Low temperature anodically grown silicon dioxide films for solar cell applications

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Australian Government

Australian Renewable Energy Agency

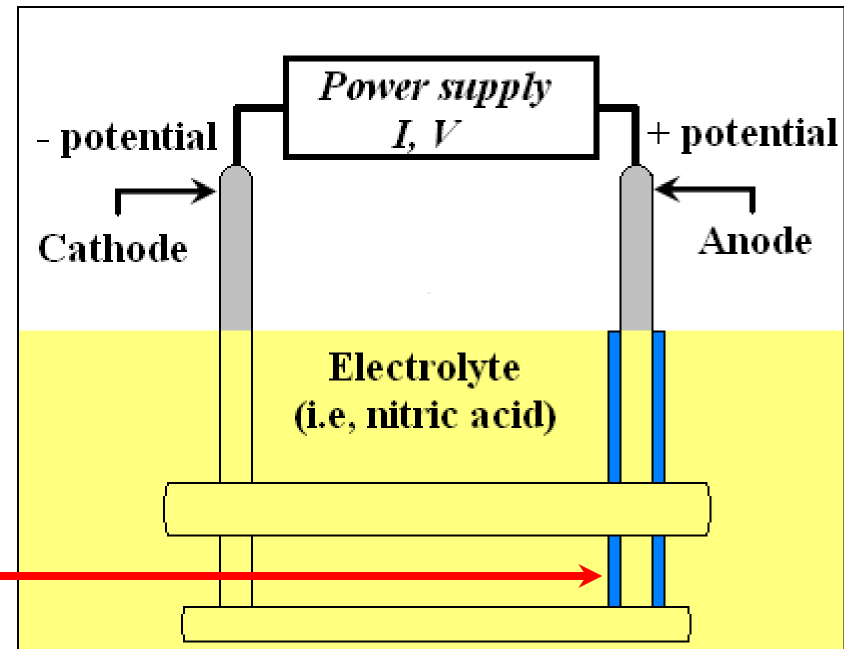
Outline

1. Electrochemical cell design and properties.
2. Direct-current anodic oxidations-Part 1 anodic oxide properties.
3. Direct-current anodic oxidations-Part 2 surface passivation.
4. Alternating-current anodic oxidations.
5. Impact of nitric acid (HNO_3) purity on the surface passivation repeatability.
6. Surface passivation degradation.
7. Masking anodic SiO_2 films.

What are anodic oxidations?

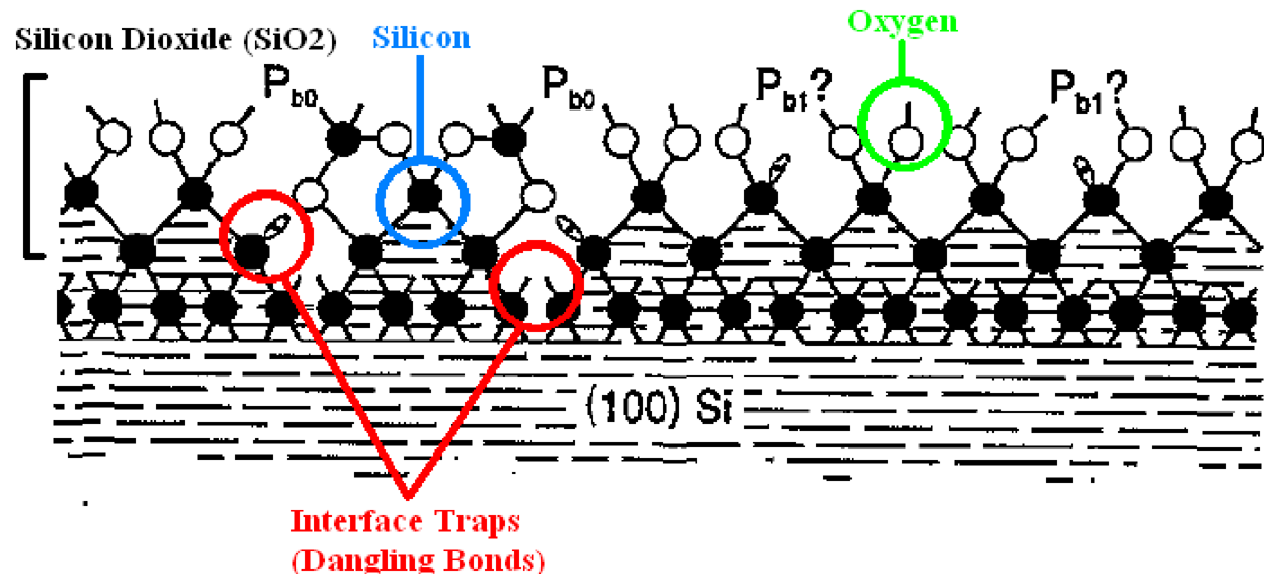
- Anodic oxidation occurs when either a constant current or a constant potential is applied across two electrodes immersed in a electrolytic solution.
- The cathode can either be a silicon wafer or a platinum wire.
- To form SiO_2 the anode must be a silicon wafer as oxidation only occurs at the anode, hence the term '**Anodic oxidation**'.

SiO_2 grows on both sides of the anode



Why investigate anodic oxidations?

- Thermal SiO_2 has been the predominant dielectric film for decades. It provides good passivation and has good masking properties.
- It is too expensive and thermally intensive. Low temperature formed SiO_2 with the same properties as thermal SiO_2 would be desirable.



C. R. Helms and E. H. Poindexter, Rep. Prog. Phys., 57, 791-852, (1994)

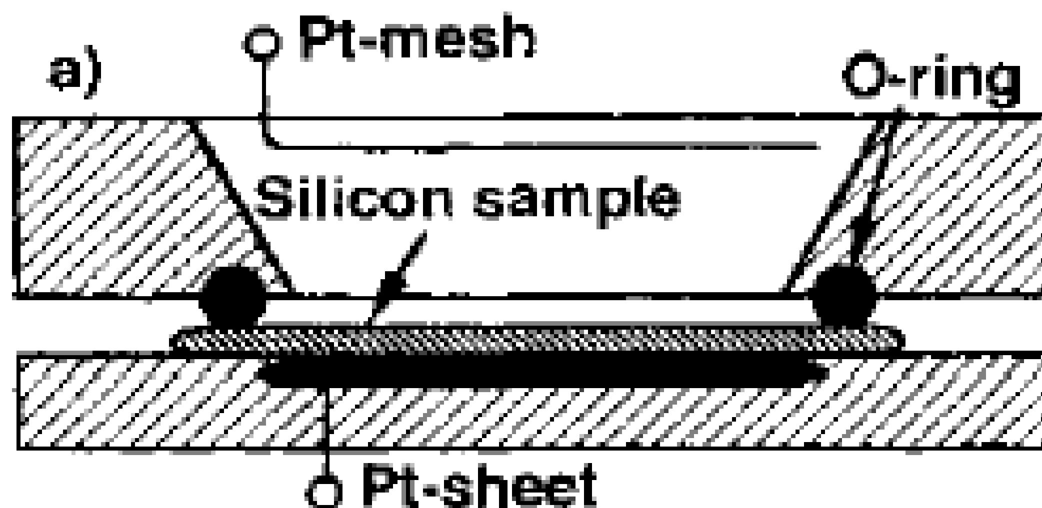
Why investigate anodic oxidations?

- Anodic oxidations can be performed at room temperature.
- They dont degrade the silicon bulk lifetime.
- Low temperatures minimise energy consumption and thus could potentially reduce cost.
- They dont require the use of complex CVD systems.

Electrochemical cell design and properties

Electrochemical cell design and properties

1. Cell design-O-ring cell

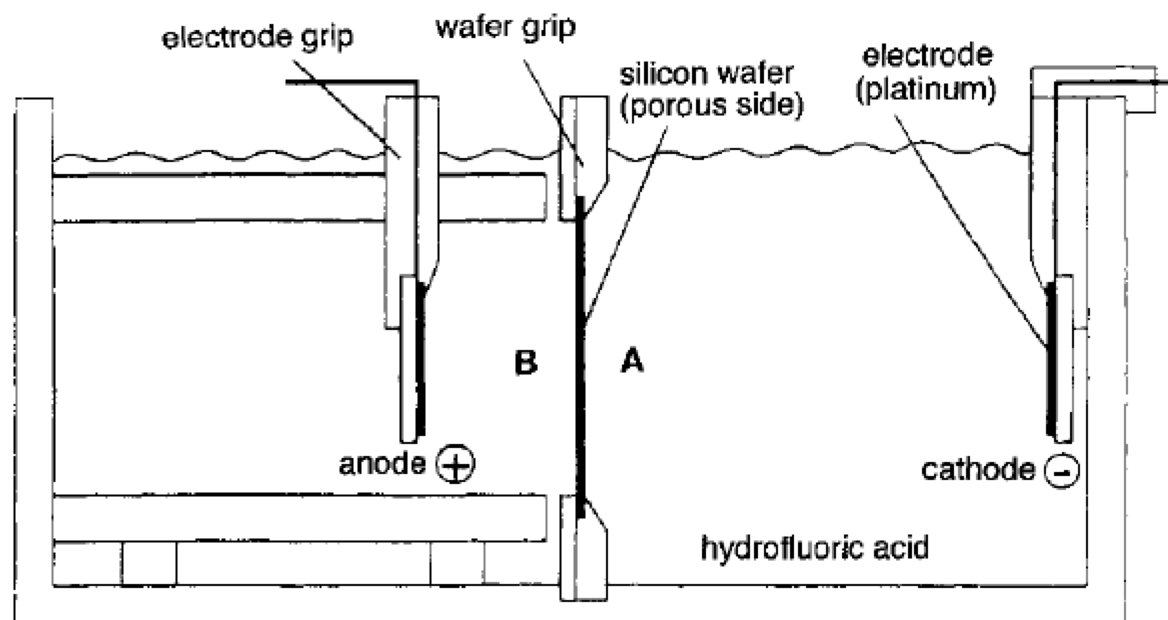


In this cell, only one side of the wafer is oxidized. The silicon sample (anode) is positively biased relative to the platinum mesh in the solution. Full area oxidation using this cell design would be difficult.

V. Lehmann. Electrochemistry of silicon: Instrumentation, science, materials and applications. Wiley-VCH, 2002.

Electrochemical cell design and properties

1. Cell design-Double cell

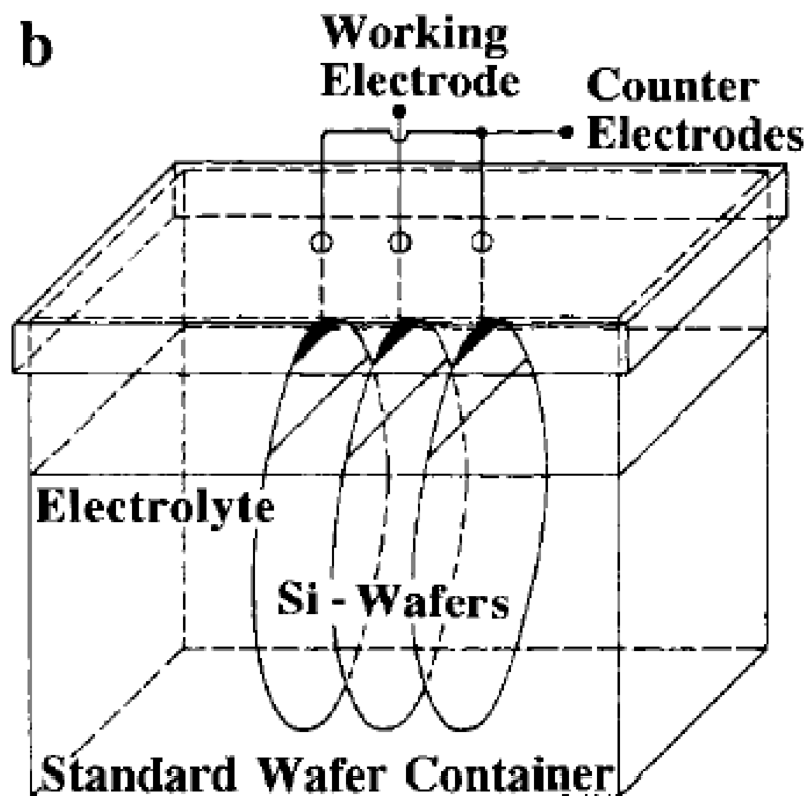


In this cell, electrical contact to the wafer is made through biased electrolytic solutions. This avoids any contact with metal. Not a simple setup.

V. Lehmann. Electrochemistry of silicon: Instrumentation, science, materials and applications. Wiley-VCH, 2002.

Electrochemical cell design and properties

1. Cell design-Immersion cell ✓



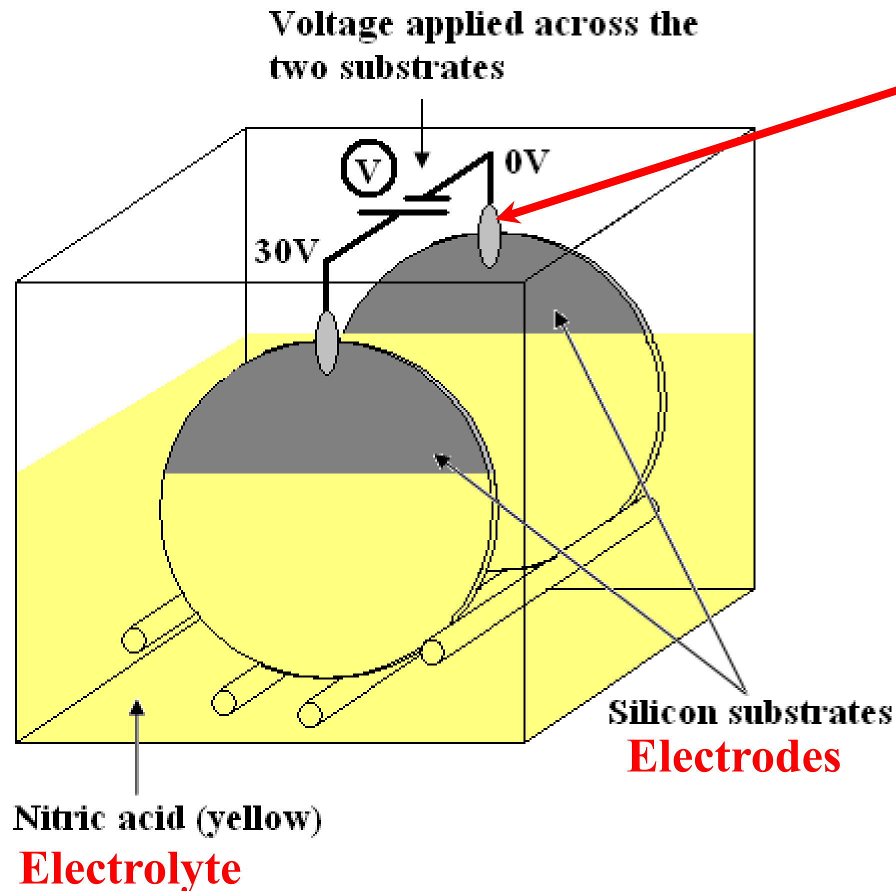
In this cell, the electrodes are simply immersed in the electrolytic solution. Contact is made to the non-immersed parts. Very simple setup.

Not practical, but the cell design is not the primary focus of this research.

V. Lehmann. Electrochemistry of silicon: Instrumentation, science, materials and applications. Wiley-VCH, 2002.

Electrochemical cell design and properties

2. Electrodes, contacting and electrolyte



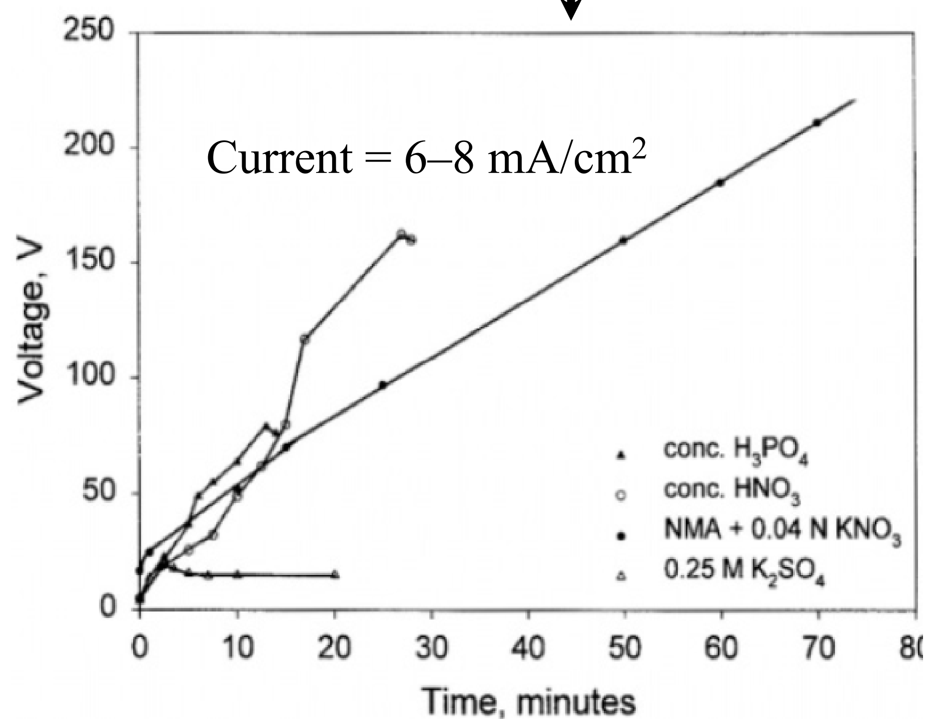
Aluminium (Al) coated alligator clips are used to contact the silicon wafer. No additional metal is deposited on the silicon.

Al was chosen because it does not corrode in nitric acid.

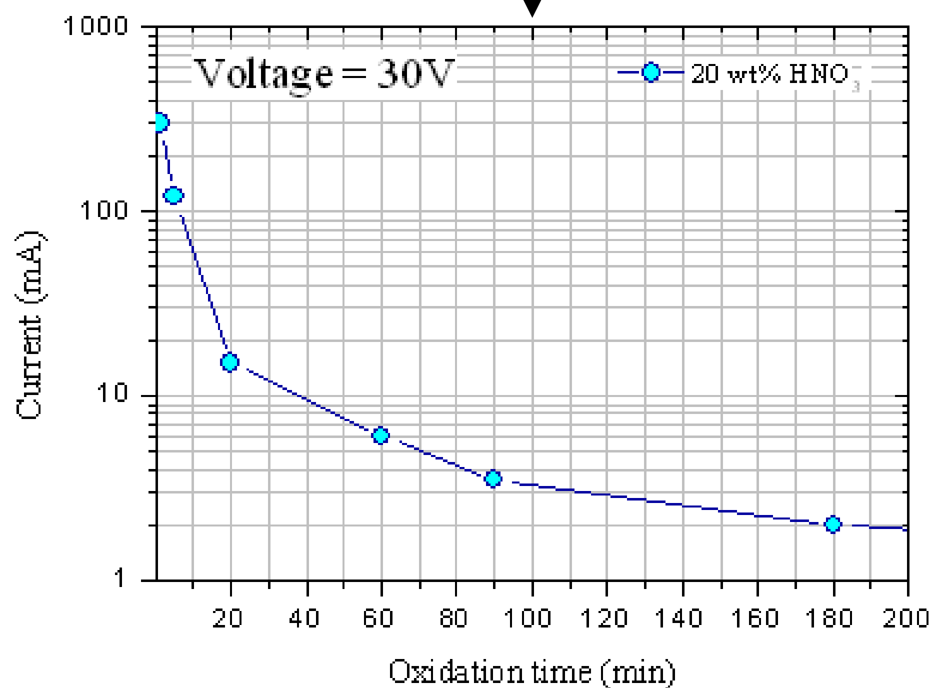
Both the anode and cathode are silicon wafers. The cathode could be a metal, provided it does not corrode in HNO_3.

Electrochemical cell design and properties

3. Constant current or constant potential?



Voltages are excessive.



Simple and safe. ✓

V. Lehmann. Electrochemistry of silicon: Instrumentation, science, materials and applications. Wiley-VCH, 2002.

Electrochemical cell design and properties

Summary

1.	Cell design–Immersion cell.	Why?–Very simple and easy to alter.
2.	Electrodes–Both are silicon wafers.	Why?–Convenient.
	Contacts–Al coated alligator clips.	Why?–Does not corrode when exposed to HNO_3 vapours.
	Electrolyte–Nitric acid (HNO_3).	Why?–Common chemical, good conduction.
3.	Constant current–Constant potential. or potential	Why?–Simple and safe.

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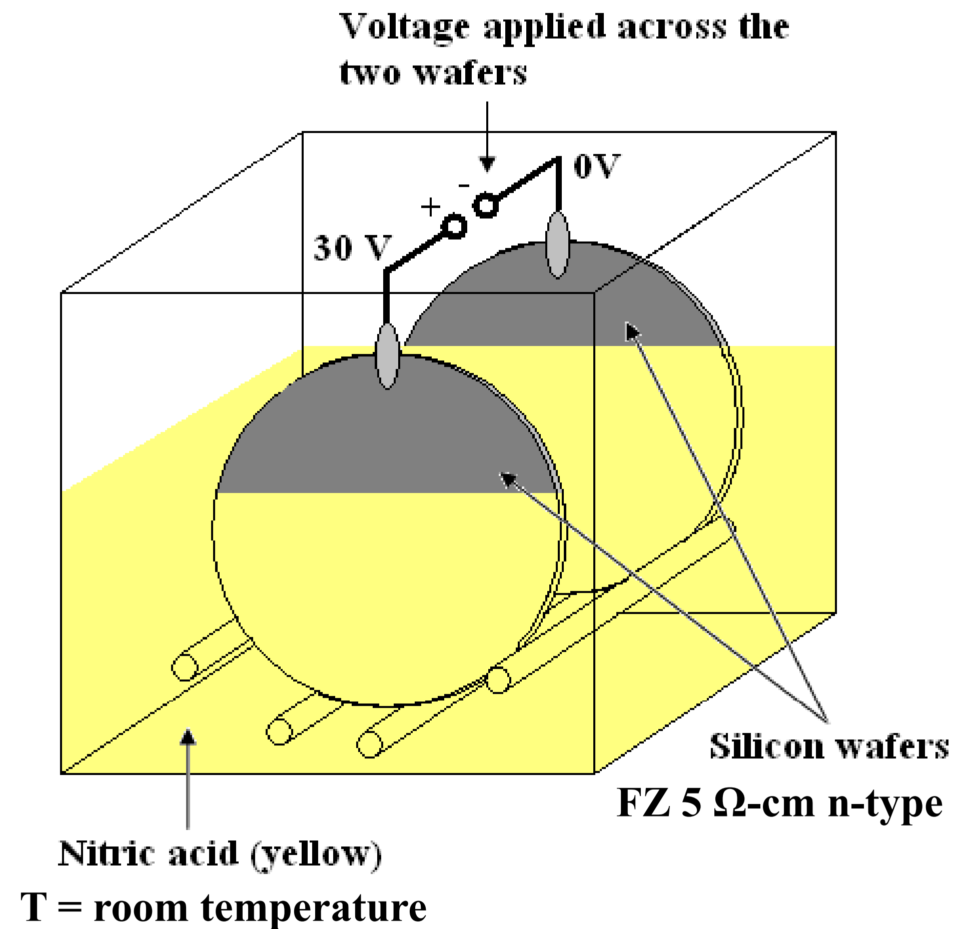
Direct-current anodic oxidations

Part 1: Anodic oxide properties

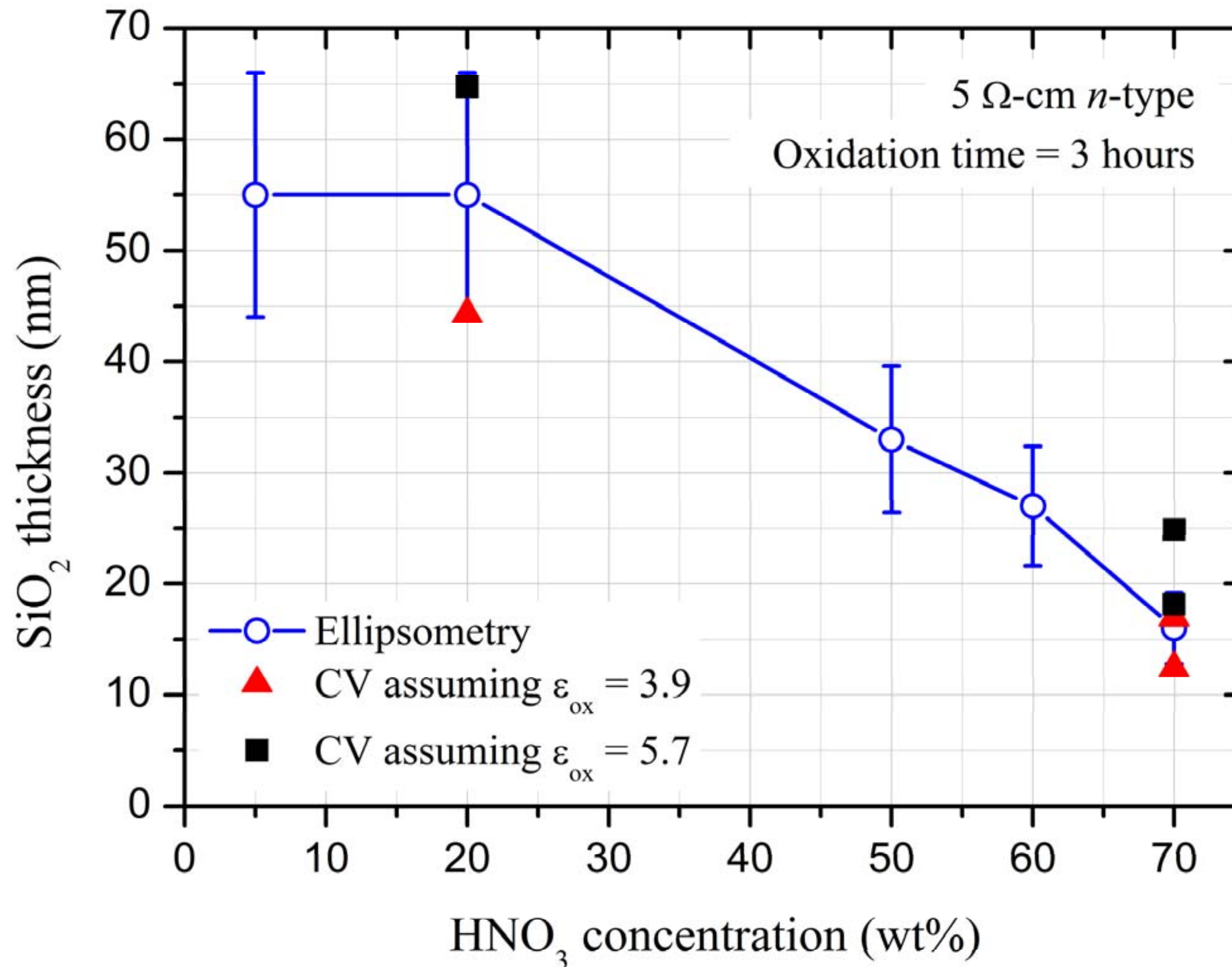
Direct-current anodic oxidation setup

Procedure:

- Apply a constant voltage across the samples while immersed in HNO_3 to grow an SiO_2 layer.
- Oxidation time = 3 hours.
- Oxidation time has yet to be optimised.



SiO_2 thickness versus H_2O concentration



H_2O concentration appears to have a substantial impact on the final oxide thickness. This suggest that H_2O is a primary source of oxygen

Oxidation efficiency is lowered at higher HNO_3 concentrations.

Sources of oxygen

- Water is the main source of oxygen for the formation of anodic SiO_2 films in various electrolytes.

$$1)\ Si + 2H_2O + nh \rightarrow 4H^+ + (4-n)e$$

- With increasing HNO_3 concentration, the oxidation efficiency is reduced because H_2O must be formed from the solvent first,

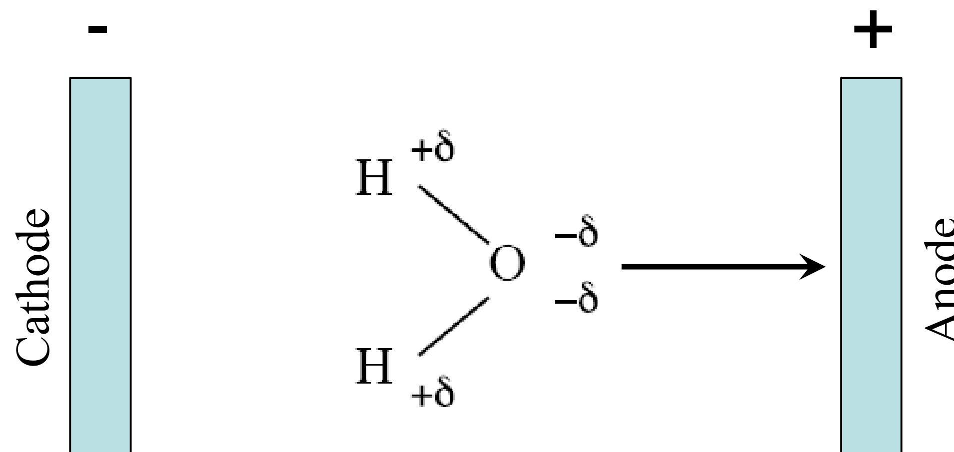
$$2)\ NO_3^- \xleftrightarrow{+H^+} HNO_3 \xleftrightarrow{+H^+} (H_2NO_3)^+ \rightarrow NO_2^+ + (H_2O).$$

- H_2O produced from reaction (2) supplies the oxygen for reaction (1), which can then form SiO_2. While oxidation still proceeds in high HNO_3 concentrated solutions, the oxidation efficiency is reduced and thus the oxide thickness is also reduced.

Migration of anions through the SiO_2 film

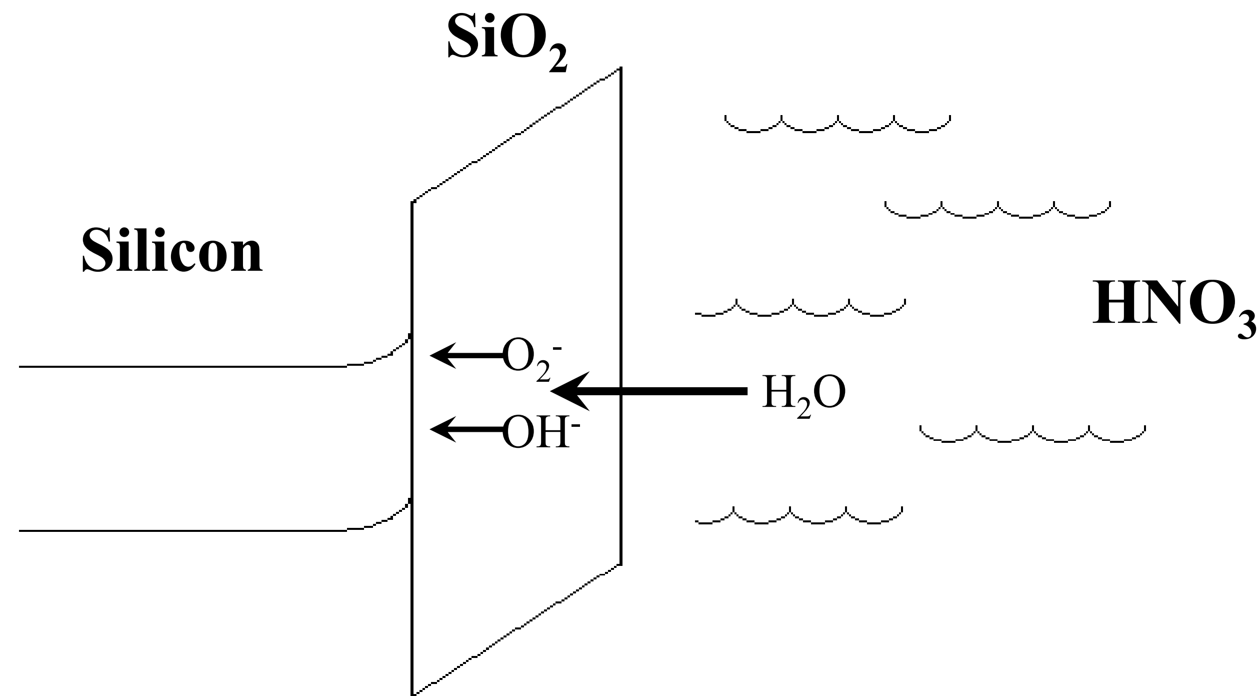
- H_2O can react with the anode in several different ways, and the details of these are unclear, however the two main ways H_2O can reach and react with the anode are:

1. H_2O has a small dipole moment, under an applied electric field the H_2O will drift towards the anode where it can form SiO_2.



Migration of anions through the SiO_2 film

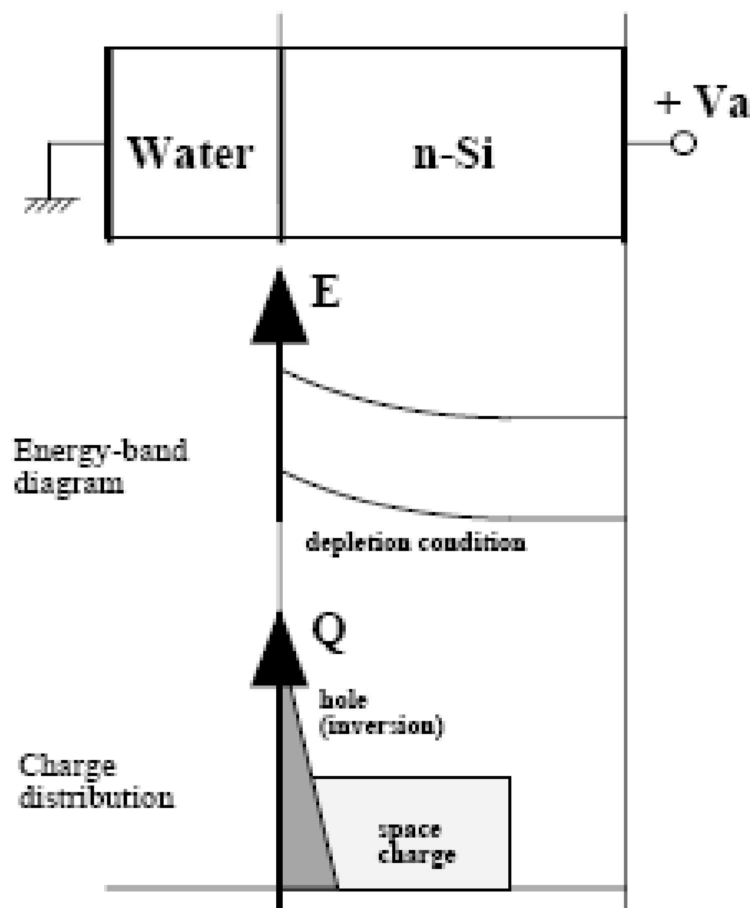
2. H_2O can dissociate upon entering the growing SiO_2 film.



3. Nitrate (NO_3^-) may also be involved in forming SiO_2???

n-type band bending under positive bias

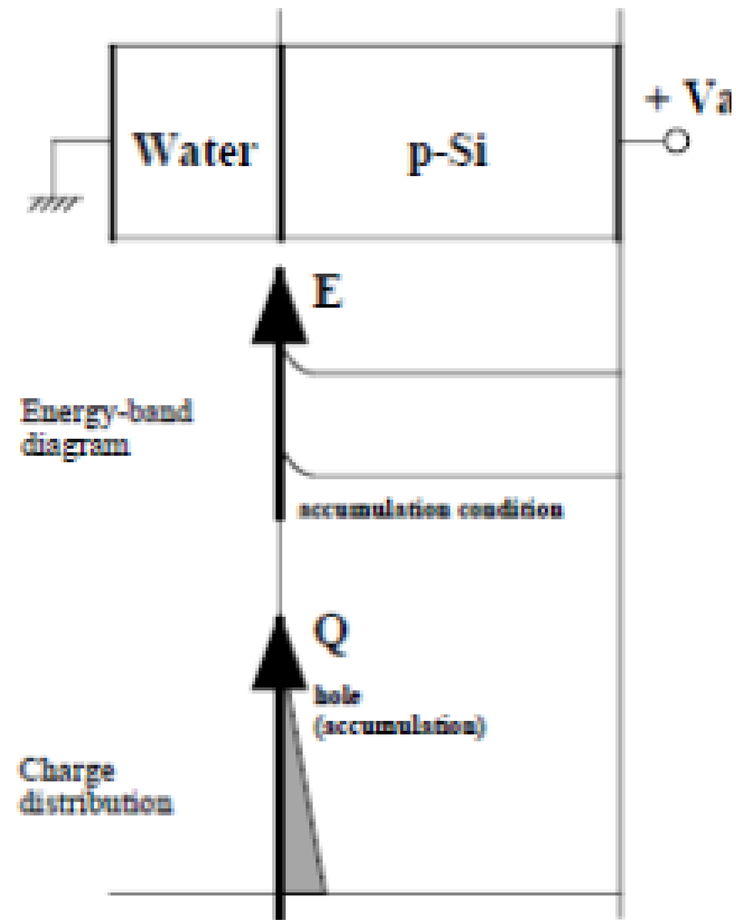
- In *n*-type silicon the positive voltage causes inversion at the interface.
- As the oxidation is a hole driven process, oxidation on *n*-type is limited by the supply of hole to the interface.
- Illumination can greatly increase the hole concentration and thus the oxidation rate.



K. OHNISHI, A. ITO, Y. TAKAHASHI and S. MIYAZAKI Jpn. J. Appl. Phys. Vol. 41 (2002) pp. 1235–1240

p-type band bending under positive bias

- In *p*-type silicon the positive voltage causes accumulation of holes at the interface.
- Because holes are the majority carrier in *p*-type silicon, illumination does not improve the oxidation rate. Therefore oxidation in the dark and under illumination results in the same oxide thickness.



K. OHNISHI, A. ITO, Y. TAKAHASHI and S. MIYAZAKI Jpn. J. Appl. Phys. Vol. 41 (2002) pp. 1235–1240

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Measured currents during anodic oxidation

Current (mA)

100
10
1

20 40 60 80 100 120 140 160 180 200

Oxidation time (min)

70 wt% HNO_3 experiment 1
70 wt% HNO_3 experiment 2
20 wt% HNO_3

d_{ox} = 50 nm

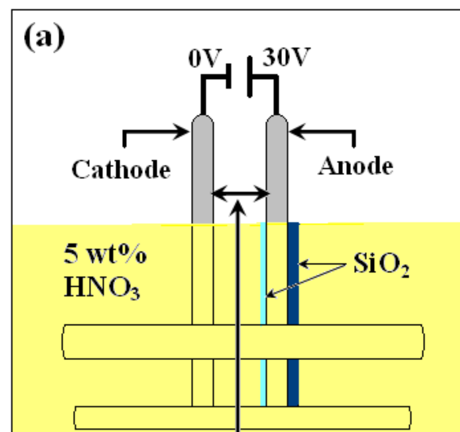
d_{ox} = 20 nm

5 Ω-cm *n*-type

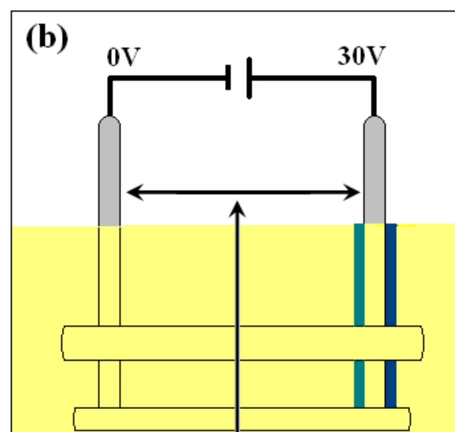
SiO_2 grows thicker in 20 wt% HNO_3 due to higher currents for longer periods of time. This is likely related to the availability of H_2O for the oxidation.

The difference in the current curves for oxidations in 70 wt% HNO_3 is likely due to ambient light variations.

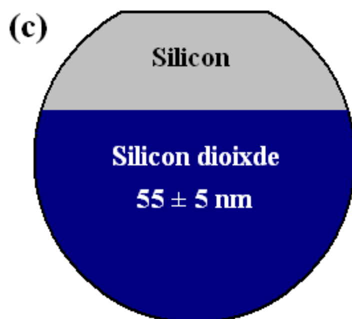
Effect of electrode spacing



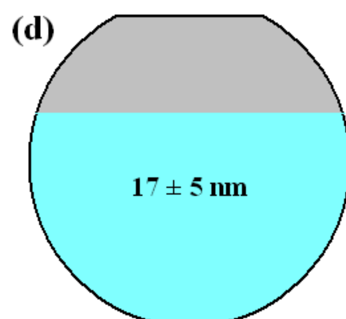
Electrode spacing = 3 cm



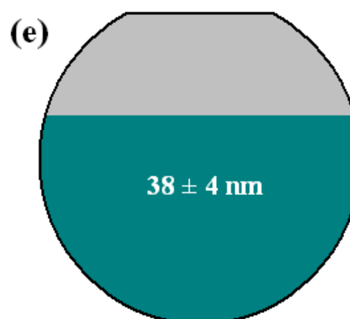
Electrode spacing = 10 cm



Side facing away from the cathode in (a) and (b)



Side facing cathode in (a)



Side facing cathode in (b)

The variation in SiO_2 thickness with electrode spacing has been observed before, however no explanation for why this occurs was given.

To ensure the oxide thickness is the same on both sides of the anode, it is best to maintain a large electrode spacing.

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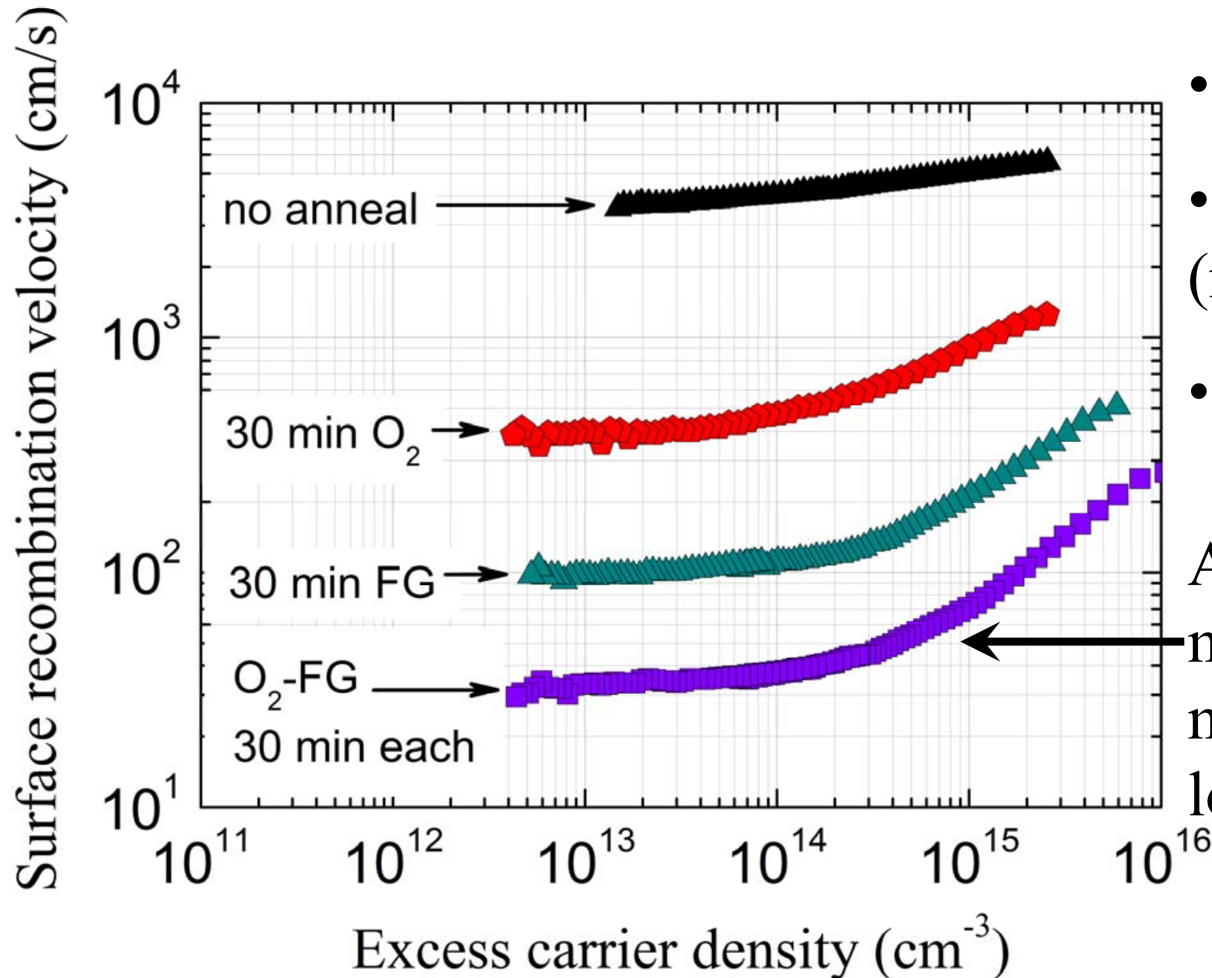
Direct-current anodic oxidations

Part 2: Surface passivation

Best annealing ambient at T=400 °C



- 5 Ω-cm *n*-type
- Oxidation time = 3hrs (not optimised yet)
- 70 wt% HNO_3

Annealing in O_2 for 30 mins followed by a 30 min FGA provides the lowest *S* of ~30 cm/s.

Passivation versus HNO_3 concentration

Post oxidation the samples were annealed in O_2 and FG at 400 °C

(a)

Surface recombination velocity (cm/s)

10^4, 10^3, 10^2

HNO$_3$ Concentration: 0 %, 20 %, 60 %, 70 %

10^{13} 10^{14} 10^{15}

Excess carrier density (cm^{-3})

(b) S

10 20 30 40 50 60 70

HNO_3 Concentration (wt%)

Passivation versus HNO_3 concentration

Post oxidation the samples were annealed in O_2 and FG at 400 °C

Surface recombination velocity (cm/s)

Modelled *S*

(a)

0 %
20 %
60 %
70 %

HNO_3 concentration

Excess carrier density (cm^{-3})

(b)

Modelled charge density

S

HNO_3 Concentration (wt%)

Modelled Charge Density x10^{11} (C/cm^2)

Capacitance-voltage measurements

Post oxidation the samples were annealed in O_2 and FG at 400 °C

(a)
○ 70 wt% HNO_3
○ 20 wt% HNO_3
d_{ox} = 20 nm
$Q_{ox} = 2.13\text{x}10^{12}$ cm^{-2}
$Q_{ox} = 1.65\text{x}10^{12}$ cm^{-2}
d_{ox} = 50 nm
Capacitance (pF)
Voltage (V)

(b)
○ 70 wt% HNO_3
○ 20 wt% HNO_3
Mid-gap
(D_{it}=2.0-3.0x10^{12} eV^{-1}cm^{-2})
E_f-E_v (eV)
D_{it} (eV^{-1}cm^{-2})

• Measurements suggest oxide charge is the cause for differences in *S* when anodic oxidation is performed in 20–70 wt% HNO_3. This is consistent with our modelling.

Summary

1. The SiO_2 thickness decreases with increasing HNO_3 concentration.
2. SiO_2 thickness is controlled by the H_2O concentration. This occurs because H_2O is a primary source for anodic oxidation of silicon.
3. Anodic oxidation is a hole driven process. Therefore if *n*-type silicon is used, the oxidation rate will be sensitive to illumination because holes are the minority carrier. Illumination does not effect the oxidation rate when *p*-type silicon is used.
4. Annealing the anodic oxide films in O_2 followed by FG at 400 °C provides the best surface passivation.
5. Lower *S* are achieved when anodic oxidations are carried out in 70 wt% HNO_3. This is primarily due to a higher positive charge in these films when compared to oxidations carried out in 20 wt% HNO_3.

Alternating-current anodic oxidations

Why investigate AC anodic oxidations?

- To further reduce the surface recombination velocity relative to DC anodic oxidations.

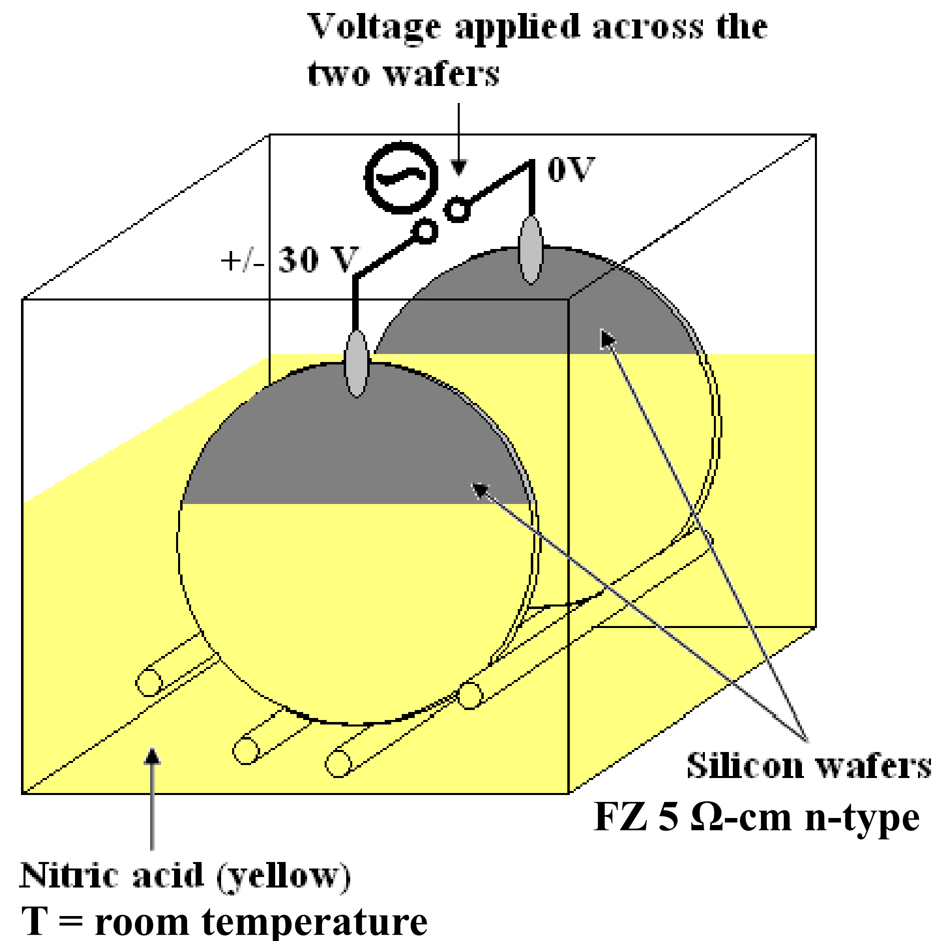
How might this be achieved?

- Anions drifting through the SiO_2 film may have multiple opportunities to passivate dangling bonds and defects in the SiO_2 film when the voltage polarity is changed periodically.

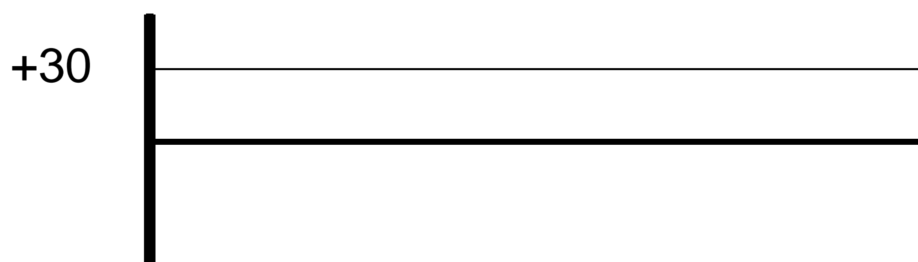
AC anodic oxidation setup

Procedure:

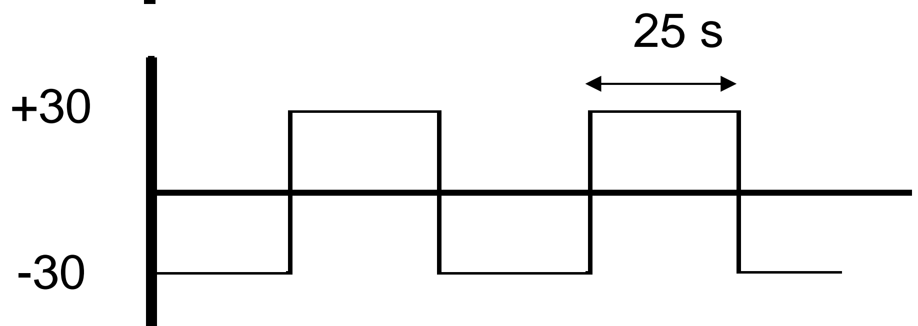
- Apply an alternating voltage across the samples while immersed in HNO_3 to grow an SiO_2 layer.
- Both wafers are oxidized simultaneously.
- Oxidation time = 3 hours.
- Oxidation time has yet to be optimised.



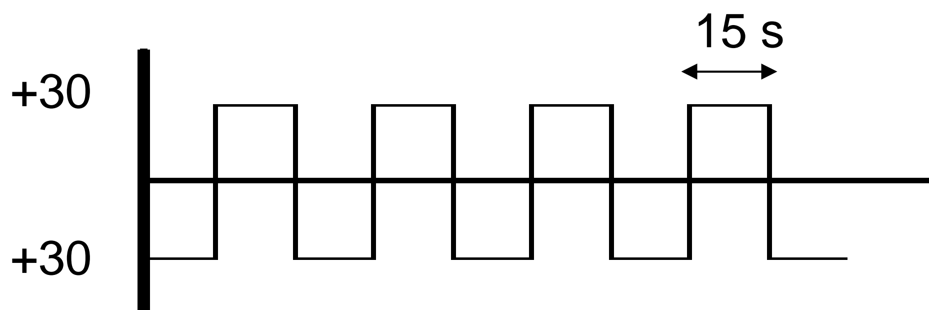
Voltage profiles for AC anodic oxidations



A constant +30 V bias (DC oxidation)



The voltage switches polarity (± 30V) every 25 seconds = 50 second cycle.



The voltage switches polarity (± 30V) every 15 seconds = 30 second cycle.

Current profile during AC anodic oxidation

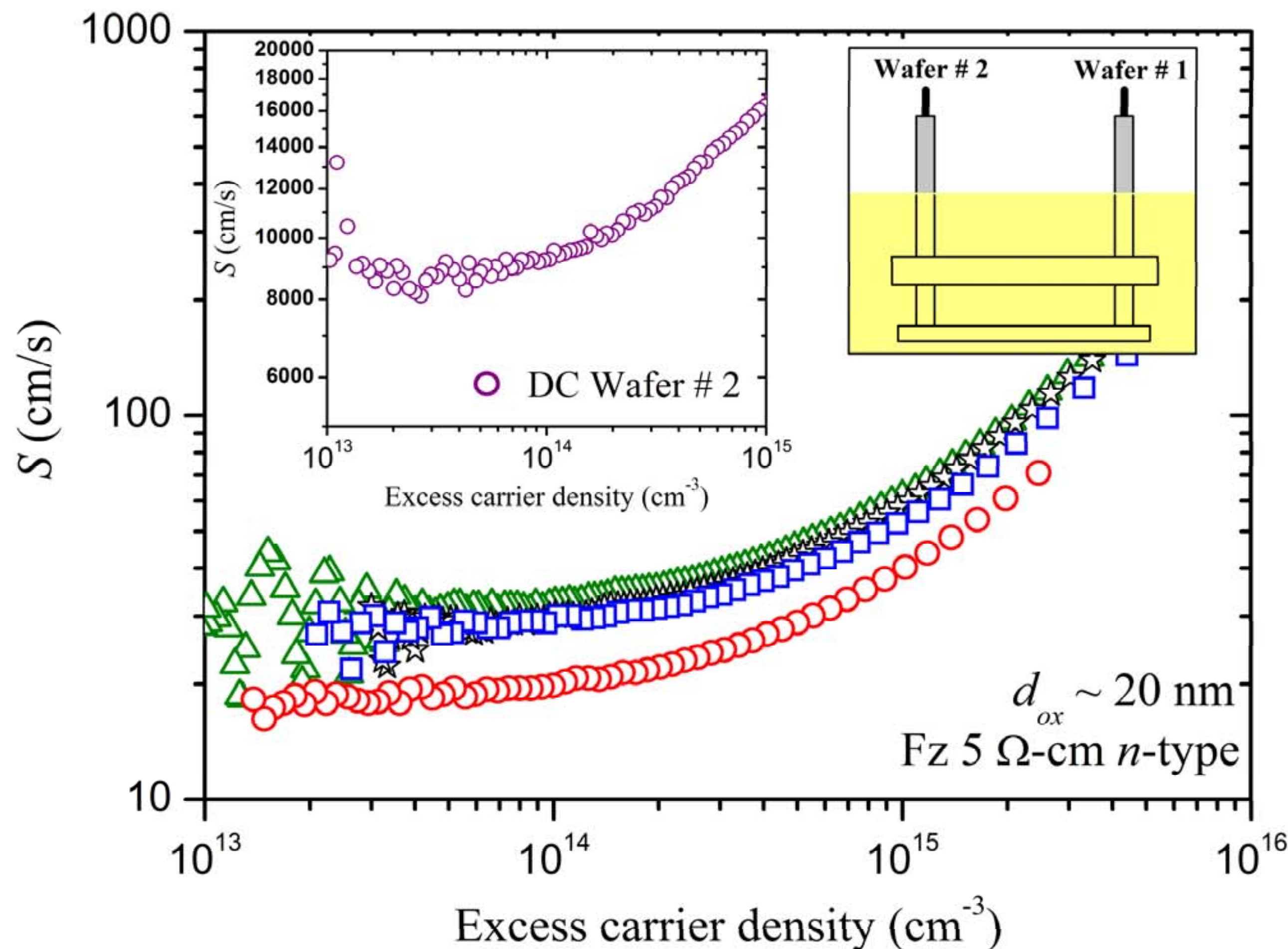
The current during the first 20 minutes of oxidation appears unstable. This is likely related to the breakdown/regrowth cycles of the oxide layer.

After ~20 mins of oxidation the current becomes much more stable. The current steadily decreases with time which is consistent with a thickening SiO_2

Positive cycle
Negative cycle
Wafer 1
Wafer 2
Wafer # 2
Wafer # 1
Current (mA)
Oxidation time (mins)

Passivation versus AC cycle time

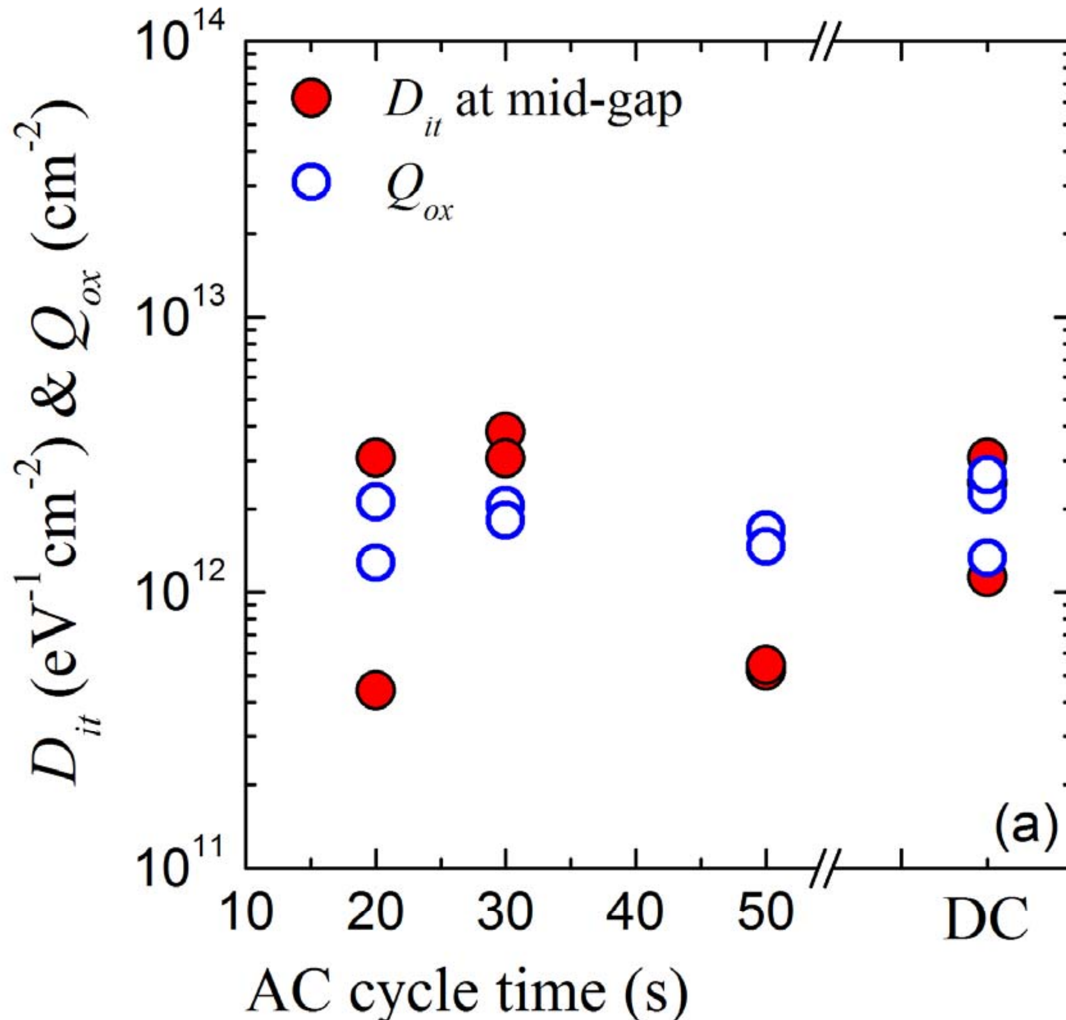
Post oxidation the samples were annealed in O_2 and FG at 400 °C



No improvement in *S* using AC cycle times of 20, 30 and 50 seconds.

Identical passivation is achieved on both wafer 1 and wafer 2 using the AC anodic oxidation process.

Passivation versus AC cycle time



No clear indication why DC anodic oxidations provide a higher level of passivation. A higher Q_{ox} maybe?

We can infer that anodic oxides provide good passivation on *n*-type silicon because the films contain a high positive fixed charge density of ~2.0×10^{12} cm^{-2}. Unfortunately the D_{it} is a little higher than we desire (i.e <1.0×10^{12}).

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Correlation between D_{it} and Q_{ox}

D_{it} at mid-gap
D_{it} at 0.7 eV
5 Ω-cm *n*-type
10^{13}
10^{12}
10^{11}
D_{it} (eV^{-1}cm^{-2})
10^{12}
2×10^{12}
3×10^{12}
Q_{ox} (cm^{-2})

It appears that when the D_{it} is high so to is Q_{ox} and vice versa.

This trend could reflect the structural and chemical quality of the oxide. When the oxide is of high quality, the density of the defects in the SiO_2 and at the interface is low.

As Q_{ox} decreases with a reduction in the D_{it}, S remains relatively constant.

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Summary

1. AC anodic oxidations form SiO_2 wafers on both silicon electrodes.

2. The current during oxidation is not stable until $t > 20$ minutes. Therefore it is unlikely high quality SiO_2 films would be formed for $t < 20$ minutes.

3. AC cycle times of 20, 30 and 50 seconds were investigated. S of ~ 30 cm/s was achieved, which is higher than that achieved by DC anodic oxidation. **Should shorter cycle times be investigated?**

4. No clear evidence to indicate why AC anodic oxides result in higher S.

5. It is clear that both the AC and DC anodic oxide films provide low S on n-type silicon because Q_{ox} is high (~2.0×10^{12} cm^{-2}). Unfortunately the D_{it} is high.

Impact of HNO_3 purity on surface passivation repeatability

Repeatability differences when using 70 wt% ppm and ppb HNO_3 solutions

Higher purity HNO_3 clearly improves the repeatability.

The first time this has occurred when τ_{eff} is high.

Cost of low purity ppm HNO_3 ~$50 per 2.5L.

Cost of high purity ppb HNO_3 ~$200 per 2.5L.

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Repeatability differences when using 20 wt% ppm and ppb HNO_3 solutions

Effective lifetime (μs) at $\Delta n = 10^{14}$

1000
800
600
400
200
0

HNO_3 (ppm)

HNO_3 (ppb)

0
2
4
6
8

Experimental number

Using 20 wt% HNO_3, it is noticeable that the surface pasivation is greatly improved using a higher purity solution.

The surface passivation is quite consistent when using pure 20 wt% HNO_3, consistent with the previous results.

Variations in current when using ppm and ppb HNO_3 solutions

70 wt% HNO_3

Bad passivation

Good passivation

Current (mA)

Oxidation time (mins)

Anodic oxidation using pure (ppb) HNO_3

Anodic oxidation using non-pure (ppm) HNO_3

10

1

1

10

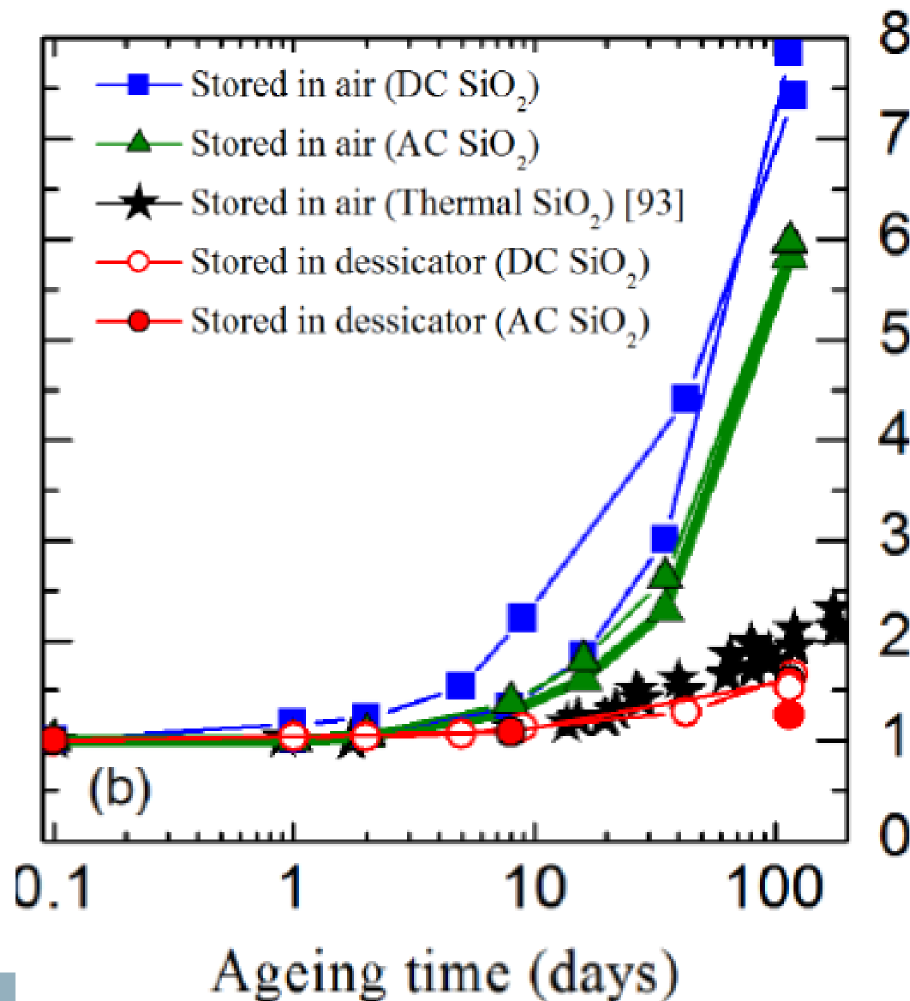
100

Summary

- HNO_3 purity has a substantial impact on the repeatability of S.
- In the case of using pure 20 wt% HNO_3 the surface passivation is greatly enhanced.
- The current profiles can potential indicate whether the oxide will provide good or bad passivation.

Surface passivation degradation

Ageing of samples stored in air and a dessicator



A dessicator is a humidity free chamber.

These results suggest that water vapour absorbed by the anodic SiO_2 film is a primary source of degradation.

The films still appear to degrade when stored in a dessicator. This could be due to water in the film resulting from the oxidation. This water may react with Si-H at the interface, breaking the bond and thereby increasing *S*.

Degradation at the interface

(a)
20 % HNO$_3$ concentration
60 %
70 %
Non-pure ppm HNO$_3$
S (cm/s)
Ageing time (days)

(b)
1 Day
8 Days
1 month
Capacitance (C/C$_{ox}$)
Voltage (V)

For samples stored in air, the degradation is primarily due to an increase in the interface defect density.

Possible solutions to prevent degradation

1. Use a capping film that is impermeable to water vapour.
2. Short (< 5 mins) high temperature (700–800 °C) anneal to remove any water in the film.
3. Avoid FG annealing unless *alnealing* can be formed where the Al is not removed. (Potential rear solar cell passivation structure)

Masking anodic SiO_2 films

Anodic oxidations using diffused silicon wafers-current profiles

20 wt% HNO_3

d_{ox}=90-100 nm

d_{ox}=120-150 nm

d_{ox}=120-150 nm

d_{ox} = 50 nm

d_{ox} = 200 nm

Boron diffusion (100 Ω/sq)

Phosphorus diffusion (30 Ω/sq)

Undiffused *n*-type silicon

Current (mA)

100

10

1

1

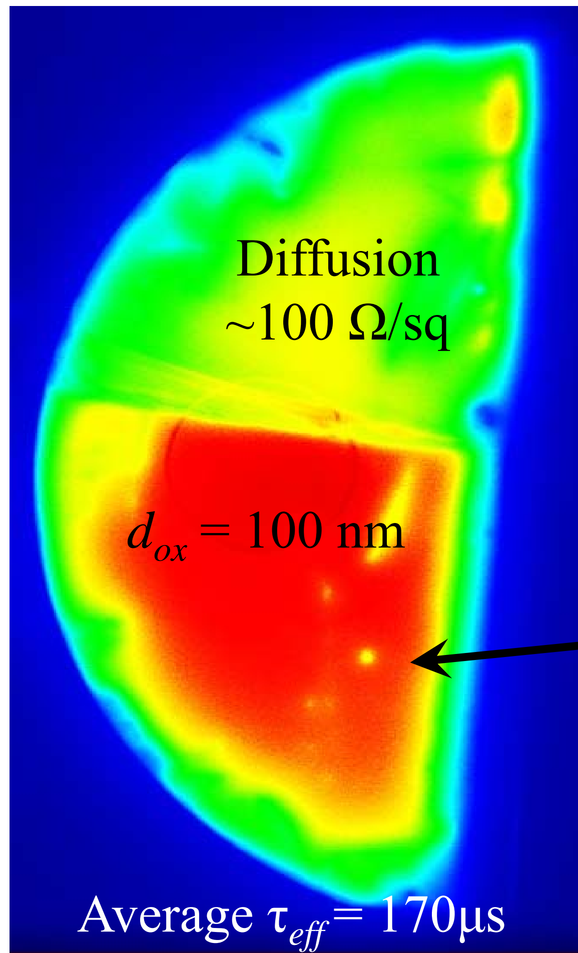
10

100

Oxidation time (mins)

Masking Boron diffusion during TMAH etching

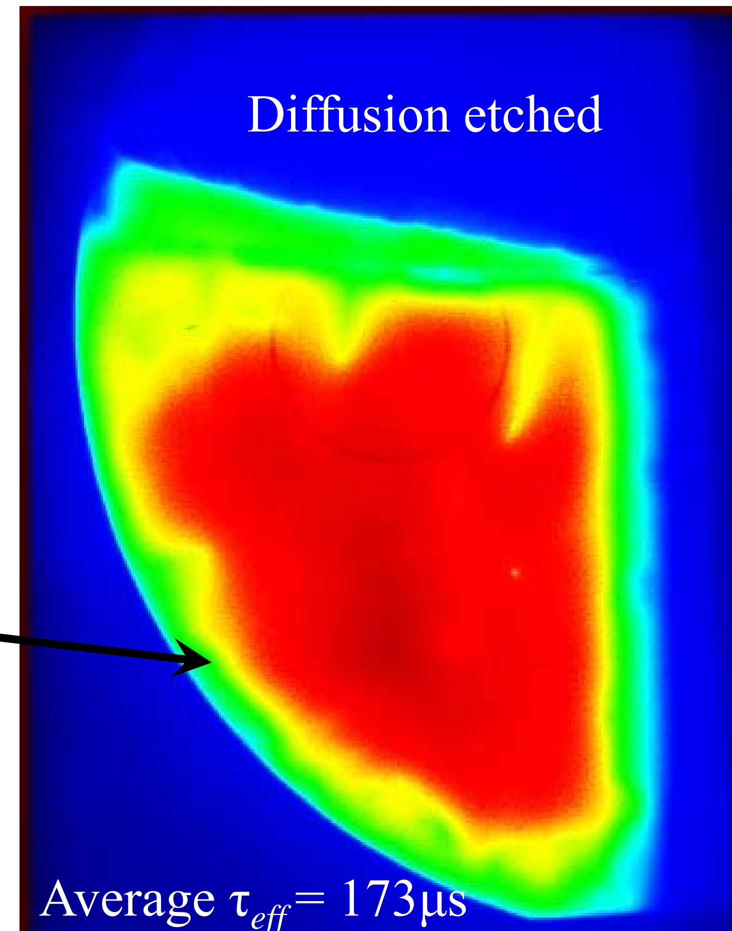
Before TMAH etching



Etching was performed in 25% TMAH at 80–90 °C for ~ 1 hour

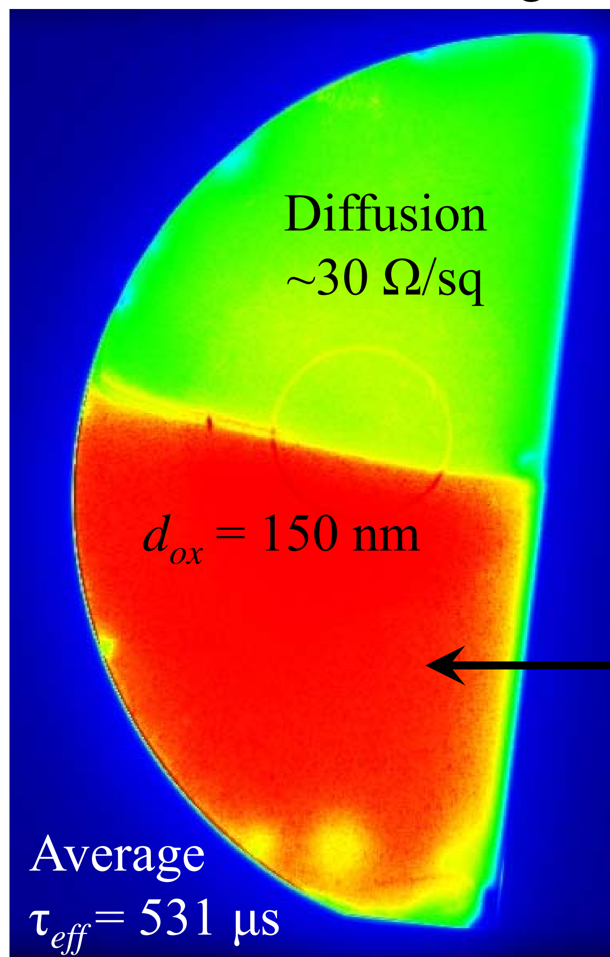
Anodic SiO_2 protecting the diffusion

After TMAH etching



Masking phosphorus diffusion during TMAH etching

Before TMAH etching

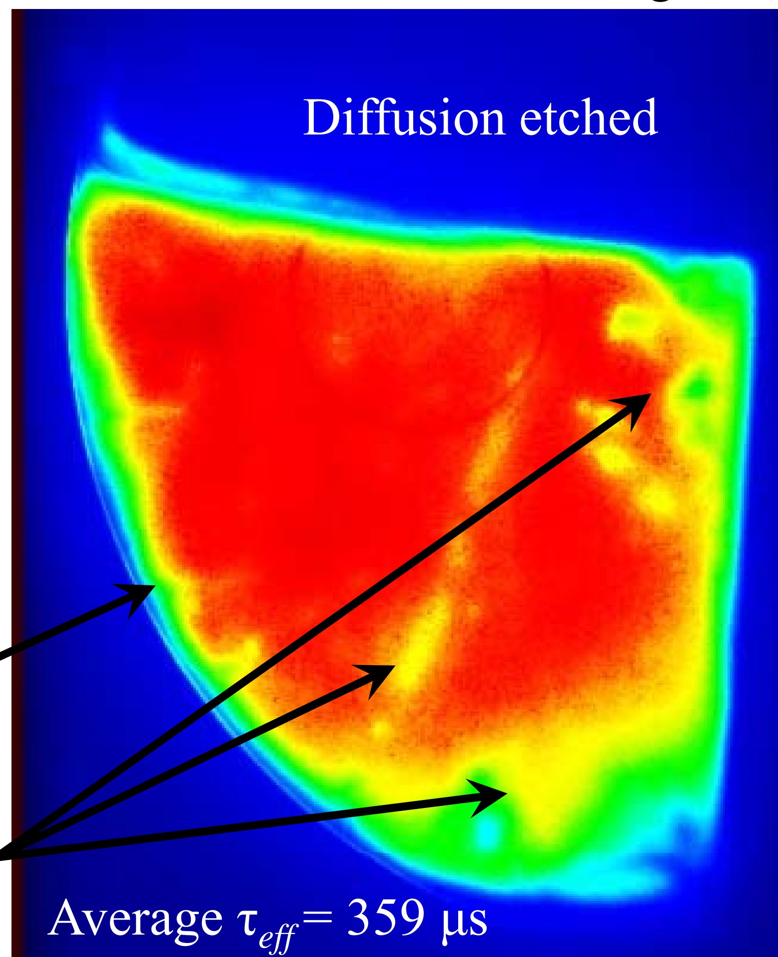


Etching was performed in 25% TMAH at 80–90 °C for ~ 1 hour

Anodic SiO_2 film

Some etching has occurred.

After TMAH etching



Masking phosphorus diffusion during TMAH etching

τ_{eff} = 511 µs

Before etching

τ_{eff} = 499 µs

Etched for 12 minutes.

τ_{eff} = 474 µs

Etched for 24 minutes.

τ_{eff} = 433 µs

Etched for 36 minutes.

τ_{eff} = 267 µs

Etched for 36 minutes.

oxide was not removed directly after etching

TMAH remains in the SiO_2 film after etching and therefore the oxide must be removed directly after TMAH etching/texturing.

Summary

1. When a boron or phosphorus diffusion is present, the measured currents are much higher and the resulting SiO_2 is much thicker.
2. Thick SiO_2 films can be formed quickly (< 30 mins)….well for anodic and thermal oxidation standards.
3. P/B diffusions can be protecting by anodic oxide films against chemical etching for long periods of time. **NOT HF**
4. The boron diffused sample was not etched at all, however the phosphorus diffused sample was slightly etched.
5. After TMAH etching, the oxide must be removed otherwise TMAH in the SiO_2 will proceed to the interface and continue to etch the diffusion.

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Collective summary

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Collective summary

1. In this work, we elected to use an immersion cell design as it is simple and easy to alter. We chose to use a constant potential because it too is simple and avoids reaching excessive voltages.
2. Nitric acid was chosen as the electrolyte because it is a common chemical, which is also conductive.
3. It was found that the anodic SiO_2 thickness decreases with increasing HNO_3 concentration.
4. It was shown that water is a primary source for the anodic oxidation process.
5. Annealing the anodic oxide films in O_2 followed by FG at 400 °C provides the best surface passivation, $S < 30$ cm/s.

Collective summary

6. Lower *S* are achieved when anodic oxidations are carried out in 70 wt% HNO_3. This is primarily due to a higher positive charge in these films when compared to oxidations carried out in 20 wt% HNO_3.
7. AC anodic oxidations were investigated and it was found that no improvement in *S* was achieved when compared to DC anodic oxidations.
8. It was shown that the HNO_3 purity has a substantial impact on the repeatability of *S*. The best *S* achieved was ~20 cm/s using pure HNO_3 and ~30 cm/s using non-pure HNO_3.
9. Although the anodic SiO_2 films provide good passivation they do degrade. The primary source of degradation was found to be due to water vapour.

Collective summary

10. When a boron or phosphorus diffusion is present, the measured currents are much higher and the resulting SiO_2 is much thicker.
11. P/B diffusions can be protecting by anodic oxide films against chemical etching for long periods of time. **NOT HF**
12. Some etching of the phosphorus diffused sample did occur. More work is required to stop this from occurring.
13. The oxide must be removed after TMAH etching to prevent any further etching of the diffusion.

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Thank you