Leakage Mechanisms

- Thin films, fully depleted
  - Leakage controlled by combined thermionic / field emission across the Schottky barrier at the film-electrode interfaces. Film quality effects barrier height, and mobilities of carriers.
- Thicker films of interest for higher voltage applications
  - Poorly understood

NC State

Much effort has gone into studying the **leakage** of perovskite-type titanate thin films, including $SrTiO_3$, $(Ba,Sr)TiO_3$, and $Pb(Zr,Ti)O_3$:

- J.F. Scott, et al., Proc. of the 1992 IEEE Int. Symp. Appl. Ferro., 356 (1992).
- T. Makita, et al., Mat. Res. Soc. Symp. Proc. **284**, 529 (1993).
- T. Kuroiwa, et al., Ceramic Transactions **43**, 219 (1994).
- C.S. Hwang, et al., Jpn. J. Appl. Phys. **34**, 5178 (1995).
- M. Kiyotoshi and K. Eguchi, Appl. Phys. Lett. **67**, 2468 (1995).
- R. Waser, in Science and Technology of Electroceramic Thin Films: NATO ASI Series Vol. 284, ed. O. Auciello and R. Waser (London: Kluwer Academic Publishers, 1995) pp. 223-248.
- G. Dietz, et al., J. Appl. Phys. **78**, 1 (1995).
- S. Dey, et al., Jpn. J. Appl. Phys. **34**, 3142 (1995).
- G. Dietz, et al., J. Appl. Phys. **82**, 2359 (1997).
- G. Dietz and R. Waser, Thin Solid Films **299**, 53 (1997)
- S. Zafar, et al., Appl. Phys. Lett. **73**, 3533 (1998)

- Proposed conduction mechanisms for BST thin films:
  - Fowler-Nordheim tunneling (interface, bulk)
  - Poole-Frenkel effect (bulk)
  - Thermionic emission across Schottky barriers (interface)
  - The **most favored** mechanism:
    Schottky-barrier limited current flow

NC State

“ELECTRICAL C ONDUCTION MECHANISMS IN SOLIDS”

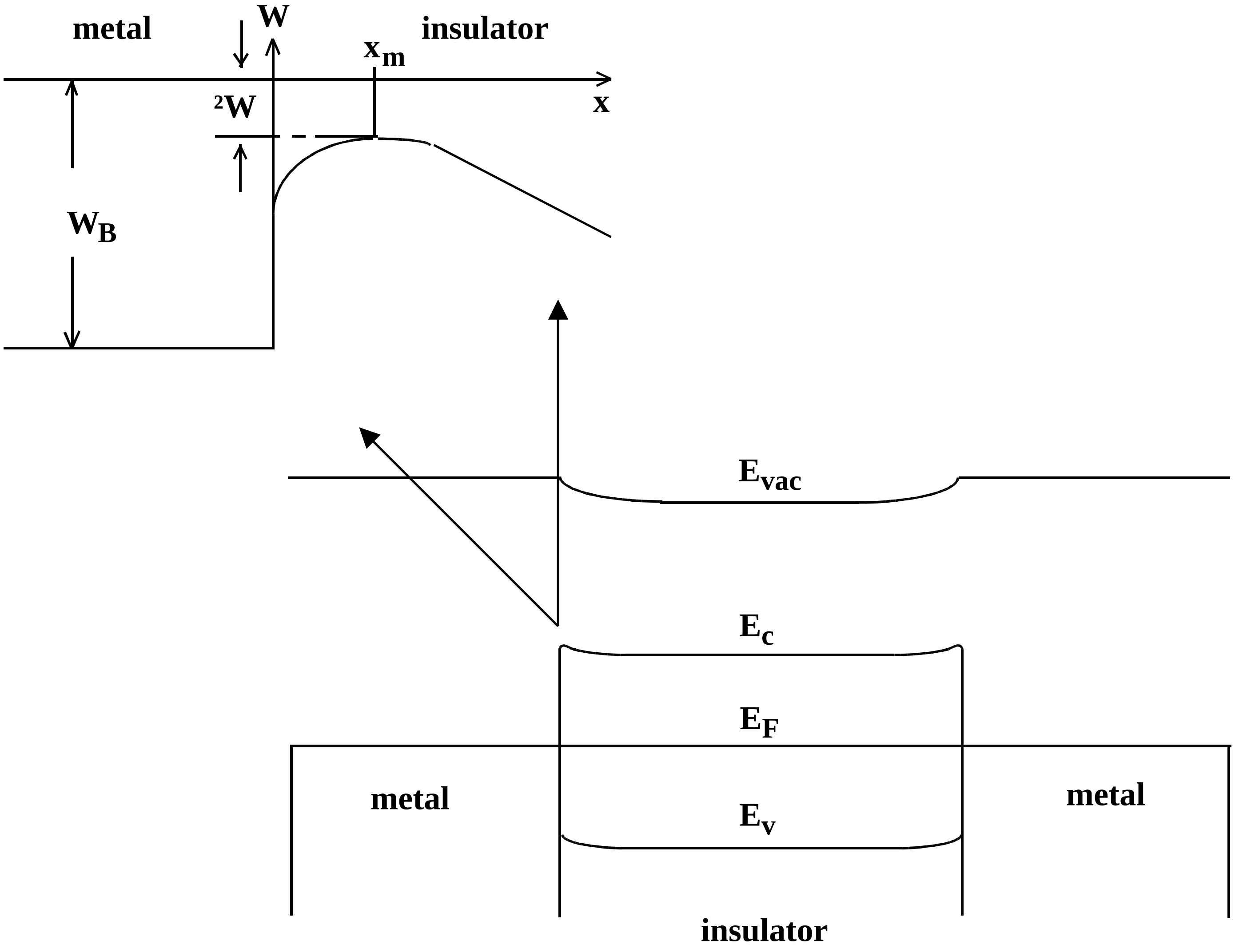
Hamann, Burghardt, and Frauenheim

“Bulk” -Controlled	**vs.**	**“Interface” -Controlled** ***(Injection-Limited)***
Ionic (high T, long time)		***Schottky Emission***
Tunneling (through film) (High E)		***Field Emission***
Bulk Doping (acceptors, donors, etc.)		*Contact Photoexcitation*
Photoexcitation (light effect)		*Fowler-Nordheim Tunneling* *(can be bulk as well)*
Trapping/Detrapping (Poole Frenkel)		*Space-Charge-Limited* *(can be bulk as well)*
Hopping Conduction (Localization)		

Thin Films **Thick(er) Films** **Failure Mode**

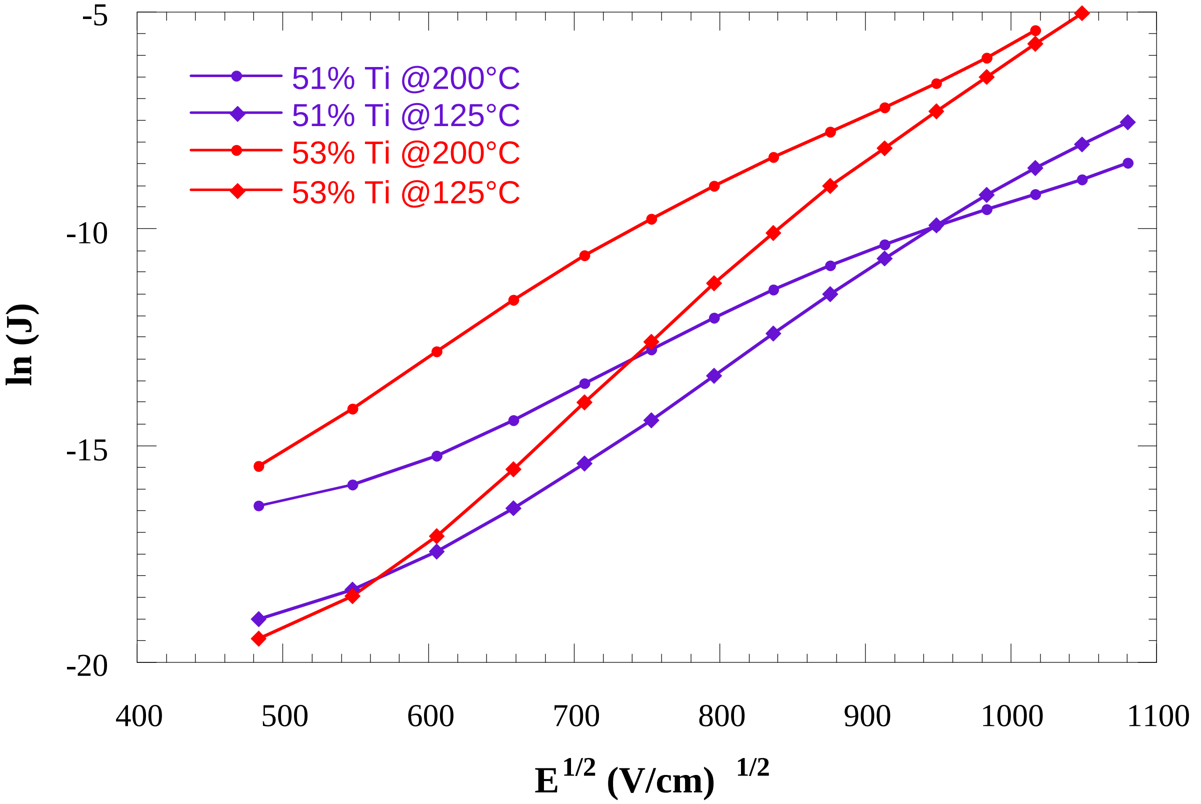
NC State

- **Lack of complete and careful analyses of leakage in BST thin films**
  - Experimental: Using a ramp or voltage step technique.
    - danger of relaxation currents contribution in the analyses
  - Field and temperature dependencies:
    - Only field- or temperature-dependent data not sufficient for understanding the mechanism !
  - Assumed values for the parameters in the model such as Richardson constant.
  - Inhomogeneity of Schottky barrier, interfacial roughness, etc.


metal
W
insulator
x_m
x
^2W
W_B
E_{vac}
E_c
E_F
metal
metal
E_v
insulator

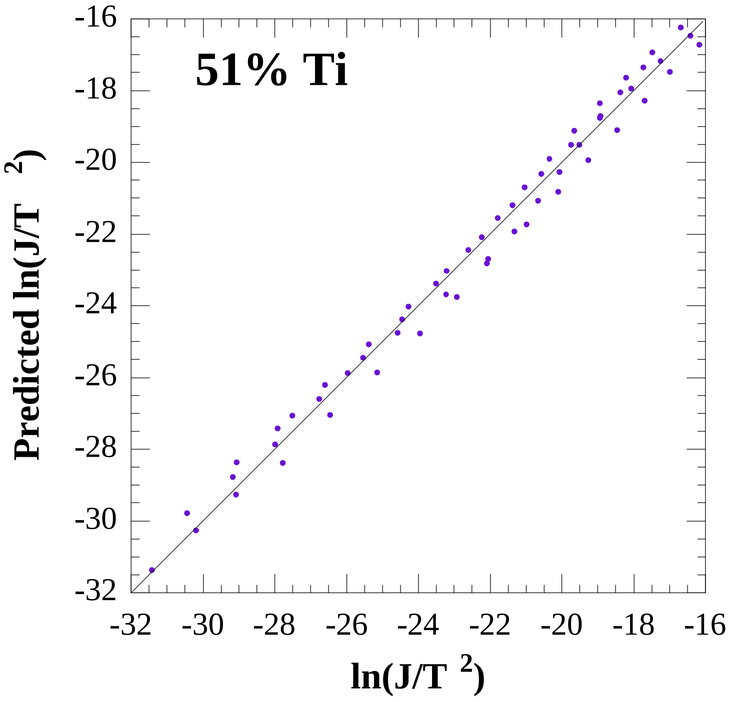
Leakage vs. A:B Site Ratio

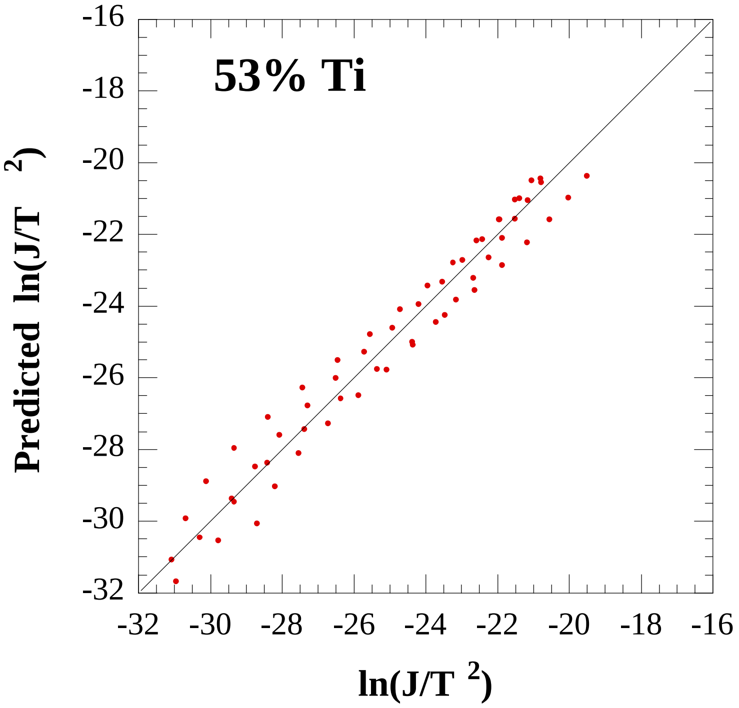
t = 30 nm; T = 125, 150, 175, & 200°C, 0 < V < 3.5V



NC State

Leakage vs. A:B Site Ratio





$$\ln\left(\frac{J}{T^2}\right) = \ln A^{**} + \frac{\alpha E^{1/2} - W_b}{k_B T}$$

NC State

Leakage vs. A:B Site Ratio

$$J = A^{**}T^2 \exp\left(\frac{\alpha E^{1/2} - W_b}{k_B T}\right)$$

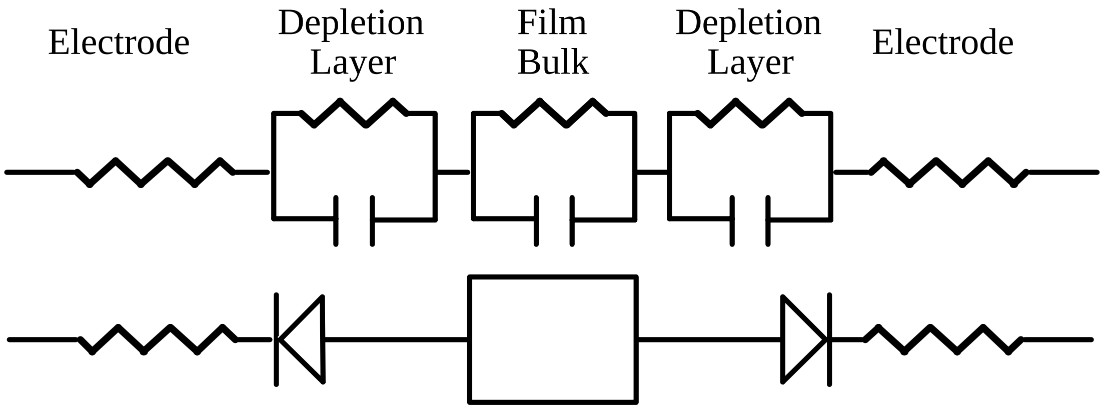
Ti Content	W_b (eV)	α	A (A/cm^2K^2)
51%	1.05	0.00085	4.0e-6
51.5	1.28	0.00066	4.2e-3
52	1.44	0.00080	1.2e-2
53	1.17	0.00069	9.1e-5
53.5	0.92	0.00084	3.3e-9

Depletion Widths

- **Issue: What are the depletion lengths?**
  - 5 – 10 nm
  - > film thickness (i.e. > 100 nm)
- **Why is this an issue?**
  - Explanation of C-V behavior
  - Affects development directions and ultimate performance predictions
- **Case for fully depleted film**
  - Field dependence in a thickness series:

    J(E,T) is almost independent of thickness ➔Field dropping across entire film thickness
  - Frequency dependence of permittivity
    - Depletion layer ➔ step frequency dependence

NC State



- **Consider 2 cases for a 200 nm film**

$$d_i = 10 \text{ nm}$$
$$\tau = C_i \times R$$

- Case 1:

$$\tau < 10^{-4} \text{ Hz}$$
$$\Rightarrow R_b \sim 10^{11}\ \Omega$$
$$\Rightarrow n \sim 10^{11} \text{ m}^{-3}$$

  - Not high enough carrier density to cause band bending

- Case 2:

$$\tau > 10^{9} \text{ Hz}$$
$$\sigma_b = \frac{d - 2d_i}{AR_b} \sim 30\ (\Omega\text{m})^{-1}$$

  - This is strongly semiconducting.

NC State

BST Depletion Widths

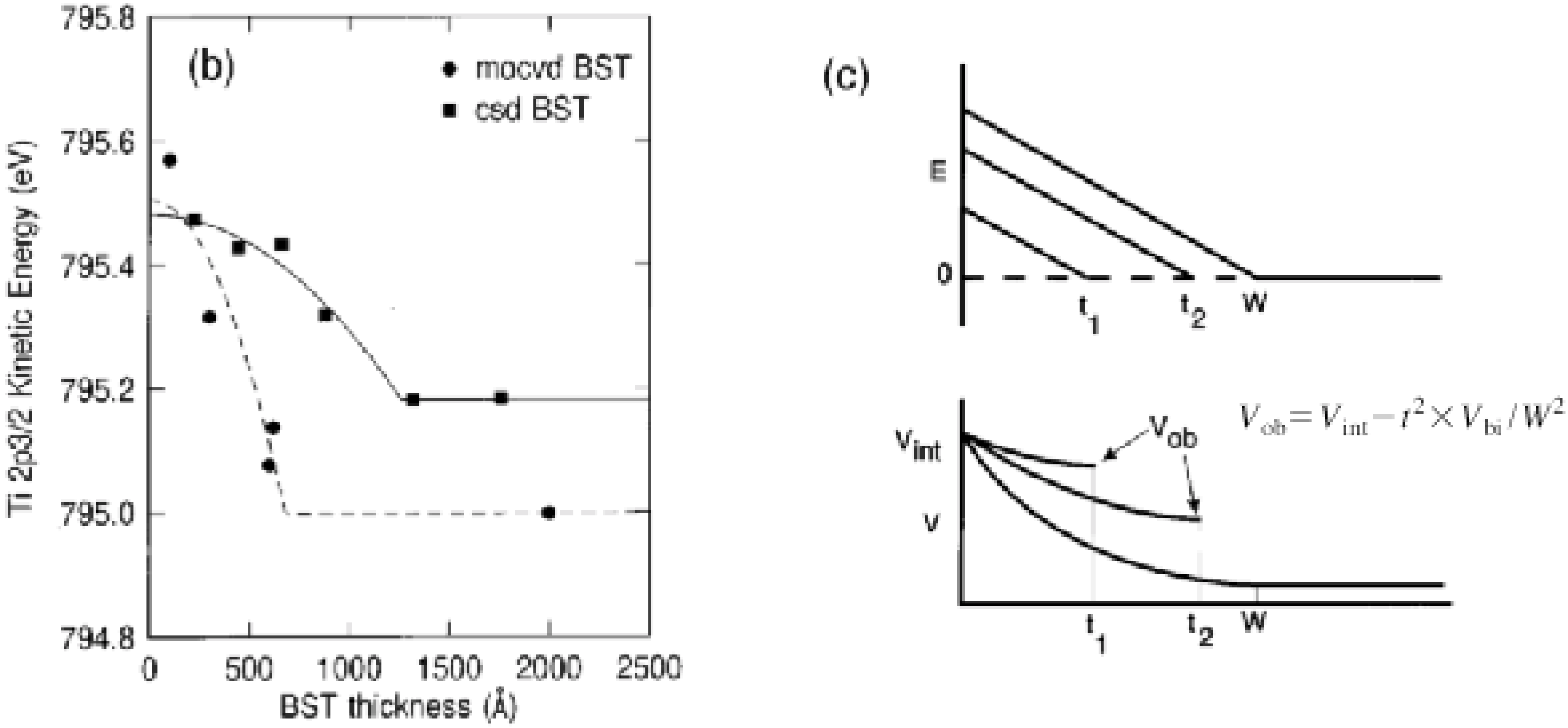


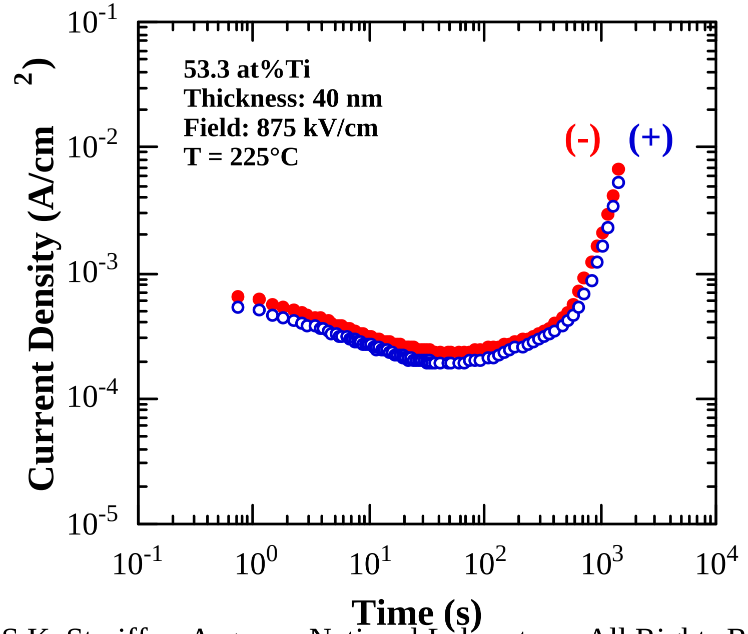
FIG. 3. (a) Ti $2p3/2$ core-level kinetic energy for nominally undoped BST thin films as a function of Pt coverage. The films are supported by a Pt coated substrate. (b) Ti $2p3/2$ initial position as a function of film thickness. Since the Pt substrate forms a back contact, the plot reveals a depth profile of the band bending. (c) Model of the film thickness dependence of the electric field and band offset.

M. Copel et al., Appl. Phys. Lett. **70**, 3227 (1997):
W = 70nm for CVD films

NC State

Failure Modes: Resistance Degradation

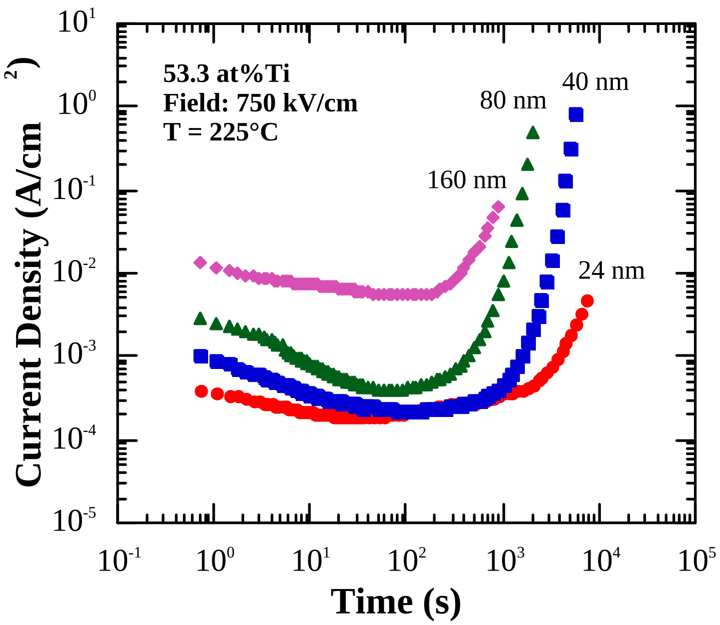
- Change in resistivity of a sample caused by migration of charged point defects, leading to increased leakage and eventually breakdown
- Bulk and single crystals: R. Waser, T. Baiatu, and K.-H. Härdtl, J. Am. Cer. Soc. **73**, 1645 (1990); **73**, 1654 (1990); J. Am. Cer. Soc. **73**, 1663 (1990).

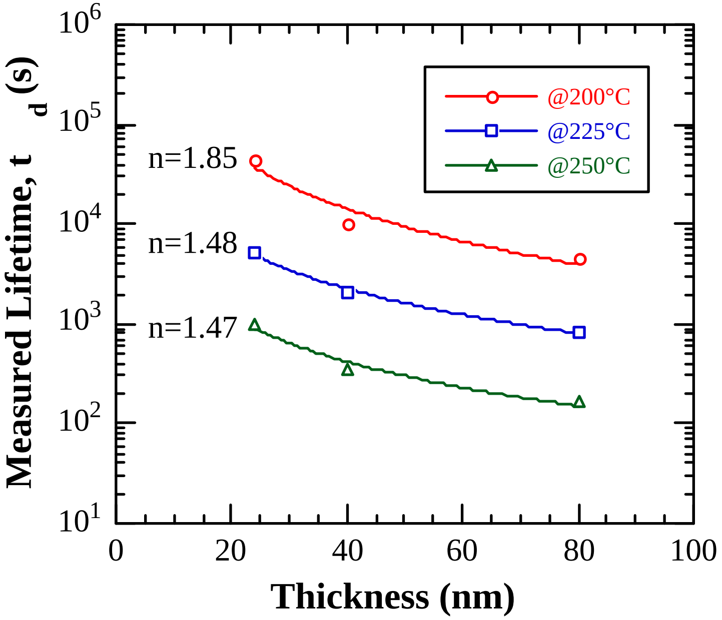


Resistance degradation in a polycrystalline (Ba,Sr)TiO_3 film, after C. Basceri et al., Ferroelectric Thin Films VI, MRS Symp.Proc. 493 (1998)

Resistance Degradation and Lifetime: Thickness Dependence

Observed thickness dependence manifests itself as a decrease in the activation energy with respect to temperature.



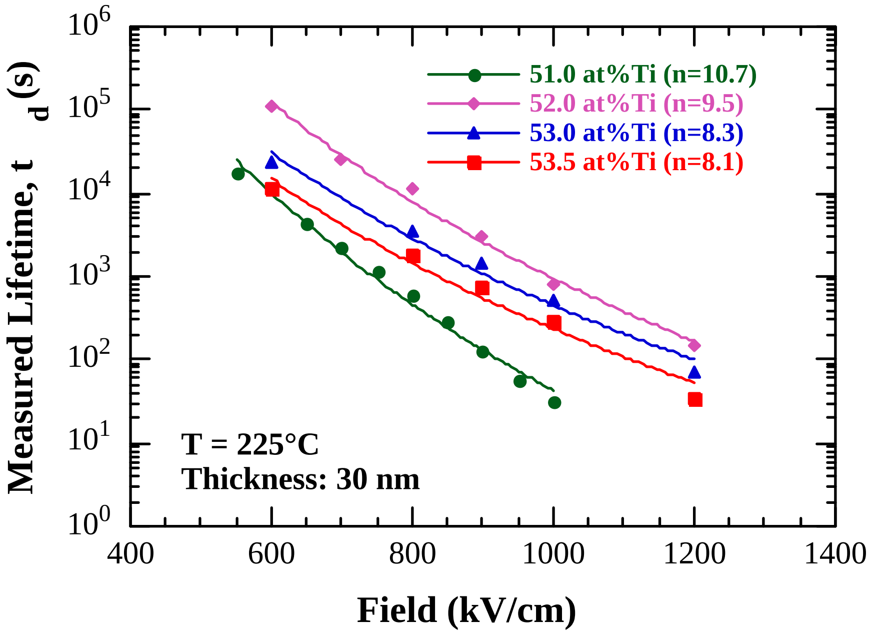


Waser: bulk $SrTiO_3$, n ~ 2.5 @ 2 kV / cm, 270°C

J. Am. Ceram. Soc. 73, 1645-1663 (1990).

NC State

Resistance Degradation and Lifetime: Composition Effect



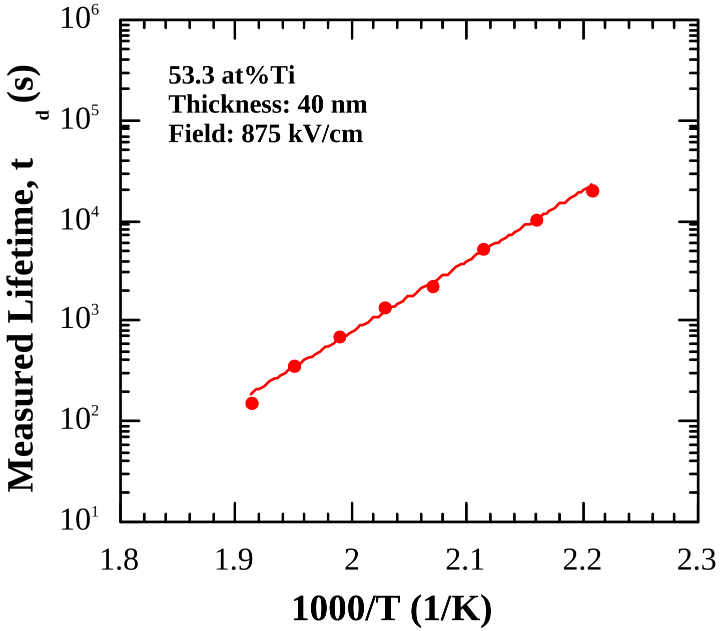
The measured resistance degradation lifetime at this temperature and in this field increases as the Ti content is increased to 52.0 at%Ti, and then decreases with higher at%Ti.

NC State

Resistance Degradation and Lifetime: Temperature Dependence

Temperature dependence clearly follows an Arrhenius-type behavior:

$$t_d = t_0 \exp\left(\frac{Q_T(V)}{kT}\right)$$



Resistance Degradation and Lifetime: Voltage/Field Dependence

It is difficult to distinguish the different functional forms of voltage/field dependence, given the electric field range investigated:

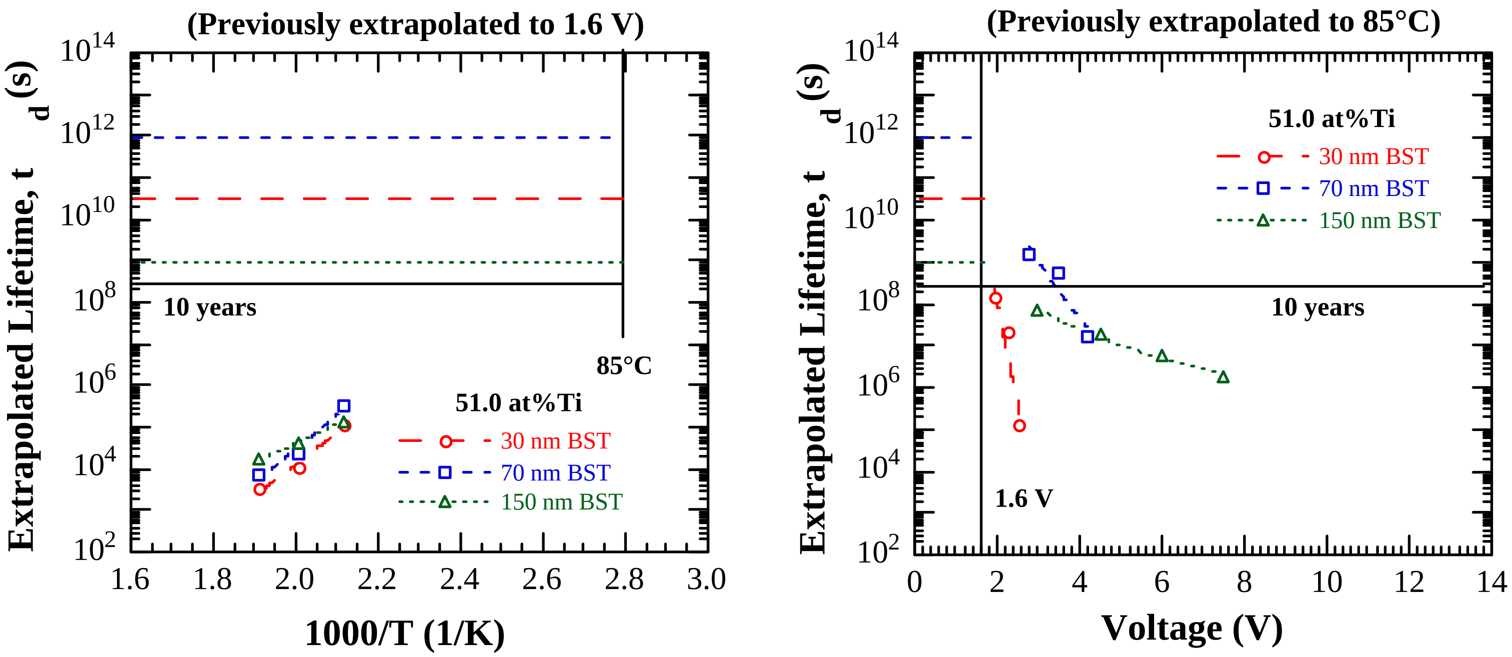
$$t_d = t_0 \exp\left(-\frac{qV}{Q_v(T)}\right)$$ most conservative

$$t_d = t_0 V^{-n}$$

$$t_d = t_0 \exp\left(\frac{Q_v(T)}{qV}\right)$$ least conservative

Resistance Degradation and Lifetime: Estimation of Lifetimes

51.0 at%Ti BST Films



NC State

Resistance Degradation and Lifetime: Modification Of Leakage Behavior

Oxygen vacancies are mobile defects under the given experimental conditions: electromigration toward cathode.

“Modification of Schotky barrier heights/band structure”

(different than bulk resistance degradation mechanism)

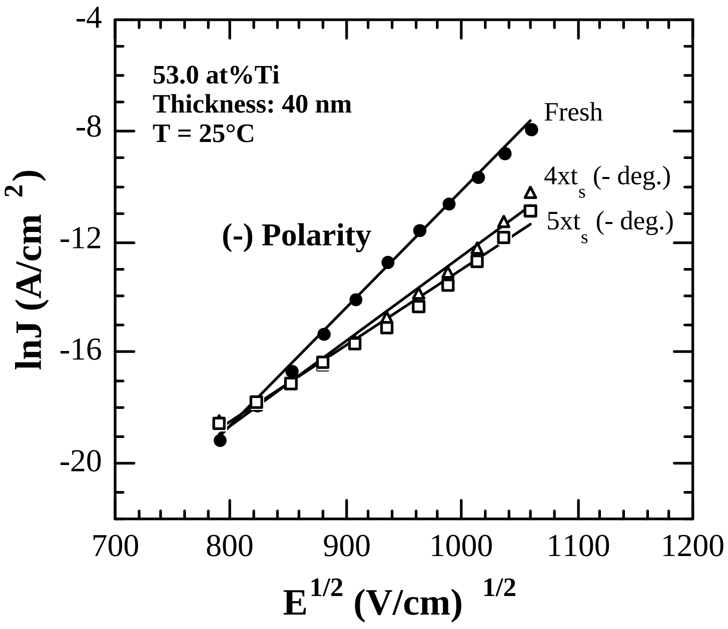
Also: Spatial modification of carrier concentrations due to the spatial variation in the oxygen vacancy concentration between the two electrode: change in conductivity of the bulk film.

The accumulation of oxygen vacancies in front of the cathode creates an internal built-in potential at the interface. This space charge modifies the band structure and thus interfacial energy barriers: The **difference in barrier heights** then appears as an **internal bias** in the film.

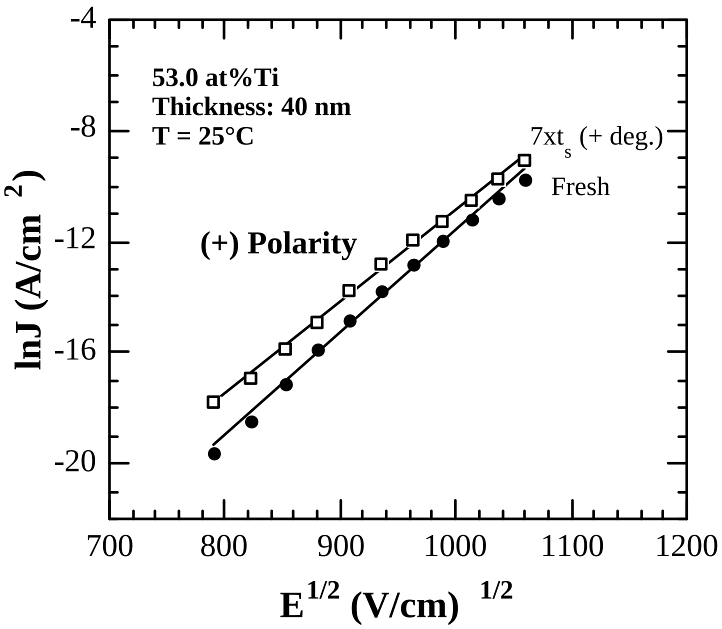
Resistance Degradation and Lifetime: Modification Of Leakage Behavior

The differences in barrier heights:

$4xt_s$: 0.13 eV
$5xt_s$: 0.21 eV



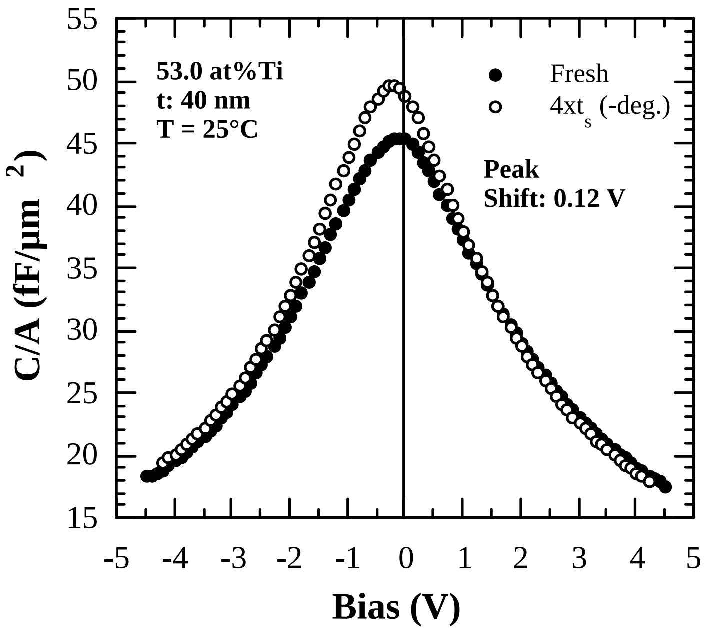
$7xt_s$: 0.22 eV

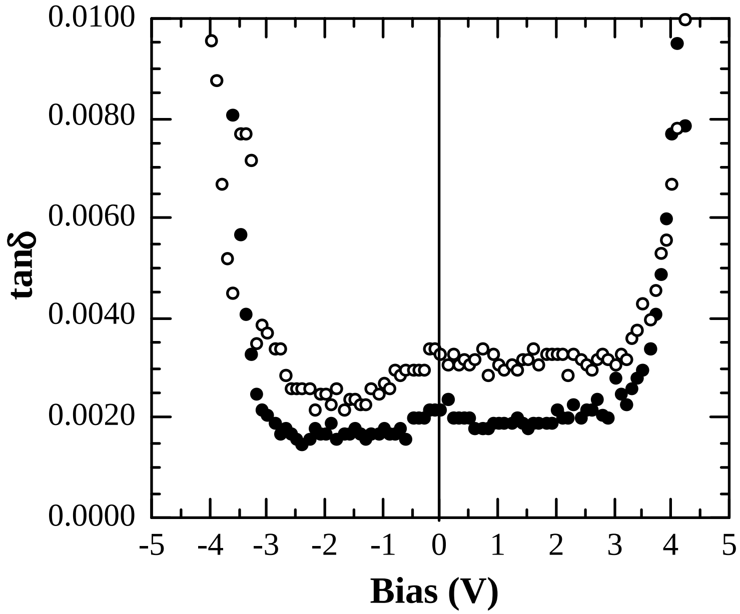


NC State

Resistance Degradation and Lifetime: Modification Of Leakage Behavior

The peak shift in C-V: 0.12 V

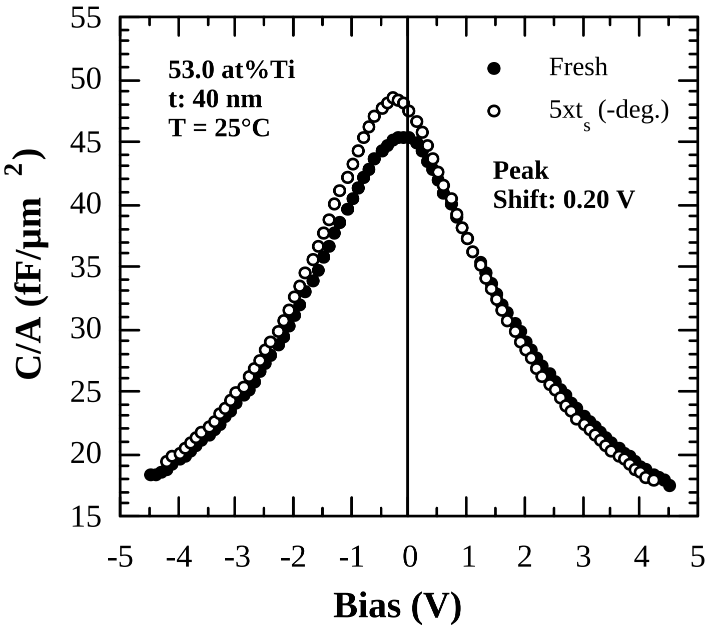


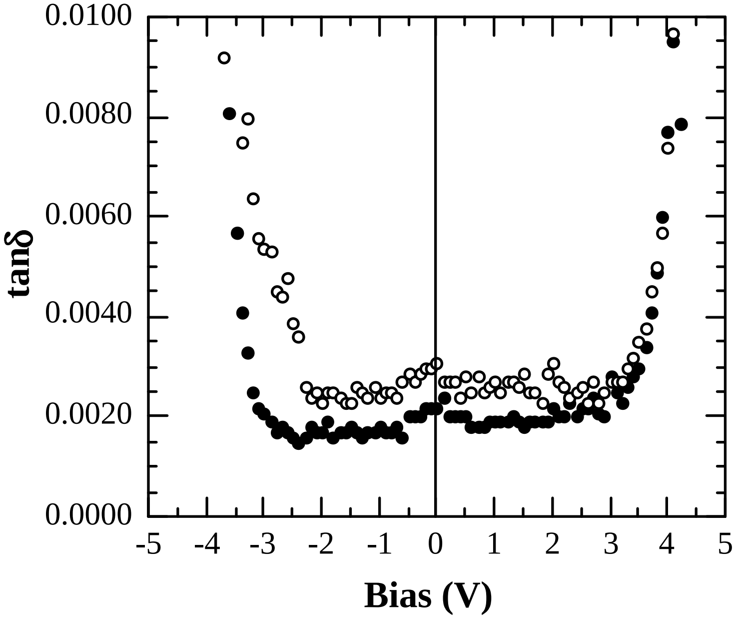


NC State

Resistance Degradation and Lifetime: Modification Of Leakage Behavior

The peak shift in C-V: 0.20 V

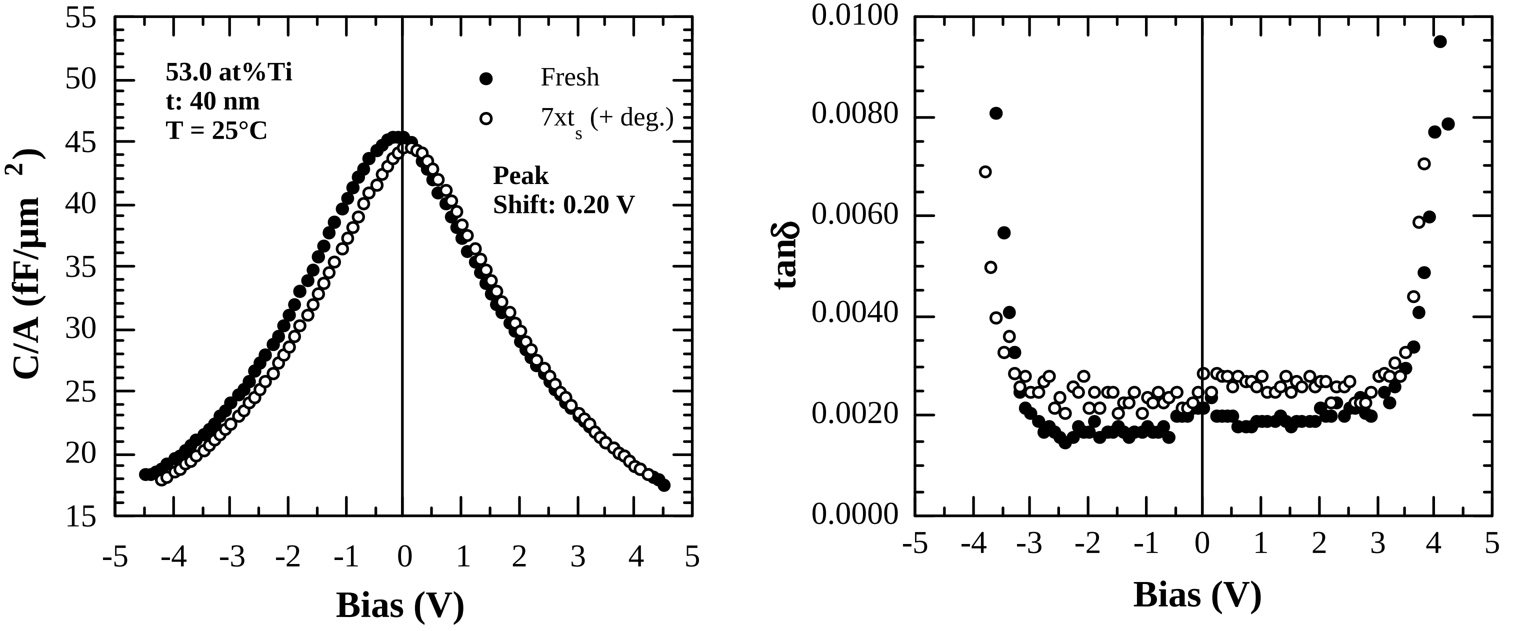




NC State

Resistance Degradation and Lifetime: Modification Of Leakage Behavior

The peak shift in C-V: 0.20 V



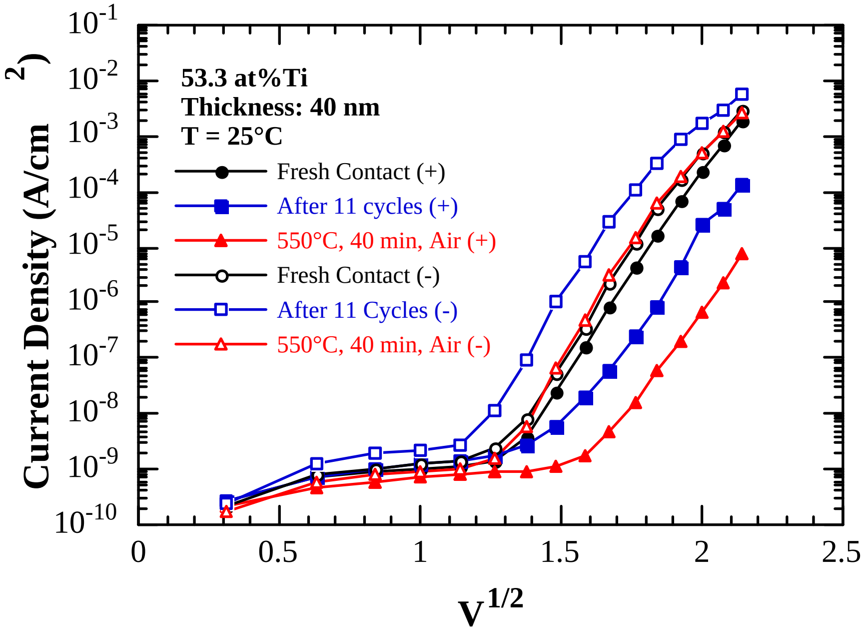
NC State

Resistance Degradation and Lifetime: Modification Of Leakage Behavior

Recovery anneal studies:

Negative polarity currents were completely recovered.

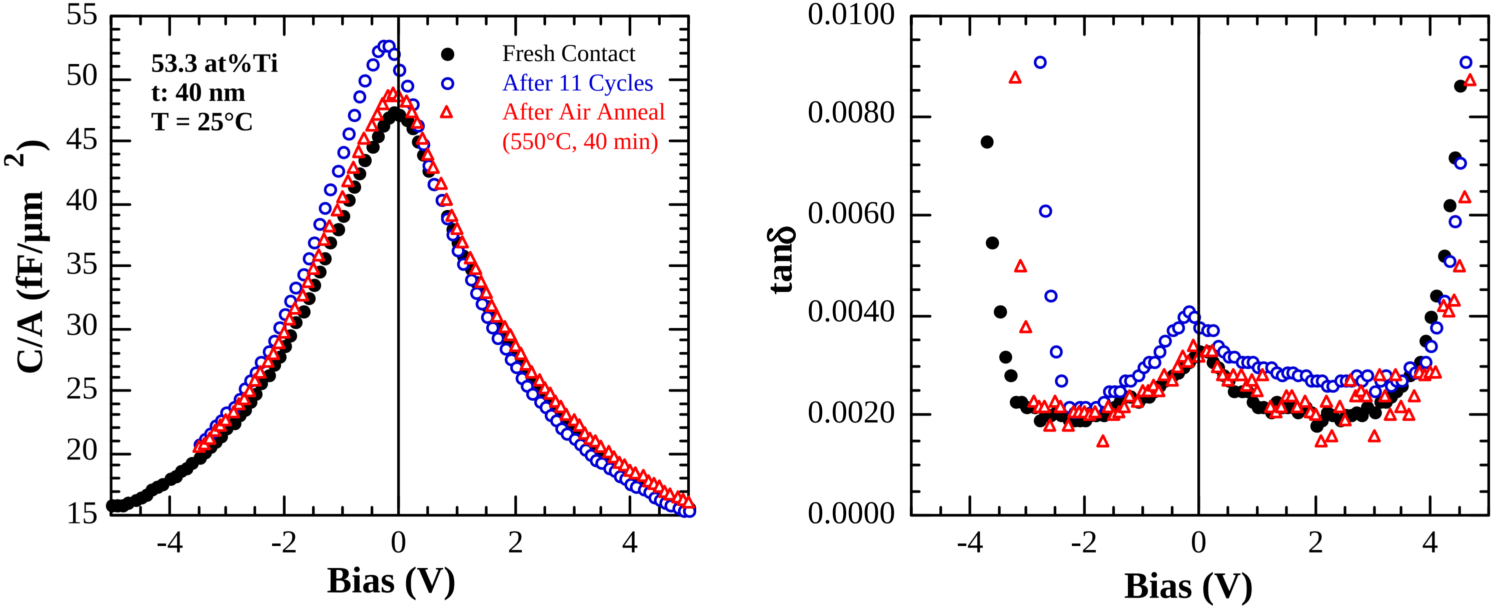
Positive polarity currents decreased further ?



NC State

Resistance Degradation and Lifetime: Modification Of Leakage Behavior

C-V behavior indicates that resistance degradation is **recoverable**.



NC State