Electron Transport across Bioelectronic Junctions: is it all about the INTERFACES ?

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Different Si wafer batches with nominally the same specifications respond differently to the same chemical surface treatments to regrow Si oxide on them. The resulting oxides differ electrically, *thereby affecting solid-state electron transport (ETp) via protein films, assembled on them.*

We studied this phenomenon using two different chemical methods to regrow oxides on the same batch of Si wafers.

We examined ETp via ultra-thin layers of the protein bacteriorhodopsin, assembled on them. **Our results point to the crucial role of (near) surface charges on/in the substrate in defining the electronic transport across proteins** as expressed strikingly in the current's temperature dependences.

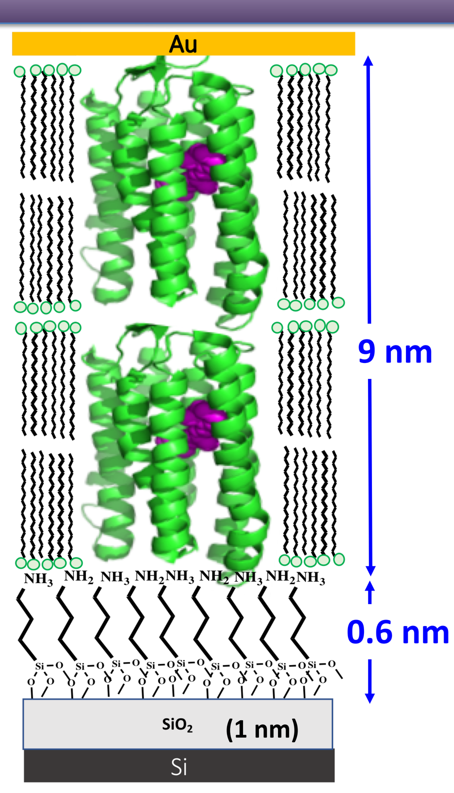
We propose that these are governed by the electric landscape at the electrode-protein interface rather than by intrinsic protein properties.

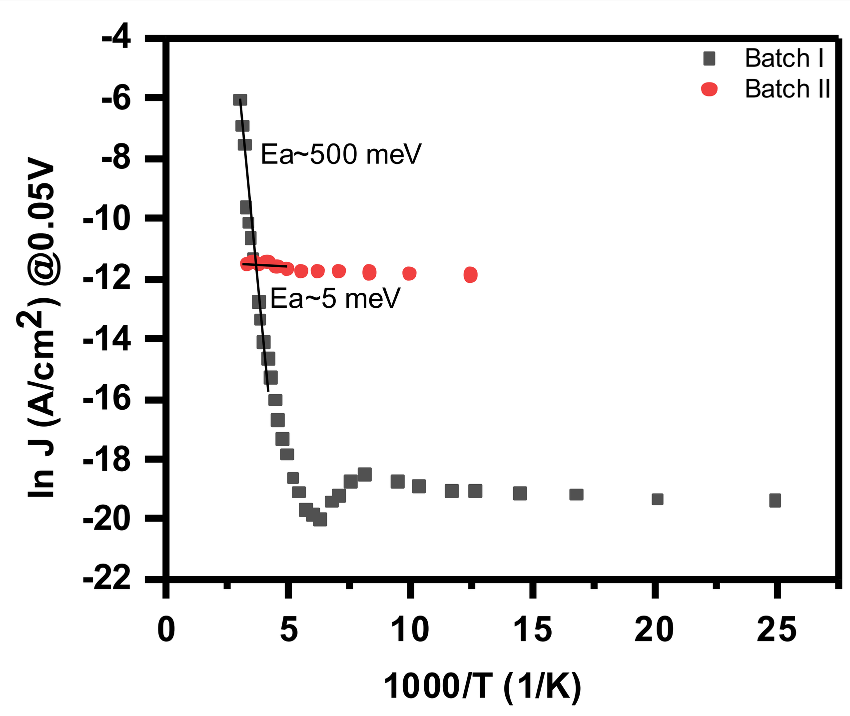
Thus, **protein-electrode coupling in junctions is a decisive factor in transport across junctions** and for interpreting the current-voltage characteristics, because this coupling can create a barrier that will dominate charge transport and control the transport mode across the junction.

Our findings' wider importance lies in their relevance to hybrid biomolecule-Si junctions, a likely direction for future bioelectronics.

The results also imply that once an electron is injected into the protein, there is no measurable barrier for transport across the protein.

Different batches of Si behave diferently





Differences in properties of Batch (I) and Batch (II) wafers

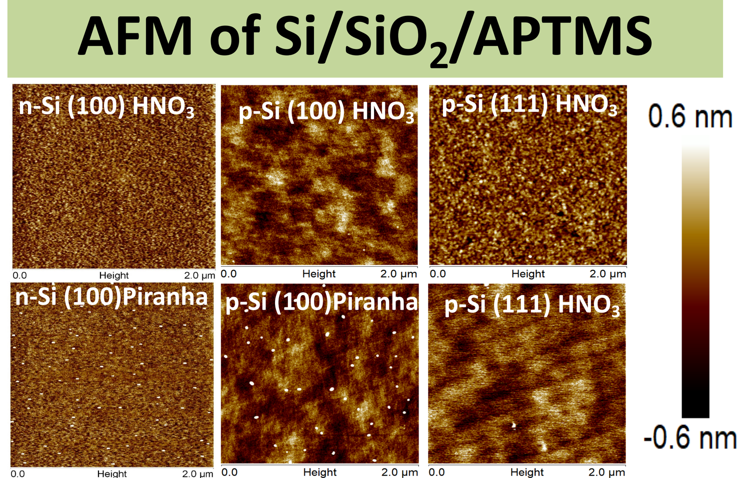
Properties	Batch (I)	Batch (II)
Time to grow oxide in Piranha	30 s	180 s
Specific resistivity (mΩ*cm)	1.1-1.5	0.7-0.9
Work function (UPS) (eV)	4.47	4.33
Current density for $Si/SiO_2/Au$ Junction @ 100mV (A/cm^2)	0.6	0.03
I-V shape ($Si/SiO_2/Au$) (-0.5V to +0.5V)	Non-linear	Linear
Si/SiO_2/APTMS/OTG-bR /Au: Ea (meV) from current T-dependence	500	20

Created differences in Si/SiO_2 using **chemical** treatments

SiO_2 formation

1. **61% HNO_3 ---10min**
2. **(2:1) H_2SO_4:H_2O_2---3min**

AFM of Si/SiO_2/APTMS



Roughness (nm)	Si(100)		Si(111)	
	p	n	n	p
HNO_3	0.23	0.37	0.26	0.3
Piranha	0.48	0.42	-	-

Work-function of Si/SiO_2/APTMS

Work function		Si(100) p	Si(100) n	Si(111) p	Si(111) n
CDP (eV)	HNO_3	4.14	3.97	4.14	4.10
	Piranha	4.08	3.85	-	-
UPS (eV)	HNO_3	3.63	3.63	3.84	3.79
	Piranha	3.57	3.55	-	-

Si(111) forms irreproducible, rough oxides with piranha

Rough oxides > 0.3 nm showed lower WF ~4.0

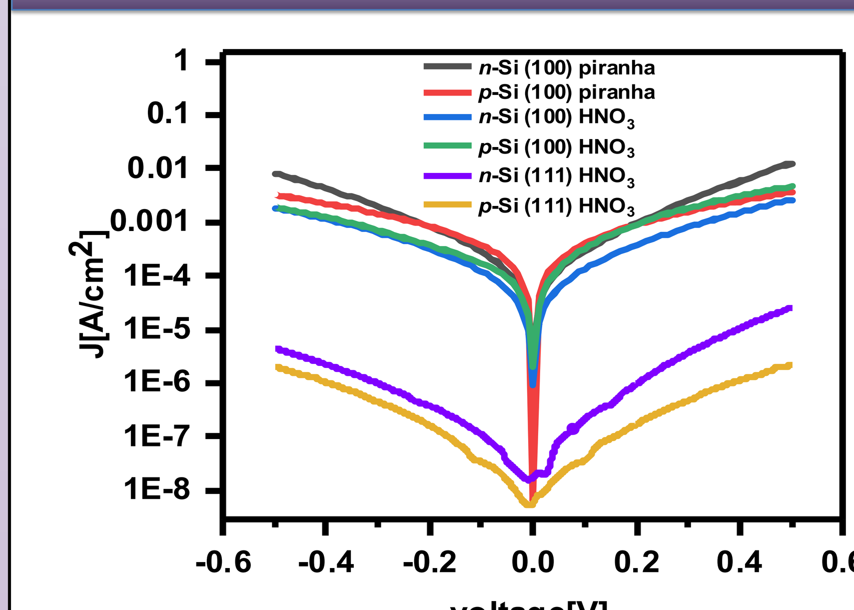
XPS analysis

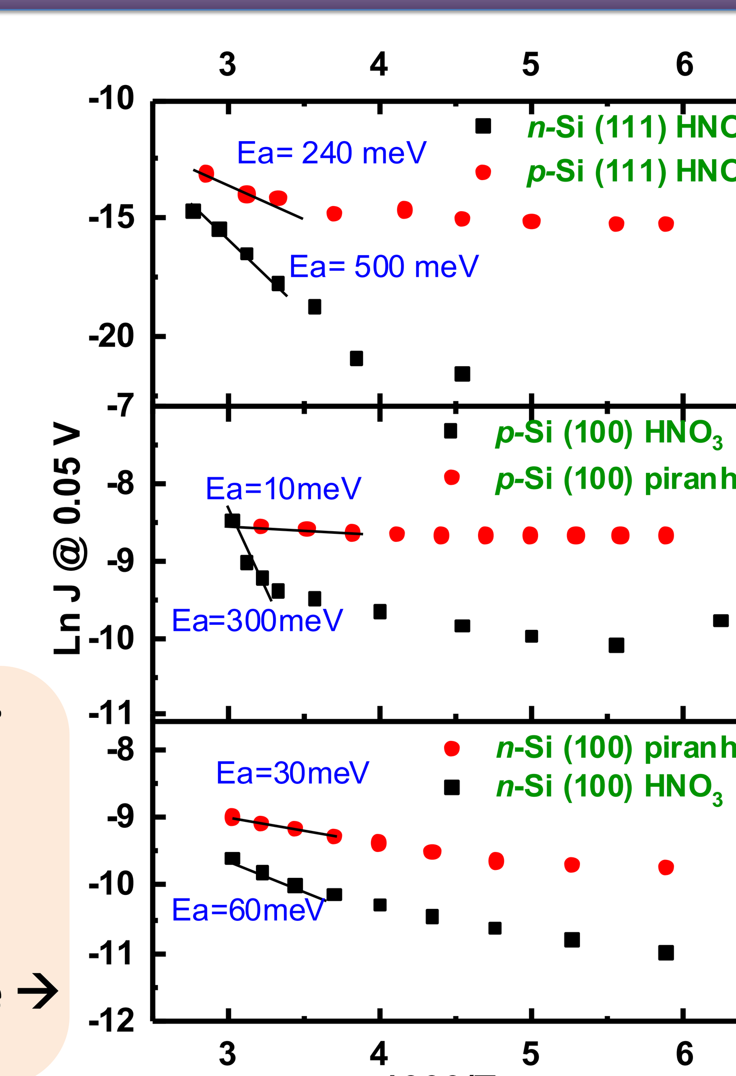
Si oxidized Species (%)	Si(100)-n type		Si(100)-p type		Si(111)	
					HNO_3	
	HNO_3	Piranha	HNO_3	Piranha	n-type	p-type
Si+	4.5	4.5	12.2	13.5	5.5	7.5
Si2+	0.5	0.7	1.6	2.0	3.0	2.0
Si3+	2.2	1.5	0.7	1.0	0.5	0.5
Si4+	22.0	16.0	21.0	20.0	23.0	23.0
NH_3^+/NH_2	1.72	2.2	0.6	1.0	0.8	0.8

HNO_3 treated samples are less positively charged

→ Less charged

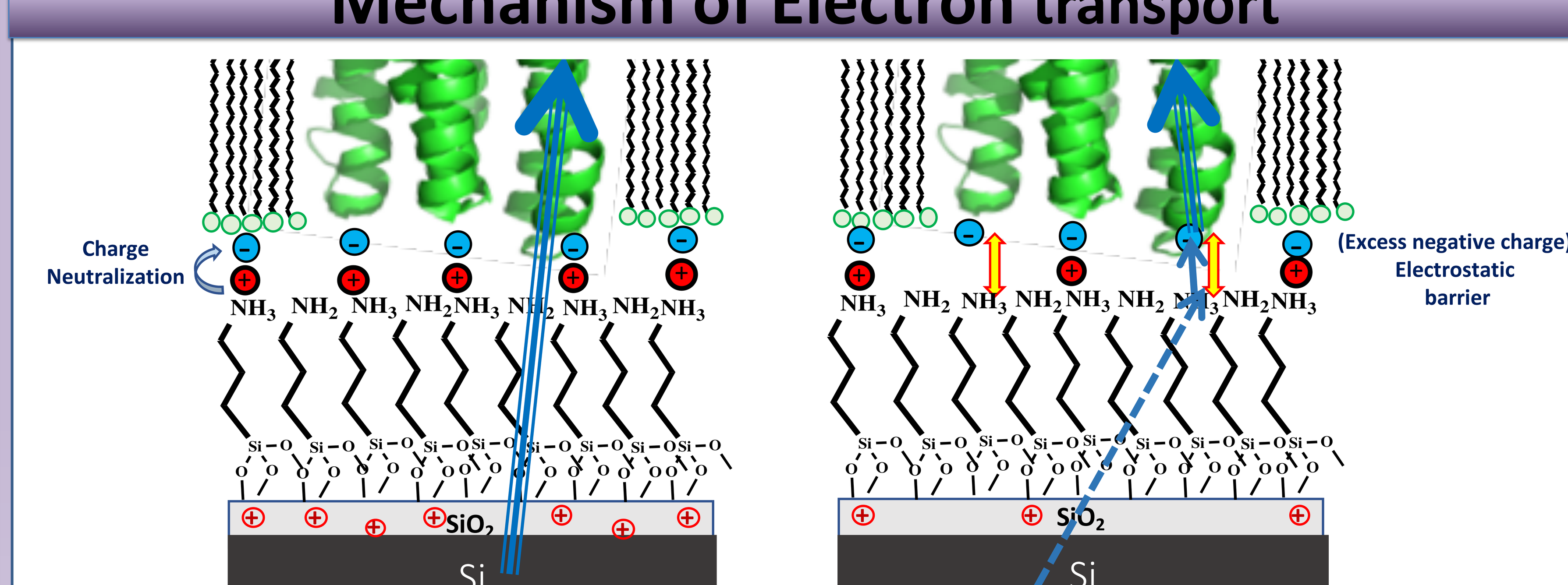
J-V characteristics





1. Si(100) samples more conducting than Si(111).
2. Si(111) with HNO_3 treatment → temperature dependence.
3. For P-Si(100) HNO_3 treated samples → temperature dependence
4. Rough oxides with low WF and low +ve charge → temperature dependent

Mechanism of Electron transport



Temperature Independent — Temperature dependent

Conclusion

1. Batches of Si with same specifications behaves differently to chemical treatments for oxide growth.
2. Homogeneity of SiO_2 surface decides the Work Function and, in turn, electron transport (ETp)
3. More positive charge →better neutralization of protein surface charge → no barrier → temperature-independent ETp
4. Less positive charge → electrostatic barrier → temperature-dependent ETp

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