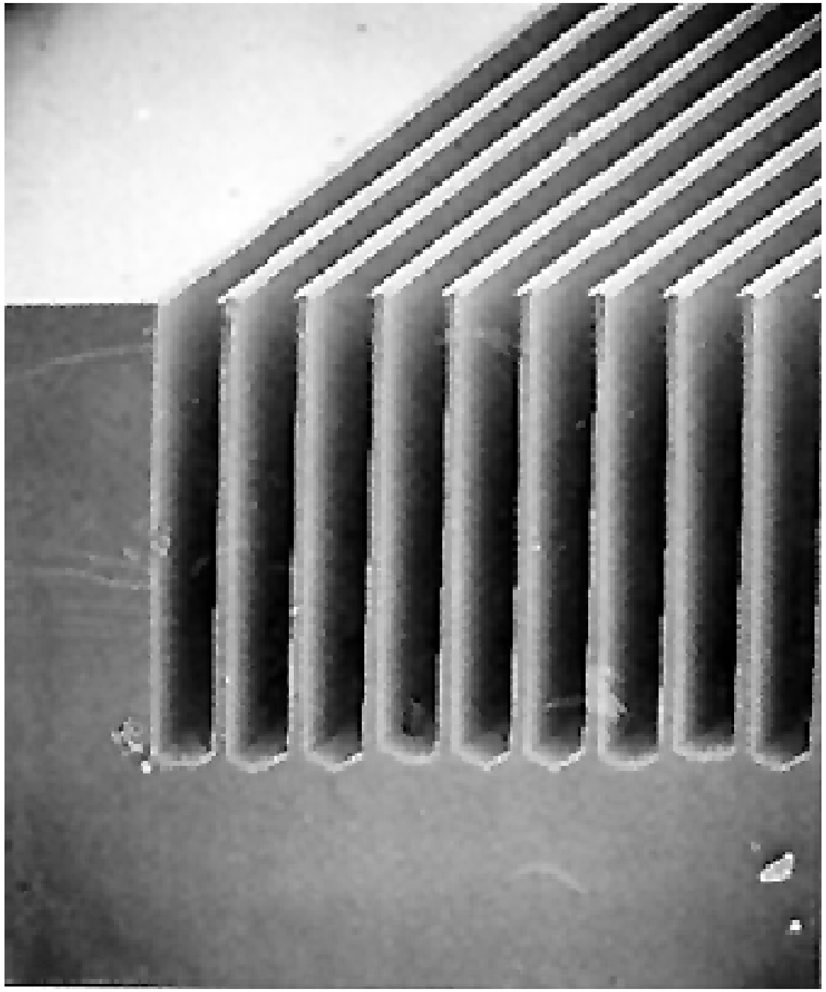
Volume removal rate:
$R = H_s V_s L_s$

Hs: Step height
Vs: Step velocity
Ls: Length of step per unit area

Difference in surface structure depending on a direction of deviation from silicon (111)

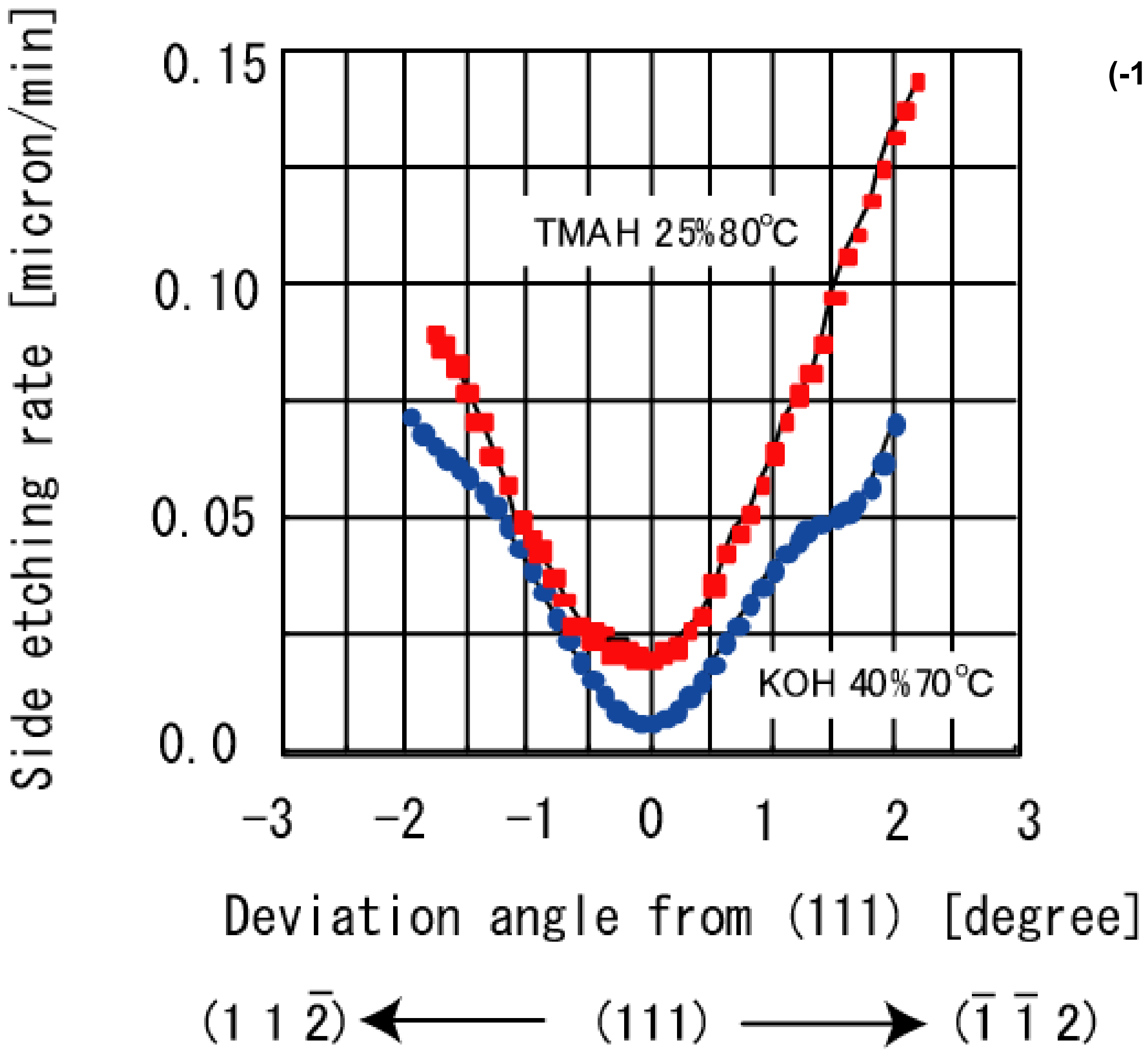


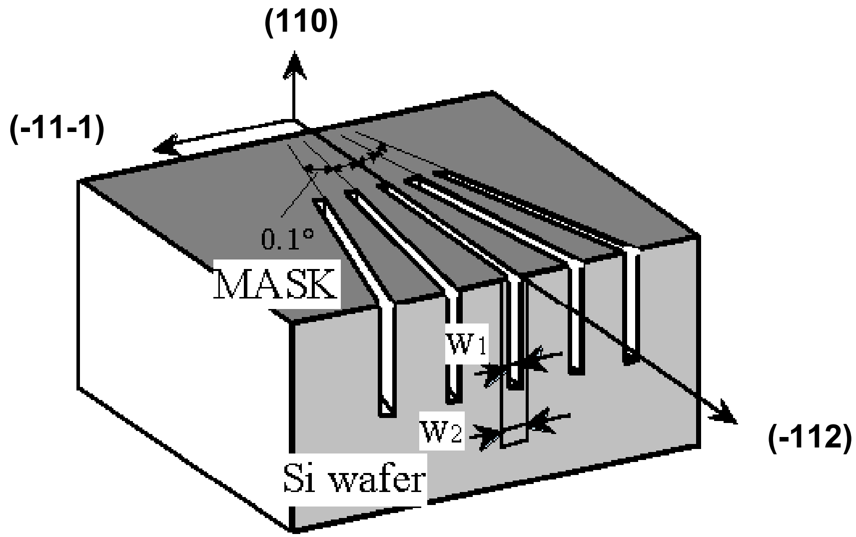
Etched deep grooves on (110) Si using a KOH water solution

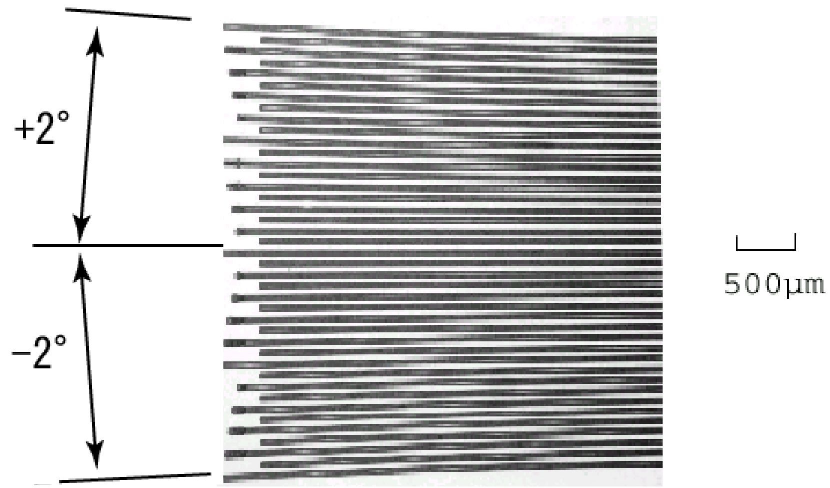


Groove depth:
90 microns

Asymmetric increase in etching rate by angular deviation from (111) orientation







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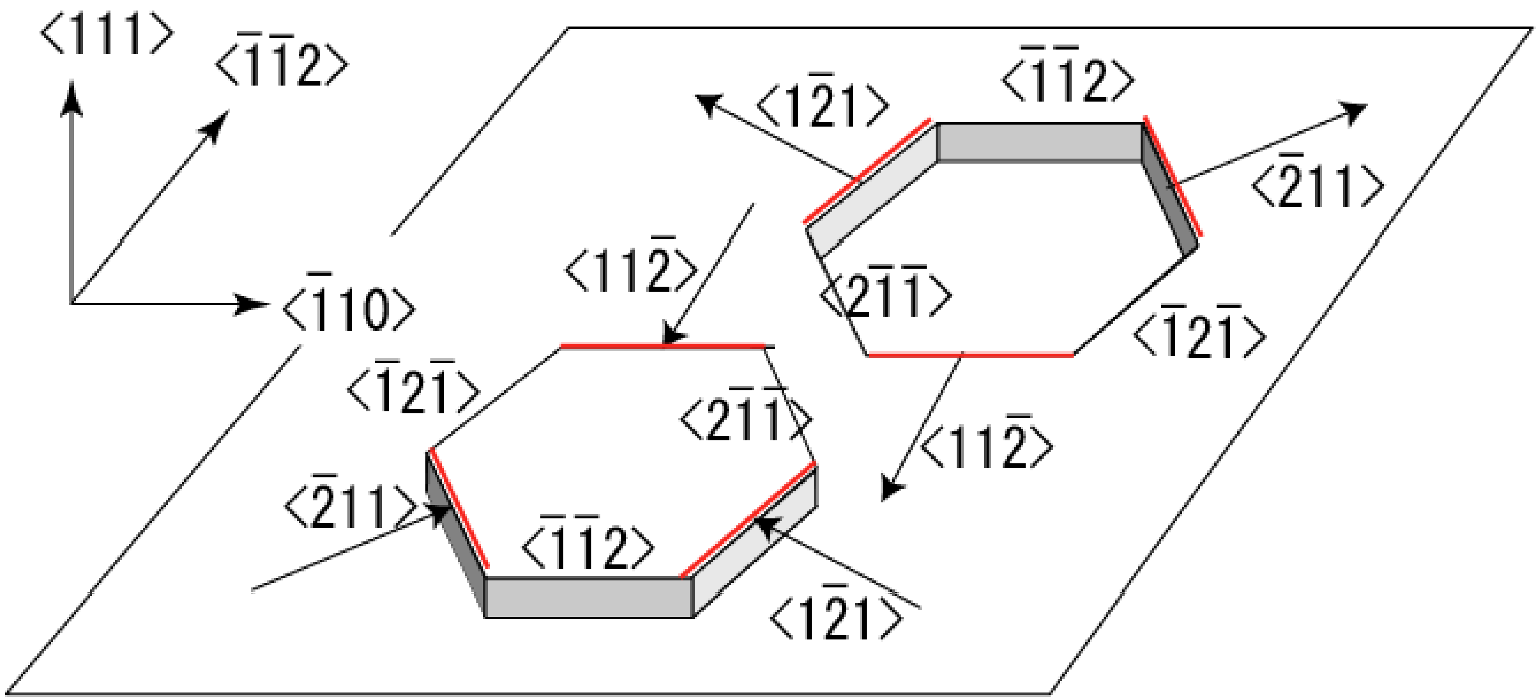

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Answers to the questions

- Is the atomic scale step flow model applicable to macroscopic etching?

  YES, in the vicinity of (111)

- Does the number of dangling bond determine the activeness of the surfaces or steps?

  NO

  (neither of the surface, nor of steps)

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References

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