ELECTRIC FIELD AND TEMPERATURE EFFECTS ON COPPER TRANSPORT IN MOS CAPACITOR WITH COPPER AS THE GATE METAL

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Waseda University
Surface resistance measurement

![Graph showing R/Ro vs Oxidation time for different samples.]

- CoMoP/Cu/CoMoP on Co sead
- CoWP/Cu/CoWP on Co sead
- CoWP/Cu/CoWP on Cu sead
- CoMoP/Cu on Cu sead
Co$_{0.9}$W$_{0.02}$P$_{0.08}$

In-situ resistivity as a function of temperature

Tracking structural changes

Heating rate ~ 2.8°C/min; Vacuum ~ 5 x 10$^{-6}$ Torr

Resistivity ($\mu\Omega \cdot \text{cm}$) vs. Temperature (°C)

After anneal:

Significant temperature independent contribution to electron scattering (imperfections including impurities)
**Crystallization and Co$_2$P phase formation processes**

**Kissinger analysis:**

\[
\ln \left( \frac{dT}{dt} \right) = -\frac{E_a}{kT_c} + \text{Constant}
\]

\( E_a \) – apparent activation energy
\( \frac{dT}{dt} \) – heating rate
\( T_c \equiv \frac{d\rho}{dT} \) is minimal
\( \text{(maximum rate of crystallization)} \)

**Resistivity (µΩ cm)**

- (a) 1.4 °C/min
- (b) 2.8 °C/min
- (c) 5.6 °C/min
- (d) 11.2 °C/min
- (e) 16.8 °C/min

**Temperature (°C)**

\(\ln\left(\frac{dT}{dt}/T_c\right)\) (-)

**Ea = 1.6 ± 0.1 eV**

**Co$_2$P**

\( E_a = 4.7 ± 0.1 \text{ eV} \)

**Schematic Diagrams**

- hcp Co + amorphous Co(W,P) → hcp Co
- hcp Co → hcp Co + orthorhombic Co$_2$P
J-M-A analysis:

Fraction crystallized as a function of time at a constant temperature:

\[ \frac{1}{\rho} = \frac{f(t)}{\rho(t \to \infty)} + \frac{1 - f(t)}{\rho(t = 0)} \]

\( f(t) \) – fraction crystallized

\[ f(t) = 1 - \exp \left[ -k(T) \cdot (t - t_0)^n \right] \]

\( k(T) \) – apparent rate coefficient
\( t_0 \) – incubation time
\( n \) – J-M-A index

\[ n = a + b \cdot c \]

\( a = 1 \); Constant nucleation rate (\( N \sim t \))
\( b = 3 \); 3D growth
\( c = 0.5 \); Diffusion controlled growth
As-deposited structure?

Cross sectional phase contrast TEM image – as deposited film
I. Electroless $\text{Co}_{0.9}\text{W}_{0.02}\text{P}_{0.08}$
II. Sputtered Co (2 nm thick)
III. $\text{SiO}_2$

Powder XRD, Bragg-Brentano geometry
Why does \( \text{Co}_2\text{P} \) nucleate at \( \sim 420°C \)?

Enrichment of P at the grain boundaries

Estimation of grain boundary coverage by P assuming 1 ML of P enveloping hcp Co grains with a side length or diameter, \( l \)

\[
\alpha = \frac{1}{1 - (1 - \frac{1}{C_{p}}) \cdot \left( \frac{r_{\text{Co}}}{r_{p}} \right)^2} + \frac{4l}{V_{\text{hcp}} \left( \frac{1}{r_{\text{Co}}^2} + (1 - \frac{1}{C_{p}}) \cdot \frac{1}{r_{p}^2} \right)}
\]

\( \alpha \) - Fraction coverage of the grain boundary
\( r_{\text{Co}} \) – Atomic radius of Co
\( r_{p} \) – Covalent radius of P
\( C_{p} \) – Atomic concentration of P in the film
\( V_{\text{hcp}} \) – Volume of hcp unit cell

Why does \( \text{Co}_2\text{P} \) nucleate at \( \sim 420°C \)?
Introduction

- Replacing Al with Cu
- Cu integration with ILD aroused some problems:
  - Adhesion
  - Corrosion
  - Cu ions transport

The solution:
- Depositing CoWP as a thin diffusion barrier layer

How to evaluate the quality of the diffusion barrier?
- Electrical monitoring of MOS capacitors
- BTS followed by electrical characterization
Ideal MOS Capacitor

- Uniform doping
- No Currents through the oxide
- $\Phi_{ms} = 0$
- There are no oxide charges or interface ones
- Ohmic contact between the semiconductor and the back contact
Ideal MOS Capacitor Under Voltage (p-Type)

- **Accumulation** \((V<0)\)
  \[ Q_{SC} = Q_S \]

- **Depletion** \((V>0)\)
  \[ Q_{SC} = -qN_A W \]

- **Inversion** \((V>>0)\)
  \[ Q_{SC} = -Q_N - qN_A W_{\text{max}} \]

---

Fig. 3: energy diagram and the charge distribution of MOS Capacitor under \(v\).
C-V Configuration of an Ideal MOS Capacitor (p-Type)

\[ C = \frac{1}{\frac{1}{C_0} + \frac{1}{C_N + C_B}} \]

\[ V_G = V_{OX} + \phi_s \]
C-V Configuration of an Ideal MOS Capacitor (p-Type)

\[ C = \frac{1}{\frac{1}{C_0} + \frac{1}{C_N + C_B}} \]

\[ V_G = V_{OX} + \phi_s \]

Fig. 4: The Equivalent Electrical Circuit of MOS Capacitor

Fig. 5: HF C-V of MOS Capacitor
\[ C = \frac{dQ}{dV} \]
Real MOS Capacitor

\[ V_G = V_{OX} + \phi_s + V_{FB} \]

\[ V_{FB} = \phi_{ms} - \frac{Q_f}{C_{OX}} - \frac{\gamma Q_m}{C_{OX}} - \frac{\gamma Q_{Ot}}{C_{OX}} - \frac{Q_{it}(\psi_s)}{C_{OX}} \]

\[
\begin{align*}
\gamma(x=0) &= 0 \\
\gamma(x=t_{ox}) &= 1
\end{align*}
\]

Fig. 7: Charges and their location for thermally oxidized Si.

Fig. 8: The influence of oxide charges and the \( \phi_{ms} \) on the C-V curve.
Real MOS Capacitor (p-type)

\[ V_G = V_{OX} + \phi_s + V_{FB} \]

\[ V_{FB} = \phi_{ms} - \frac{Q_f}{C_{OX}} - \frac{\gamma Q_m}{C_{OX}} - \frac{\gamma Q_{Ot}}{C_{OX}} - \frac{Q_{it}(\psi_s)}{C_{OX}} \]

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\gamma(x=0) &= 0 \\
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\end{align*} \]

Fig. 8: The influence of oxide charges and the \( \phi_{ms} \) on the C-V curve.
C-t Measurement & Zerbst technique

$$t_g = \frac{t_F}{(N_D / n_i) \cdot (C_O / C_F)}$$

Fig. 9: Deep depletion MOS-C characteristics: (a) the C-V curve. (b) the C-t transient.

Fig. 10: Space-charge region (SCR) and quasinutral region generation components of a depletion MOS-C.

$$-\frac{d}{dt} \left( \frac{C_O X}{C} \right)^2 = \frac{2n_i}{t_g N_A} \frac{C_O X}{C_F} \left( \frac{C_F}{C} - 1 \right) + \frac{2n_i C_O X S'}{K_S \varepsilon_0 N_A}$$

Fig. 11: Zerbst plot of the C-t transient
Fig. 9: Deep depletion MOS-C characteristics: (a) the C-V curve. (b) the C-t transient.

\[ \tau_g' \approx \frac{t_F}{(N_D/n_i) \cdot (C_O/C_F)} \]
Zerbst technique

\[
\frac{dQ_N}{dt} = -\frac{q_n}{\tau_g} \left( W - W_F \right) - q_n s'
\]

\[
- \frac{d}{dt} \left( \frac{C_{OX}}{C} \right)^2 = \frac{2n_i C_{OX}}{\tau_g N_A} \left( \frac{C_F}{C} - 1 \right) + \frac{2n_i C_{OX} S'}{K_S e_0 N_A}
\]

Fig. 11: Zerbst plot of the C-t transient
Barrier integrity

Questions:

1. How to evaluate the quality of a diffusion barrier?

2. What is the barrier integrity of electroless deposited Co alloy films?
How to evaluate the quality of a diffusion barrier?

Evaluation of barrier integrity depends on the sensitivity of the characterization method

Most sensitive methods:

Metal – Oxide – Semiconductor (MOS) capacitors and Metal – Semiconductor diodes

MOS is also a functional approach
**Evaluation of D.B. quality using MOS capacitors:**

**Capacitance-Voltage**

- **Quasi – static C-V measurements (1 MHz)**

![Graph showing capacitance-voltage measurements with different temperatures and durations.](image)

- **ΔV_{fb}**
  - Cu\(^+\) ions in the oxide – requires electric field in order to enhance drift of Cu\(^+\) ions
  
  \[ \Delta V_{fb} < 0 \]

- **C_{INV}**
  - Decreased minority lifetime as a result of Cu generated deep levels
  
  \[ \Delta C_{INV} \text{ increases for a fixed a.c. frequency} \]
Evaluation of D.B. quality using MOS capacitors: Capacitance-transient

Capacitance time measurements (1 MHz)

- Inversion
- Deep depletion

Cu/Co$_{0.9}$P$_{0.1}$
- 300°C / 30 min
- 450°C / 4 hrs
- 450°C / 12 hrs

Zerbst plot of a C-t measurement

- $\tau' = 630 \pm 50$ $\mu$sec
- $s' = 0.08 \pm 0.01$ cm/sec

Effective generation lifetime: om the slope: 
$$\tau'_{g} = \frac{2n_{i}C_{0}}{N_{B}C_{F} \cdot \text{slope}}$$

Effective generation velocity: om the intercept: 
$$s' = \frac{K_{S} \varepsilon_{0}N_{B} \cdot \text{intercept}}{2n_{i}C_{0}}$$
### Evaluation of diffusion barrier quality

Results

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Thermal Stress(^1)</th>
<th>Bias and Thermal Stress(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 MV/cm at 300°C / 30 min</td>
</tr>
<tr>
<td>Co(<em>{0.96}W</em>{0.04})</td>
<td>Fails after 450°C / 1 hr</td>
<td>Fails</td>
</tr>
<tr>
<td>Co(<em>{0.9}P</em>{0.1})</td>
<td>Fails after 450°C / 10 hr</td>
<td>Stable</td>
</tr>
<tr>
<td>Co(<em>{0.9}W</em>{0.02}P_{0.08})</td>
<td>400°C/30 min: Stable</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>500°C/30 min: Fails</td>
<td></td>
</tr>
</tbody>
</table>

1 – Evaluated by C-t

2 – Evaluated by C-V

A. Kohn, M. Eizenberg, Y. Shacham-Diamand

B. Israel, and Y. Sverdlov

*Microelectronic Eng. 55, 297 (2001)*

Electroless Co\(_{0.9}\)P\(_{0.1}\), 30 nm thick, are stable barriers at 450°C during approximately 10 hours

Current allowed total thermal budget:
Thermal cycles equivalent to 400°C, 10 – 60 minutes
Investigation of the structure of electroless Co alloys and its evolution as a result of heat treatments

Questions:
1. What is the as-deposited structure?
2. How does the structure change with thermal anneal?
3. What is the structure during failure of the diffusion barrier?

Case study: $\text{Co}_{0.9}\text{W}_{0.02}\text{P}_{0.08}$

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
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<tbody>
<tr>
<td>Electroless $\text{Co}<em>{0.9}\text{W}</em>{0.02}\text{P}_{0.08}$</td>
<td>10 – 100 nm</td>
</tr>
<tr>
<td>Sputtered Co or Cu</td>
<td>2 – 20 nm</td>
</tr>
<tr>
<td>(Sputtered Ti)</td>
<td>(5 nm)</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>100 nm</td>
</tr>
<tr>
<td>Si wafer</td>
<td></td>
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</tbody>
</table>
How to evaluate the quality of a diffusion barrier?

Evaluation of barrier integrity depends on the sensitivity of the characterization method

Most sensitive method:
Metal Oxide Semiconductor (MOS) and Metal Semiconductor diodes
MOS is also a functional approach
**Evaluation of D.B. quality using MOS diodes: Capacitance-Voltage**

- **$\Delta V_{FB}$** provides a measure of $Cu^+$ ions in the oxide:
  \[ V_{FB} = \phi_ms - \frac{Q_f + Q_m + Q_{ot}}{C_o} \]
  \[ \rightarrow \Delta V_{FB} < 0 \]

- **$C_{inversion}$** decreases minority lifetime as a result of $Cu$ generated deep levels:
  \[ \rightarrow \text{increases for a fixed a.c. frequency} \]

- Requires electric field to enhance drift of $Cu^+$ ions:
  \[ \text{In order to enhance drift of } Cu^+ \text{ ions} \]
Applying bias – enhanced drift of Cu$^+$, and degradation of the dielectric

Reference: Al / SiO$_2$ / n-Si

**Cu / SiO$_2$ / n-Si**
Evaluation of D.B. quality using MOS diodes: Transient Capacitance

Evaluation of D.B. quality using MOS diodes: Transient Capacitance

$V_G$

+ 0 0 t

Accumulation

Strong inversion

Deep depletion
Deep depletion MOS-capacitor

- Using the expression for capacitance as a function of gate voltage and inversion capacitance:

\[
\frac{dQ_N}{dt} = -(qK_s\varepsilon_0 C_o N_B/C^3) \frac{dC}{dt}
\]

(d\(Q_N/dt \sim -d(C_o/C)^2/dt\)

Thermal generation of electron-hole pairs:

\[
\frac{dQ_N}{dt}(\text{bulk scr}) = -q \int_{W_F}^{W} G_{\text{scr}} \, dx = -q \int_{W_F}^{W} \left( n_i/\tau_g \right) \, dx = -qn_i(W - W_F)/\tau_g
\]

\[C\ - \text{capacitance (F/cm}^2)\]
\[C_0\ - \text{oxide capacitance (F/cm}^2)\]
\[\varepsilon_0\ - \text{permittivity of free space (F/cm)}\]
\[N_B\ - \text{net doping concentration (cm}^{-3})\]
\[n_i\ - \text{intrinsic carrier concentration (cm}^{-3})\]
\[K_s\ - \text{s.c. dielectric constant (Si:11.8) (-)}\]
\[Q_N\ - \text{electron surface charge density (Cb/cm}^2)\]
\[G_{\text{SCR}}\ - \text{steady-state scr generation rate (cm}^{-3}s^{-1})\]
\[W\ - \text{scr width (cm)}\]
\[W_F\ - \text{final scr width for MOS capacitor in heavy inversion (cm)}\]
\[\tau_g\ - \text{generation lifetime (sec)}\]
Zerbst plot of the C-t transient

Example: Cu/Co\textsubscript{0.9}P\textsubscript{0.1} after 300°C/30min

$$\frac{-d(C_0/C)^2}{dt} = \left(\frac{2n_iC_0}{N_BC_F\tau'_g}\right) \cdot \left(\frac{C_F}{C} - 1\right) + \frac{2n_iC_0s'}{K_S\varepsilon_0N_B}$$

From the slope:
$$\tau'_g = \frac{2n_iC_0}{N_BC_F \cdot \text{slope}}$$

From the intercept:
$$s' = \frac{K_S\varepsilon_0N_B \cdot \text{intercept}}{2n_iC_0}$$
MOS Samples

Thermal Stress, 300° - 600°C vacuum anneal (≤10⁻⁶ Torr)
Bias Thermal Stress 1 MV/cm 300 °C , N₂ ambient
Evaluation of diffusion barrier quality – 450°C

Co$_{0.96}$W$_{0.04}$ diffusion barrier

Quasi–static capacitance voltage measurements at 1 MHz
Evaluation of diffusion barrier quality – 450°C

**Co_{0.96}W_{0.04} diffusion barrier**

Typical example

Capacitance transient measurement at 1 MHz
Evaluation of diffusion barrier quality – 450°C

$\text{Co}_{0.9}\text{P}_{0.1}$ diffusion barrier

Typical example

![Graphs showing capacitance and time with different temperatures and times.](image)
Evaluation of diffusion barrier quality – 450°C

Typical example

- \( \tau_g \) (\( \mu \)sec)
- \( V'_s \) (cm/sec)
- \( \Delta V_{FB} \) (mV)

- Co\(_{0.9}\)P\(_{0.1}\)
- Cu
- Co\(_{0.9}\)P\(_{0.1}\)
- SiO\(_2\)
- p-Si

Significant increase (+order of magnitude)
Bias Thermal Stress - 300°C / 0.5 hr, 1 MV/cm, N₂ environment:

- Co₀.₉P₀.₁ diffusion barrier stable
- Co₀.₉₆W₀.₀₄ diffusion barrier fails

Typical example

Quasi-static C-V measurements of MOS capacitors at 1 MHz
Motivation for Cu metallization
I. Reducing the RC delay time

\[ RC = 2 \rho k \varepsilon_0 \left( \frac{4L^2}{P^2} + \frac{L^2}{T^2} \right) \]

- \( \rho \) – metal resistivity
- \( \varepsilon_0 \) – vacuum permittivity
- \( k \) – relative dielectric constant
- \( L \) – line length
- \( P \) – line pitch
- \( W \) – line width
- \( S \) – line spacing
- \( T \) – line thickness

(\text{the dielectric thickness above and below the interconnect is equal})

Mark T. Bohr,
Interconnect Scaling - The Real Limiter to High Performance ULSI
I995 International Electron Devices Meeting
Deep depletion

Strong inversion

Accumulation
Electroless deposition of Co alloys

Process:

Reduction of Co ions (complexed with the citrate)

\[ \text{Co(II)Cit} + e^- \rightarrow \text{Co(I)Cit}_{\text{ads}} \]
\[ \text{Co(I)Cit}_{\text{ads}} + e^- \rightarrow \text{Co(s)} + \text{Cit} \]

Reducing agent is hypophosphosphate: In parallel, a competing reaction of hypophosphite deposits P:

H2PO2⁻ → HPO2⁻_{ads} + e⁻

Reaction with OH⁻ ions:

HPO2⁻_{ads} + OH⁻ → H2PO3⁻ + e⁻

Reaction of H atoms is dependant on the catalytic seed layer:

H_{ads} + OH⁻ → H₂O + e⁻  Catalytic seed layer: Pd, Pt,
Rh 2H_{ads} → H₂  Catalytic seed layer: Cu, Au, Ag

W deposition? Induced co-deposition: iron group ion + refractory metal


Induced co-deposition of MoO₄²⁻ and ion M (Fe²⁺, Co²⁺, Ni²⁺) complexed with a ligand L

\[ \text{MoO}_4^{2-} + \text{M(II)L} + 2\text{H}_2\text{O} + 2e^- \rightarrow [\text{M(II)LMoO}_2]_{\text{ads}} + 4\text{OH}^- \]
\[ [\text{M(II)LMoO}_2]_{\text{ads}} + 2\text{H}_2\text{O} + 4e^- \rightarrow \text{Mo(s)} + \text{M(II)L} + 4\text{OH}^- \]
Periodicity in P depth profile

AES depth profiles

Co$_{0.9}$W$_{0.02}$P$_{0.08}$
Co
Ti
SiO$_2$
Si

as-deposited

500$^\circ$C

300$^\circ$C

700$^\circ$C

400$^\circ$C

$\sim$12 nm
Chemical binding states

Co, W – no observable change in chemical binding (XPS, EELS)
P – significant changes

X-ray photoelectron spectroscopy

Suggested fitting of $2p_{3/2}$ and $2p_{1/2}$ P states:

P1 and P2 2p binding states

1. $p_{3/2}$ and $p_{1/2}$ $\Delta E = 0.84$ eV  

2. $p_{3/2}$ and $p_{1/2}$ area ratio = 2:1

3. FWHM, G/L ratio equal for $p_{3/2}$ and $p_{1/2}$ for P1, P2

4. $0.2 \leq G/L \leq 0.8$

Results:

1. P1 and P2 – equal B.E., FWHM, G/L ratio for all samples
   → validates assumptions

2. Area ratio of P1:P2 → ratio of binding states

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area ratio P1/P2 (-)</th>
<th>±10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$<em>{0.9}$W$</em>{0.02}$P$_{0.08}$ as-dep</td>
<td>1:1.1</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{0.9}$W$</em>{0.02}$P$_{0.08}$ 400°C</td>
<td>1:2</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{0.9}$W$</em>{0.02}$P$_{0.08}$ 600°C</td>
<td>1:4.9</td>
<td></td>
</tr>
<tr>
<td>Co$_2$P Reference</td>
<td>1:5</td>
<td></td>
</tr>
</tbody>
</table>
Structure of $\text{Co}_{0.9}\text{W}_{0.02}\text{P}_{0.08}$ and its evolution with thermal treatments

Cu: Influence of seed layer and/or phase interaction?

Same results on Co and Cu seed layer

No phase reaction between Cu and the electroless film up to 700°C

Copper seed

Thermal anneal:
1 hour
Vacuum $\leq 10^{-6}$ Torr

Powder XRD, Bragg-Brentano geometry
The Main Goals

- The effectiveness of CoWP as a Barrier Layer against Cu transport
- Failure characterization
- Comparison between the various kinds of electrical measurements
- The effect of the temperature and the bias on the Cu transport
- Calculation of the $D_{eff}$ of Cu under BTS
Capacitors’ type

1. Test capacitors: CoWP/Cu/CoWP/Co/Ti/SiO₂
2. Reference capacitors #1: CoWP/Cu/Co/Ti/SiO₂
3. Reference capacitors #2: CoWP/Cu/SiO₂
Experimental Setup

- The main parameters that were derived from the electrical measurements are:
  - **C-V curve:** $C_{FB}$, $N_d$, $Q_{it}$, $Q_m$, $d_{ox}$
  - **C-t curve:** $\tau_g$, $s$
  - **I-V curve:** $E_{critical}$, Conduction mechanism
  - **I-t curve:** $I_p$, Leakage currents

- Annealing at 300°C for 1/2 hr
- Performing C-V, C-t and I-V Measurements at 25°C
- BTS at 250-300°C, under various fields; 0.3-1.4MV/cm
- Going down to room temperature and performing C-V, C-t and I-V measurements

Results presentation methodology

I. TS and BTS measurements under:
   - low electric field.
   - high electric field.

II. Data of BTS results under wide range of temperatures and fields.

III. Calculating the effective diffusion coefficient

IV. Proposing a model for Cu$^+$ transport in the oxide.
I. TS and BTS measurements under:
   - low electric field.
   - high electric field.

II. Data of BTS results under wide range of temperatures and fields.

III. Modeling using the effective diffusion coefficient

IV. Proposing a model for Cu transport in the oxide.
C-V of test cap.: CoWP/Cu/CoWP/Co/Ti/SiO$_2$

**TS: 250°C**

- PreAnn.
- TS1
- TS4

**BTS: 250°C, 0.3MV/cm**

- PreAnn.
- BTS1
- BTS2
- BTS3
- BTS4

<table>
<thead>
<tr>
<th>Accumulate Time(hr)</th>
<th>Stress No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TS1/BTS1</td>
</tr>
<tr>
<td>2.5</td>
<td>TS2/BTS2</td>
</tr>
<tr>
<td>25.83</td>
<td>TS3/BTS3</td>
</tr>
<tr>
<td>97</td>
<td>TS4/BTS4</td>
</tr>
</tbody>
</table>

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$\Delta V_{FB}$ vs. time of ref. #1

C-t of ref. #1 under BTS: 250°C, 0.3MV/cm

$\tau_c$=26 µs
$S$=0.63 cm/sec
C-V & C-t of ref. #1: CoWP/Cu/Co/Ti/SiO₂

BTS: 250°C, 0.3MV/cm

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<td>BTS2</td>
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</tr>
<tr>
<td>BTS3</td>
<td>3.5</td>
</tr>
<tr>
<td>BTS4</td>
<td>20.5</td>
</tr>
<tr>
<td>BTS5</td>
<td>26</td>
</tr>
<tr>
<td>BTS6</td>
<td>45</td>
</tr>
</tbody>
</table>

Zerbst Plot

\[
\frac{d(C/C)}{dt} = \frac{1}{\tau_g} \frac{S}{E} \times \left(\frac{C}{C_m}\right) \left(1 - \frac{C}{C_m}\right) \text{[1/sec]}
\]

\[
t = 26.12 \times 10^{-6} \text{ sec}
\]

\[
S = 0.63 \text{ cm/sec}
\]
I-V & I-t of ref. #1: CoWP/Cu/Co/Ti/SiO₂

BTS: 250°C, 0.3MV/cm

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</tbody>
</table>
C-V & I-t of ref. #2: CoWP/Cu/SiO₂

BTS: 250°C, 0.3MV/cm

<table>
<thead>
<tr>
<th>Stress No.</th>
<th>Accumulate Time(hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTS1</td>
<td>0.5</td>
</tr>
<tr>
<td>BTS2</td>
<td>1.5</td>
</tr>
<tr>
<td>BTS3</td>
<td>3</td>
</tr>
<tr>
<td>BTS4</td>
<td>4</td>
</tr>
<tr>
<td>BTS5</td>
<td>6</td>
</tr>
<tr>
<td>BTS6</td>
<td>8</td>
</tr>
</tbody>
</table>
Temperature effect under low electric field

in ref. #1

<table>
<thead>
<tr>
<th>BTS</th>
<th>type</th>
<th>Stress time (hr)</th>
<th>$\Delta V_{FB}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250°C, 0.3MV/cm</td>
<td>A</td>
<td>20.50</td>
<td>-0.15</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>26.00</td>
<td>-0.20</td>
</tr>
<tr>
<td>275°C, 0.3MV/cm</td>
<td>A</td>
<td>19.15</td>
<td>-0.25</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>33.50</td>
<td>-0.32</td>
</tr>
<tr>
<td>300°C, 0.3MV/cm</td>
<td>B</td>
<td>29.38</td>
<td>-0.57</td>
</tr>
</tbody>
</table>

* A-flat-band shift after 20 hours.
* B-critical change in the C-V curve after 26-33 hours.
I. TS and BTS measurements
   - low electric field.
   - high electric field.

II. Data of BTS results under wide range of temperatures and fields.

III. Modeling using the effective diffusion coefficient

IV. Proposing a model for Cu transport in the oxide.
**C-V, C-t & I-t of ref. #1: CoWP/Cu/Co/Ti/SiO₂**

**BTS: 250°C, 1.2MV/cm**

<table>
<thead>
<tr>
<th>Stress No.</th>
<th>Accumulate Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTS1</td>
<td>4.5</td>
</tr>
<tr>
<td>BTS2</td>
<td>9.5</td>
</tr>
<tr>
<td>BTS3</td>
<td>22.5</td>
</tr>
<tr>
<td>BTS4</td>
<td>2.2hr</td>
</tr>
</tbody>
</table>

**Graphs:**

- **Graph a:**
  - **X-axis:** Accumulate Time (min)
  - **Y-axis:** Stress No.
  - **Legend:**
    - PreAnn.
    - BTS1
    - BTS2
    - BTS3
    - BTS4

- **Graph b:**
  - **X-axis:** C(pF)
  - **Y-axis:** V(v)
  - **Legend:**
    - PreAnn.
    - BTS1
    - BTS2
    - BTS3
    - BTS4

- **Graph c:**
  - **X-axis:** t(sec)
  - **Y-axis:** C(pF)
  - **Legend:**
    - PreAnn.
    - BTS1
    - BTS2
    - BTS3
    - BTS4

- **Graph d:**
  - **X-axis:** $\frac{d\log(C)}{dt}$
  - **Y-axis:** Time (sec)
  - **Legend:**
    - PreAnn.
    - BTS1
    - BTS2
    - BTS3
    - BTS4

- **Graph e:**
  - **X-axis:** t(µs)
  - **Y-axis:** Zerbst Plot
  - **Legend:**
    - BTS3
    - BTS4

**Equation:**

$$\tau = 143 \mu s$$

$S = 0.48 \text{ cm/s}$
C-V & I-t of test cap.: CoWP/Cu/CoWP/Co/Ti/SiO$_2$

BTS: 250°C, 1.2MV/cm

*BTS - accumulate stress time of 27.5hr
**C-V of ref. #2: CoWP/Cu/SiO₂**

**BTS: 250°C, 1.2MV/cm**

**ΔV<sub>FB</sub> vs. time of ref. #2 under low and high electric field**

<table>
<thead>
<tr>
<th>Accumulate Time(min)</th>
<th>Stress No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>BTS1</td>
</tr>
<tr>
<td>9</td>
<td>BTS2</td>
</tr>
<tr>
<td>22.33</td>
<td>BTS3</td>
</tr>
<tr>
<td>37.66</td>
<td>BTS4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>E</th>
<th>Cu⁺[ions/cm²·sec]</th>
<th>Cu⁺[ions/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3MV/cm</td>
<td>2.51·10⁷</td>
<td>7.24·10¹¹</td>
</tr>
<tr>
<td>1.2MV/cm</td>
<td>5.31·10⁸</td>
<td>1.2·10¹²</td>
</tr>
</tbody>
</table>
**Temperature effect under high electric field in ref. #1**

<table>
<thead>
<tr>
<th>BTS</th>
<th>From C-V</th>
<th>From I-t</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta V_{FB}$</td>
<td>Arrival time to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a significant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>shift</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Current</td>
</tr>
<tr>
<td></td>
<td></td>
<td>threshold</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Arrival time to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>the current</td>
</tr>
<tr>
<td></td>
<td></td>
<td>threshold</td>
</tr>
<tr>
<td>1</td>
<td>250°C, 1MV/cm</td>
<td>-12.61</td>
</tr>
<tr>
<td>2</td>
<td>275°C, 1MV/cm</td>
<td>-9.29</td>
</tr>
<tr>
<td>3</td>
<td>300°C, 1MV/cm</td>
<td>-8.32</td>
</tr>
</tbody>
</table>

![Graph showing temperature effect](image_url)
Electric field effect on the flatband shift in ref. #1 and #2

Under low electric field the flat band shift is gradual

The CO/Ti seed layer serves as a barrier layer against Cu at low electric fields

<table>
<thead>
<tr>
<th>type</th>
<th>Electric field strength</th>
<th>Initial stress time</th>
<th>Advance stress time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SiO₂</td>
<td>Low</td>
<td>☺</td>
<td>☺</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>☺</td>
<td>☺</td>
</tr>
<tr>
<td>Cu/Co/Ti/SiO₂</td>
<td>Low</td>
<td>☺</td>
<td>☺</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>☺</td>
<td>☺</td>
</tr>
</tbody>
</table>

☺ Gradual increase in $\Delta V_{FB}$
● Exponential increase in $\Delta V_{FB}$

![Graph showing $\Delta V_{FB}$ vs. time for different electric field strengths and materials.](image)
Our observations concerning to the electric field and temperature

Capacitors without a barrier layer (ref. #2):
Linear increase in the flat band shift under low and high electric fields.

Capacitors with a seed layer (ref. #1):
Linear increase in the flat-band shift only under low electric fields. A sudden increase in progress steps of the BTS under high electric fields.

Capacitors with the full stack (test cap.) or capacitors that were subjected to TS only:
Minor shifts.

The temperature effect becomes significant in a lower value at BTS under high electric field, comparing to BTS under low electric field.
I. TS and BTS measurements under:
   - low electric field.
   - high electric field.

II. Data of BTS results under wide range of temperatures and fields.

III. Modeling using the effective diffusion coefficient

IV. Proposing a model for Cu transport in the oxide.
BTS under different kind of fields and temperatures

\[ t_f = \frac{d^2}{\mu V_G} = \frac{d^2}{\mu_0 V_G} = \frac{Q}{e kT} \]

![Graph showing the variation of \( t_f \) with temperature and electric field strength](image)
The activation energy vs. electric field comparing to the literature

The effective time to failure vs. field

\[
\frac{1}{t_f} \approx \frac{1}{t_{\text{diff.}}} + \frac{1}{t_{\text{drift}}}
\]

\[
t_{\text{drift}} \approx \frac{x}{\mu E}
\]

\[
t_{\text{diff.}} \approx \frac{x^2}{4\alpha^2 D}
\]

---

The slope:

\[t_f E = \frac{d}{\mu} = \frac{d}{\mu_0} e^{Q \sqrt{E}}\]

0.18MV/cm, 4hr

3.03e-3 [1/eV]^{0.5}
Results presentation methodology

I. TS and BTS measurements under:
   ➢ low electric field.
   ➢ high electric field.

II. Data of BTS results under wide range of temperatures and fields.

III. Calculating the effective diffusion coefficient

IV. Proposing a model for Cu transport in the oxide.
Calculating the effective diffusion coefficient of Cu in the oxide

\[ D_{\text{eff},BTS}(x,T,E) = \left( -\alpha + \sqrt{\alpha^2 + \frac{E}{kT/q}} \right) \left( \frac{E\sqrt{t}}{kT/q} \right)^2 \]

- \( t \)-time,
- \( x \)-distance,
- \( \mu \)-mobility,
- \( D_{\text{eff},BTS} \)-effective diffusion coefficient,
- \( k \)-Boltzmann constant,
- \( T \)-temperature in Kelvin,
- \( q \)-electron charge
The effective diffusion coefficient

![Graph showing the effective diffusion coefficient vs. electric field (E) for different temperatures (250°C, 275°C, 300°C) and processes (BTS, TS). The y-axis represents $D_{\text{eff}}$ in cm²/sec, and the x-axis represents E in MV/cm. The graph includes data points and lines for each condition, indicating the diffusion coefficient increases with electric field and temperature.](image-url)
Experimental result:
- Cu diffusivity in oxide depends on the electric field at high electric fields

Problem:
- How to take into consideration the electric field effect?

Model:
- Assume that the electric field modifies the energy barrier for emission of the Cu ions that are trapped in the oxide.
What affects the diffusivity at high fields?

\[ D, \text{Diffusivity} = \lambda^2 \nu_0 \exp[-qE_a/kT] \]

- \( \nu_0 = \) lattice vibration frequency
- \( E_a = \) Activation energy for de-trapping
- \( \lambda = \) jump distance (between trapping sites)

**Diffusivity definition in a 3D random walk model between traps**

- Ea is a function of the electric field
- It is a local effect, hence it affects diffusivity directly

**What affects the diffusivity at high fields?**

- Ea is a function of the electric field
- It is a local effect, hence it affects diffusivity directly
Modifying Poole-Frenkel emission

\[ D(E, T) = A e^{-\frac{q}{kT}(\phi_B - \Delta \phi)} = D_0 e^{\frac{q}{kT} \Delta \phi} \]

\[ \Delta \phi = \frac{qE}{\pi \varepsilon_0 \varepsilon_{SiO_2}} \]

\[ \text{slope} = \frac{q}{kT} \sqrt{\frac{q}{\pi \varepsilon_0 \varepsilon_{SiO_2}}} \]

<table>
<thead>
<tr>
<th></th>
<th>The slope [1/eV](^{0.5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>From the (D_{\text{eff}}) vs.</td>
<td>4.02e-3</td>
</tr>
<tr>
<td>From Poole-Frenkel</td>
<td>4.50e-3</td>
</tr>
</tbody>
</table>

(\(D\)-diffusion coefficient, \(A\)-constant, \(\phi_B\)-barrier height, \(\Delta \phi\)-barrier lowering, \(D_0\)-diffusion constant, \(T\)-temperature in Kelvin, \(E\)-electric field, \(k\)-boltzman constant, \(q\)-electron charge, \(\varepsilon_0\)-permittivity in vacuum, \(\varepsilon_{SiO_2}\)-dielectric constant)
Results presentation methodology

I. TS and BTS measurements under:
   - low electric field.
   - high electric field.

II. Data of BTS results under wide range of temperatures and fields.

III. Modeling using the effective diffusion coefficient
Cu\textsuperscript{+} transport in the oxide under BTS

Our assumptions:
- The barrier to Cu\textsuperscript{+} movement is anisotropic
- Assuming Poole-Frenkel model modification

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
E [MV/cm], T=300\textdegree C & D/D_0 & e^8/B \\
\hline
0.3 & 17.5 & 16.1 \\
0.6 & 165 & 65 \\
0.8 & 220 & 142 \\
1 & 265 & 287 \\
1.2 & 300 & 547 \\
\hline
\end{tabular}
\end{table}

(r-the distance between the sites, E-electric field, \theta-the angle projection on x, \Delta \phi-barrier lowering, \nu_0-jumping frequency, \psi-statistic function, \varepsilon-permittivity dielectric constant, k-boltzman constant, T-temperature in Kelvin, e-electron charge)
The effective time to failure

- The time to failure, depending on the components’ diffusion:
  \[ t_{\text{diff.}} \approx \frac{x^2}{4\alpha^2 D} \]

- The time to failure, as depending on the components’ drift:
  \[ t_{\text{drift}} \approx \beta \frac{x}{\mu E} \]

\[ \frac{1}{t_f} \approx \frac{1}{t_{\text{diff.}}} + \frac{1}{t_{\text{drift}}} + \frac{1}{2t_{\text{diff.}} \left( \frac{4t_{\text{diff.}}}{t_{\text{drift}}} - 1 \right)} \]

\[ \Rightarrow \quad \frac{1}{t_f} = \frac{1}{t_{\text{diff.}}} + \frac{1}{t_{\text{drift}}} \]

\[ t_f E = \frac{d}{\mu} = \frac{d}{\mu_0} e^{Q\sqrt{E}} \]

The slope:
\[ 3.03e-3 \, [1/eV]^{0.5} \]
The capacitance techniques are more sensitive to the penetration of Cu into the oxide than current measurements.

The transient capacitance measurement have been proven to be the most sensitive in identifying the penetration of Cu onto the Si substrate.

The I-t measurement let us know the exact time to failure and control the stress in-situ.
The major effects that indicate a coming failure are:

- The curve distortion and a noticeable shift of the flat-band voltage.
- Hysteresis effects
- An increase in the inversion capacitance and a decrease in the accumulation capacitance
- Apart of the capacitors loses its ability to form an inversion layer so a deep depletion layer appears
- Minority’s lifetime decreased sharply
- The leakage currents become stronger, exceeding to values greater than $10^{-6}$A
Conclusions

- The effectiveness of CoWP as a Barrier Layer against Cu transport was demonstrated.
- In BTS under low electric field the temperature assists the Cu transport, while during BTS under high electric field the magnitude of the phenomenon determines mainly by the electric field.
- The $D_{\text{eff}}$ of Cu under BTS was calculated and correlated under various conditions.
- Cu$^+$ transport though the oxide under BTS in a modification of the Poole-Frenkel mechanism.