Low-k/Cu Resistive 2-Level PROM Memory Collocated with CMOS Backend-of-Line

A. Verma, G. Ghosh, Y. Fan, M. Orlowski

Bradley Department of Electrical and Computer Engineering,
Virginia Tech, Blacksburg VA, USA

J. Bielefeld, S. King

Logic Technology Development
Intel Corporation, Hillsboro, OR, USA

AVS Conference, San Jose, October 20, 2015

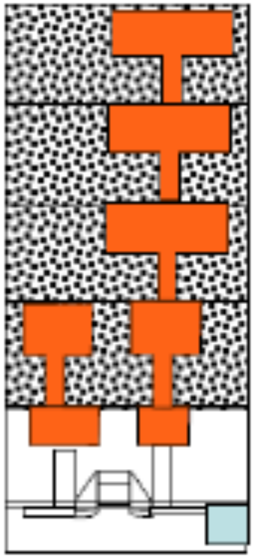
Virginia Tech

Outline

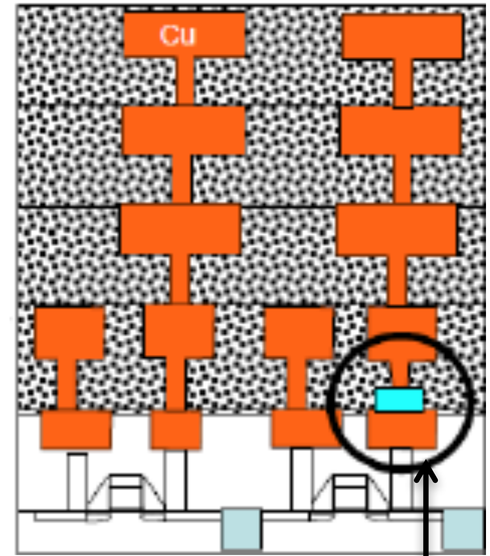
- Motivation: CMOS BEOL materials not readily compatible with RRAM but with PROM and FPGA
- Switching properties Low-k dielectric BEOL MIM structures
- Nature of conductive filaments
- Beyond PROM and FPGA: “electric definition” of vias
- Conclusions

Motivation for the work

BEOL



BEOL + RRAM MEMORY



- Mitigation of latency issues
- Low cost
- High speed
- Multiple layer
- Rad-hard

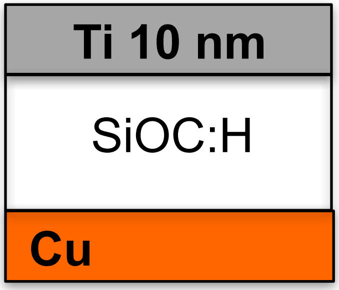
- **Issue for resistive switching: compatibility of materials used in BEOL**

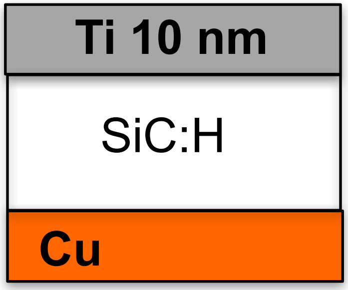
RRAM

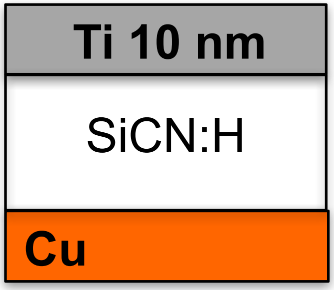
- **But present materials suitable for PROM or FPGA**

- **Cu diffusion causes many ILD and MOSFET reliability issues**
- **Cu diffusion beneficial for RRAM, PROM, electric via manufacturing**

Low-k dielectric BEOL MIM structures





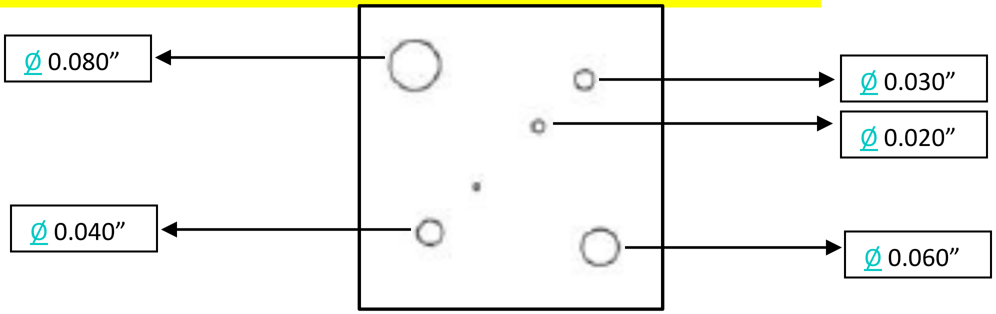


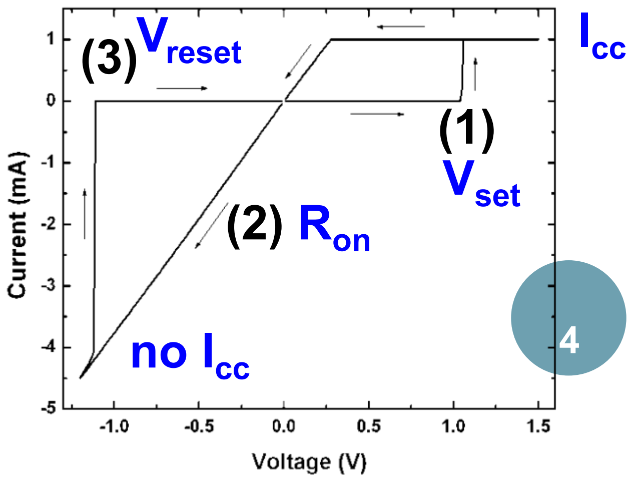
Dielectric	Purpose	Dielectric constant k	Density (g/cm3)	Young's Mod. (Gpa)	Porosity %
SiOC:H	low-k ILD	3.3	1.5	20	< 2
SiC:H	etch stop	5	1.8	80	0
SICN:H	etch stop	5.85	2.25	120	0

S. King et al ECS J. Sol. Stat. Scie. & Tech. 1(6) N115-N122 (2012)

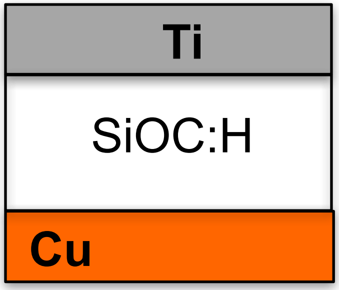
Characterization of Resistive switching.

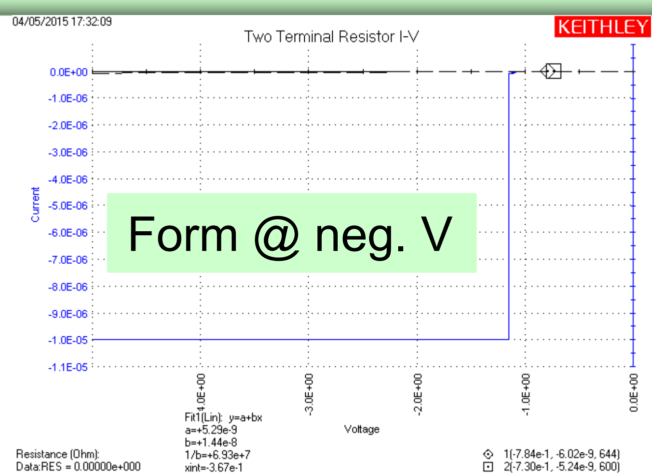
Device layout:
- bottom electrode (ground plate) Cu
- top electrode: islands of Ti/Al





Characterization of Ti/SiOC:H/Cu



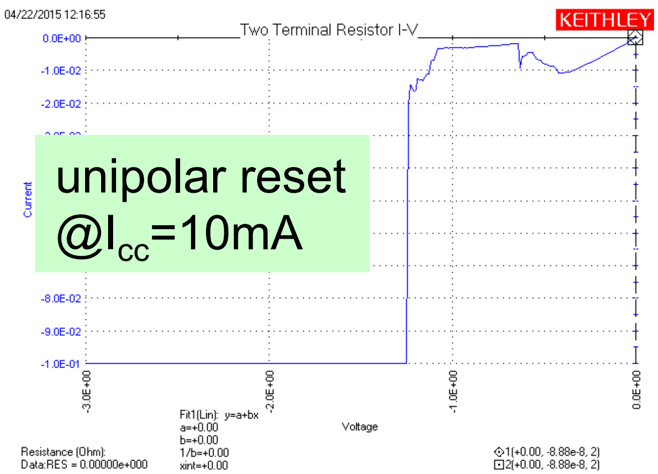


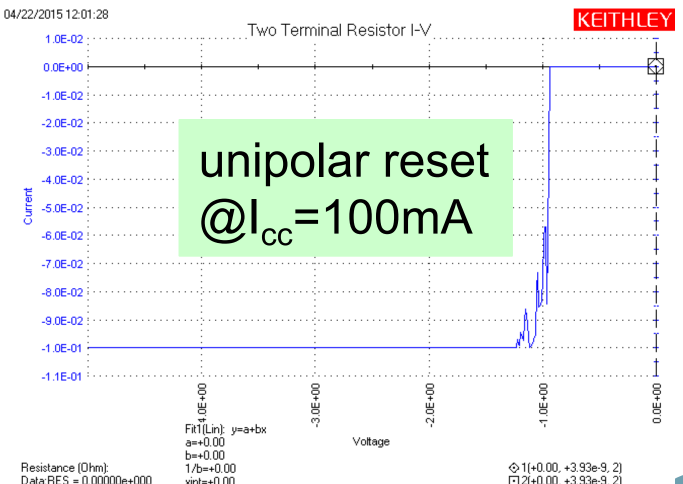
R_{off}=200 MΩ

I_{cc}=0.01mA
V_{form}=0.9 – 1.45 V
R_{on}=120-150 kΩ

cannot be reset

Surprising result: Reset leads to a secondary set with resulting R_{on} dependent on I_{cc} independent of voltage polarity.

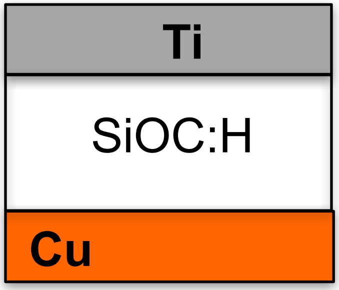


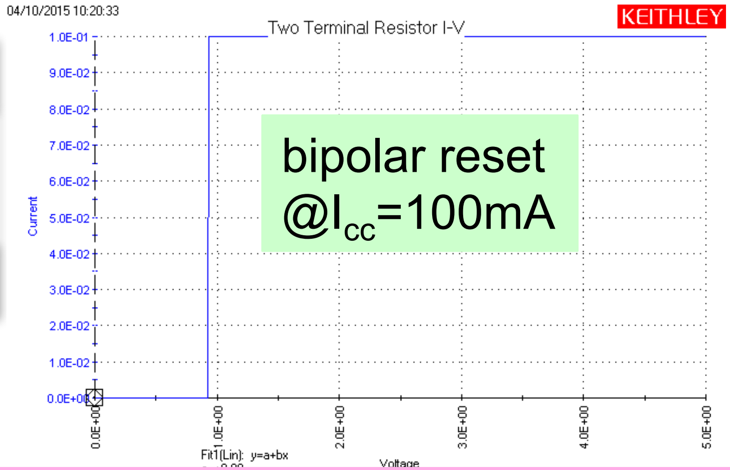


Secondary set V_{set}=1.25 V
$R_{on}(1)$=150 kΩ ➔ $R_{on}(2)$=34.2 Ω

Secondary set V_{set}=1.00 V
$R_{on}(1)$=150 kΩ ➔ $R_{on}(2)$=12 Ω

Characterization of Ti/SiOC:H/Cu





bipolar reset
@I_{cc}=100mA

Secondary set V_{set}=0.90 V
$R_{on}(1)$=150 kΩ ➔ $R_{on}(2)$=12 Ω

Two-level set of $R_{on}(1)$ and $R_{on}(2)$

Log (R)

R_{off}=200 MΩ

$R_{on}(1)$=120-150 kΩ

Form operation
@ Icc=0.01 mA
V_{form}=0.9-1.5 V

$R_{on}(2)$=34 Ω @I_{cc}=10mA

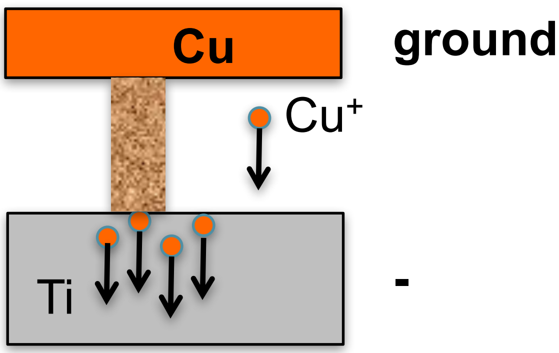
Reset leads to a secondary set
V_{set}=0.8-1.1V
@ Icc=10 mA, @ both polarities;
$R_{on}=R_{on}(I_{cc})$

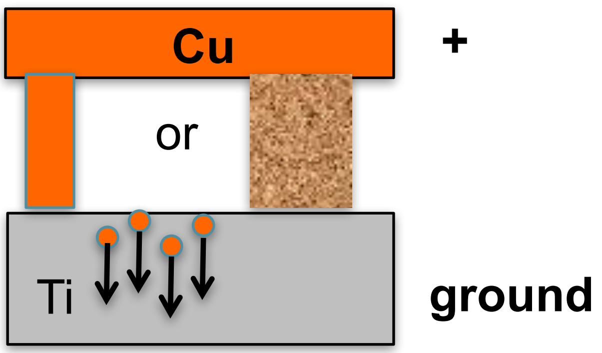
$R_{on}(3)$=2-10 Ω @I_{cc}=100mA

Form operation
@ Icc=100 mA
V_{form}=0.9-1.5 V

$R_{on}(3)$=10 Ω @I_{cc}=100mA

Nature of Filament in Ti/SiOC:H/Cu





At negative bias $R_{on}(1)$ @ low I_{cc}.

Filament attributed to Cu ions.

$R_{on}(1) \sim 140k\Omega$.

Cu diffuses into Ti electrode preventing a cone shape of the filament. Filament cannot be ruptured.

Secondary set $R_{on}(2)$=2-35 Ω depending at I_{cc} =5 -100 mA.

Since secondary set does not depend on bias polarity a lateral growth of the filament with Cu can be excluded.

Filament undergoes a dramatic phase transformation to a very low conductivity material.

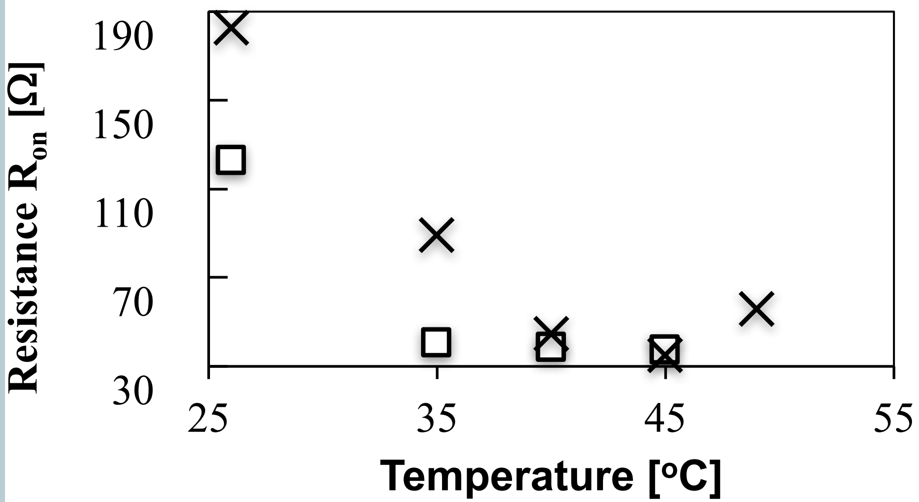
2^{nd} phase transformation mysterious. Since currents and Joules heating are very high, some kind of melting is possible.

A 5 Ω cylindrical filament of L=25 nm, assuming bulk Cu resistivity would require a diameter of 11 nm. Since resistivity of the filament is smaller than bulk Cu, its diameter would have to be significantly larger than 11 nm.

Temperature coefficient of resistance (α=TCR) of (high) R_{on}

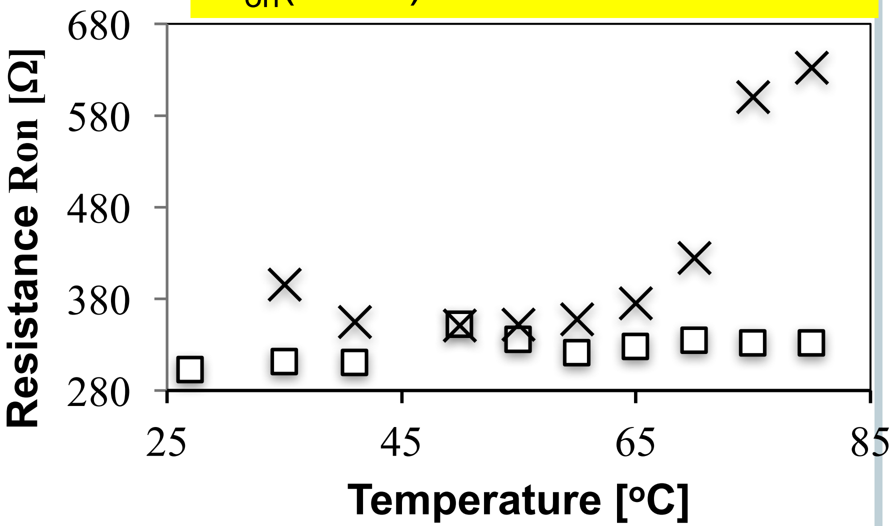
$$R(T) = R(T_o) \times [1 + \alpha(T - T_o)]$$

Sample 1
@ I_{cc}=1 mA V_{form}=0.96V
R_{on}(300K)=123 Ω



Two consecutive runs on the same device. TCR is negative. ΔR is largest between 26 C and 35 C.

Sample 2
@ I_{cc}=1 mA V_{form}=1.02V
R_{on}(300K)=302 Ω



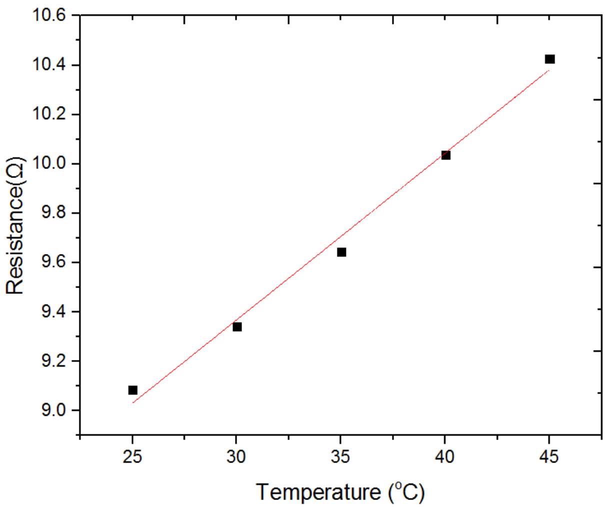
Two consecutive runs on the same device. TCR is negative. During the 1st run resistance almost independent of temperature. During 2nd run sharp

The resistance of the filament very sensitive with temperature. Negative TCR indicates defects with energy levels below the Fermi level. The transport effects are masked by reconstruction of the defect states.

This behavior is in stark contrast with TCR for Cu and Vo filament in Cu/TaO_x/Pt devices where TCR of 0.003 K^{-1} for Cu CF, and 0.001 K^{-1} for V_o CF are measured.

Temperature coefficient of resistance (TCR) of (low) R_{on}

Sample 1
@ I_{cc}=100 mA V_{form}=4.8 V
R_{on}(300K)=9 Ω



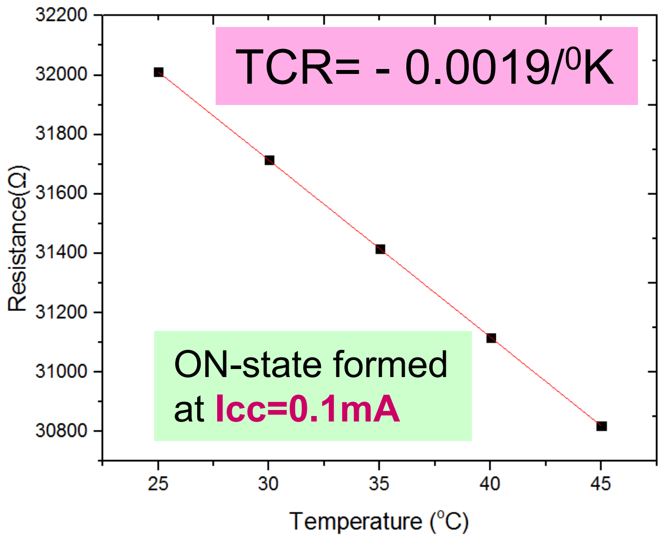
For low R_{on} formed @ 100 mA we find for SiOC:H, SiC:H, and SiCN:H that the filament is metalic with a TCR=0.008 K^{-1}. This three-time higher value than for Cu filament in Cu/TaO_x/Pt. Thus the filament is not likely to be Cu filament.

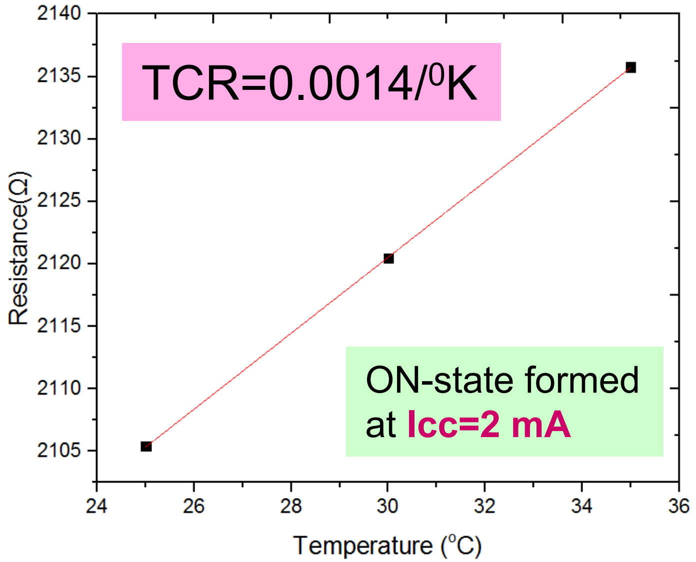
Similar results have been obtained for Ti/TaOx/Pt devices (see paper # at this conference

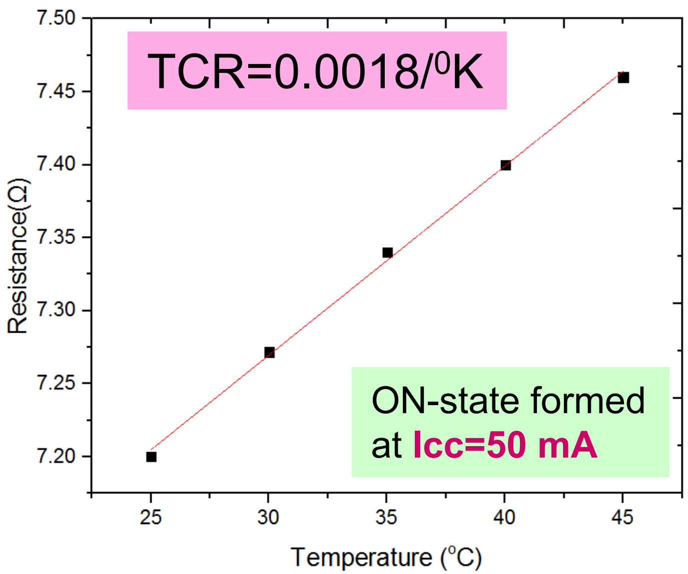
The TCR measurement is an important probe into the nature of the filament. We observe that highly resistive R_{on} formed at low I_{cc} (< 0.5 mA) display semiconductive conduction, while low resistance R_{on} formed at high I_{cc} (>5 mA) display metallic conduction.

Temperature coefficient of resistance (TCR) of (low) R_{on}

Device Cu/SiC:H/Ti

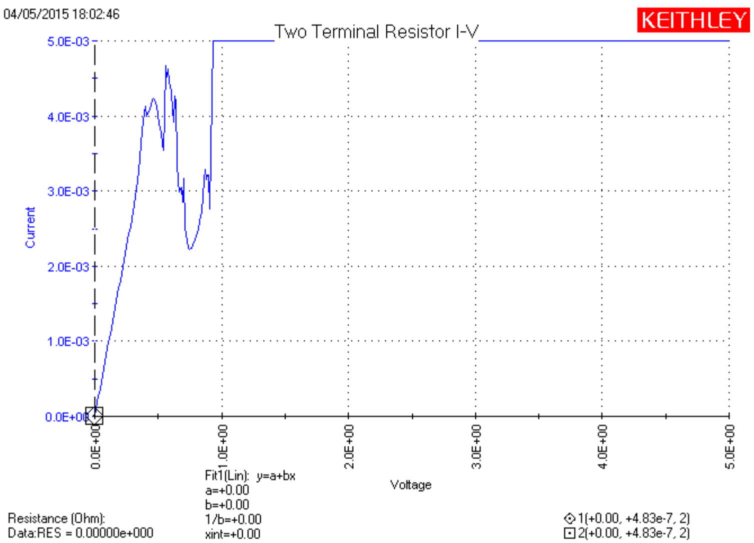






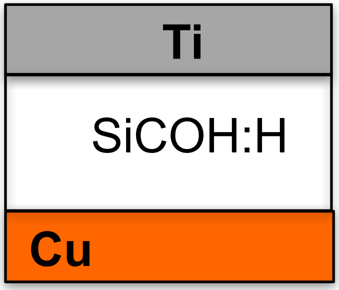
Clear transition from semiconductive to metallic conductivity with increasing I_{cc}.

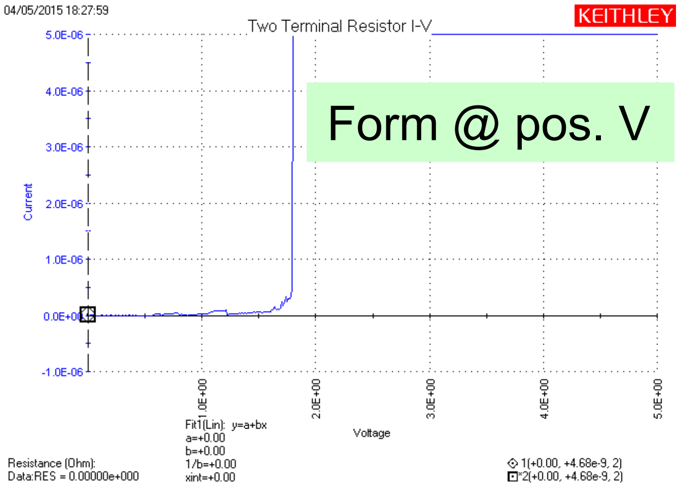
Tendency at Reset for Ti/SiOC:H/Cu



At positive voltage when the supply of Cu^{+} ions is cut off one can observe some predisposition to reset. But the attempt is followed by a strong set transition.

Set at positive bias of Ti/SiOC:H/Cu

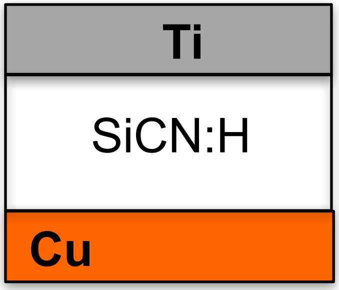


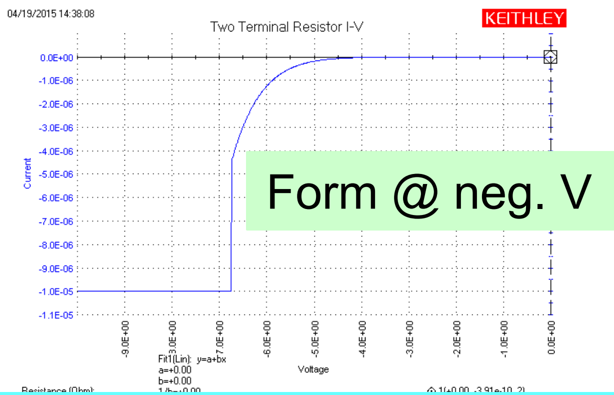


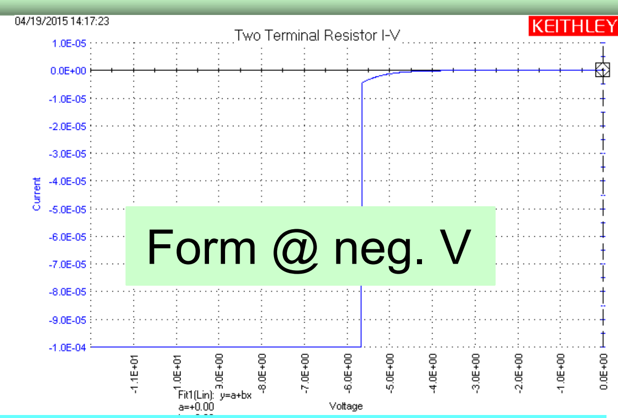
R_{off}=200 MΩ

I_{cc}=0.005mA
V_{set}=1.8 V
R_{on}= 53 Ω

Characterization of Ti/SiCN:H/Cu

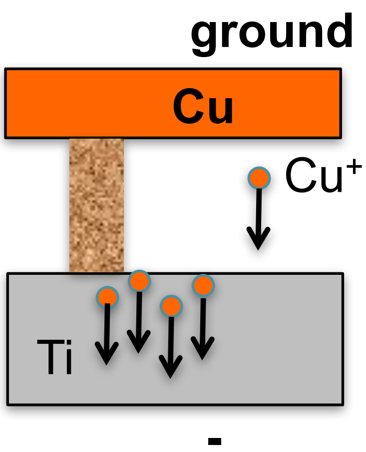






R_{off}=500 MΩ V_{form}=5-7V R_{on}~10 Ω

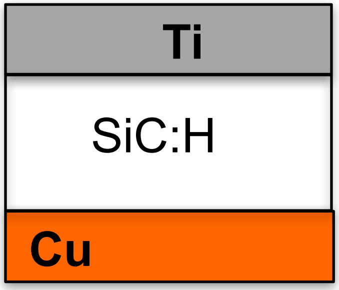
Cannot be reset and does not undergo a secondary reset.

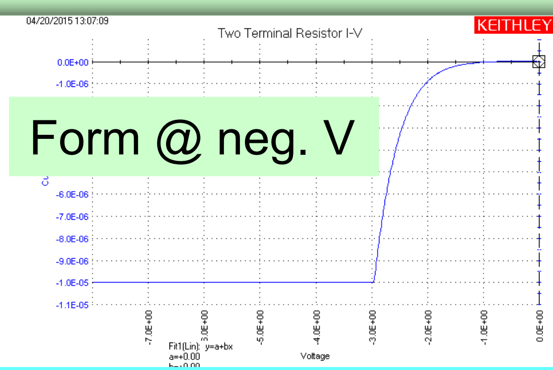


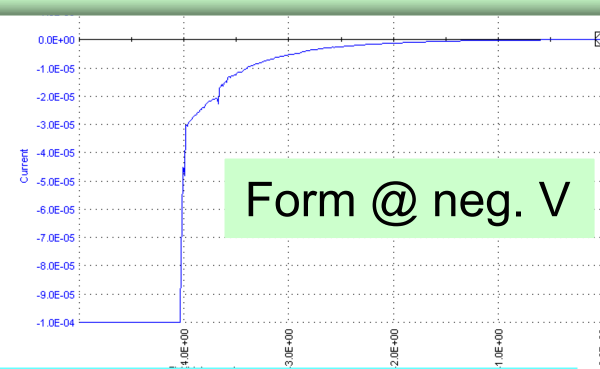
Filament is attributed to a Cu filament.
The much higher form voltage is attributed to much slower diffusivity of Cu in SiCN than in SiCOH.

As previously shown, a diameter of Cu filament would have to be 10 nm -15 nm. It is hard to imagine how such massive filament can be created.
Alternatively, multiple filaments could form over the device cross-section. Nevertheless, the diameter of the hypothesized filament is much smaller than the top electrode.

Characterization of Ti/SiC:H/Cu

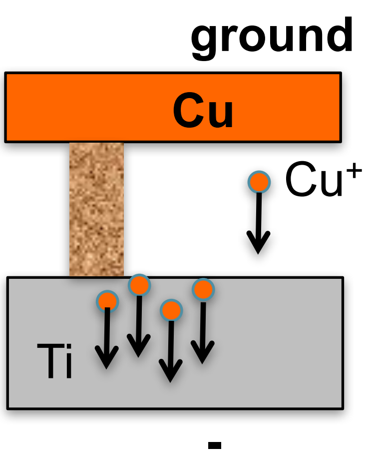






No (volatile) form I_{cc} < 0.3 mA; @ I_{cc}> 5mA V_{form}=4 V R_{on}=5 Ω

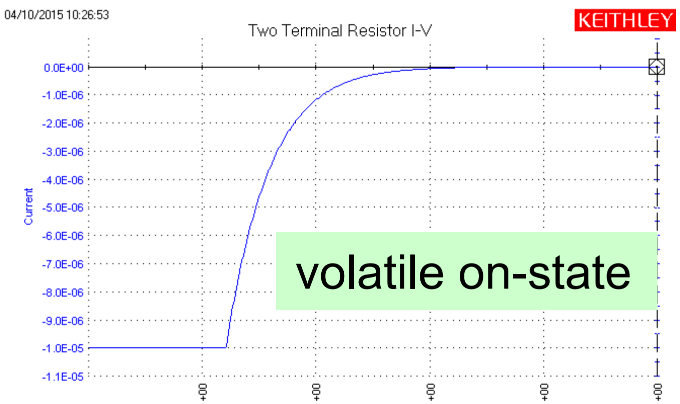
Cannot be reset and does not undergo a secondary reset.

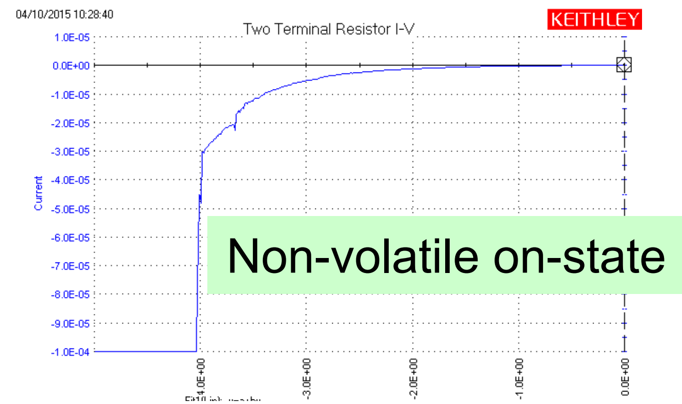


Filament is attributed to a (Cu+defects) filament.
V_{form} is much higher than V_{form} in SiCN but slightly lower than in SiCN and hence one may conclude that the diffusivity of Cu in SiCOH is much higher than in SiC and SiCN. However, the issue of Cu migration could be masked by the availabity of Cu^+ ions.

Final ON-resistance, however is about the same as in SiCN and SiC.

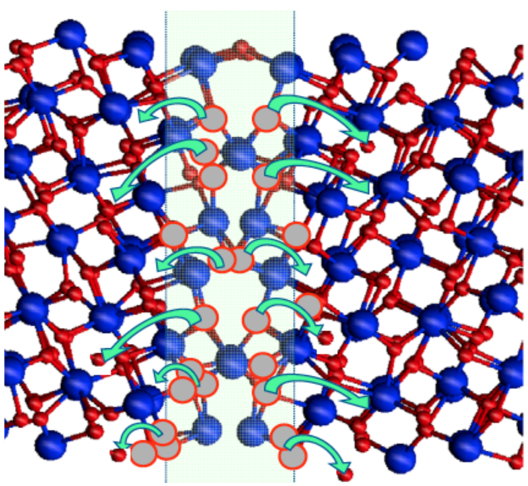
Volatile vs Non-Volatile ON-STATE

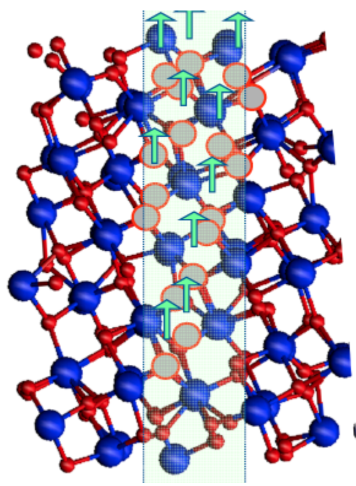




A gradual current increase is indicative of volatile formation and can be attributed to some bulk conduction mechanisms such as field assisted Pool-Frenkel mechanisms which relies on static (native) defects

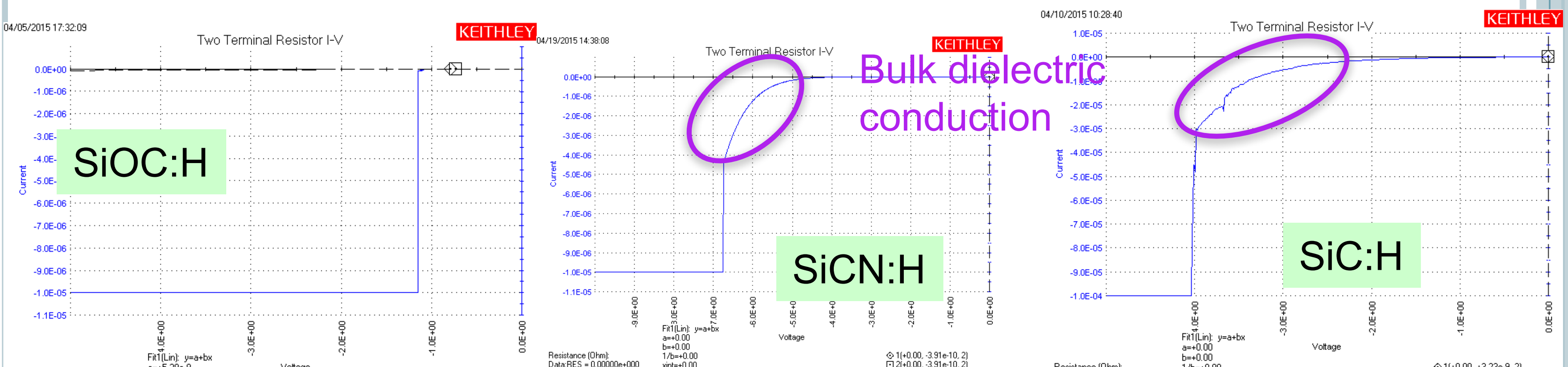
A sudden increase of current is indicative of a non-volatile conductive path. As it is shown above it is not only a function of the effective electrical field but also of current allowed to flow through the device.





This leads us to postulate that a structural damage to create a conductive path requires not only energy from the electric field but also a thermal energy to effect structural changes to the dielectric.
The thermal energy comes form local Joules heating.

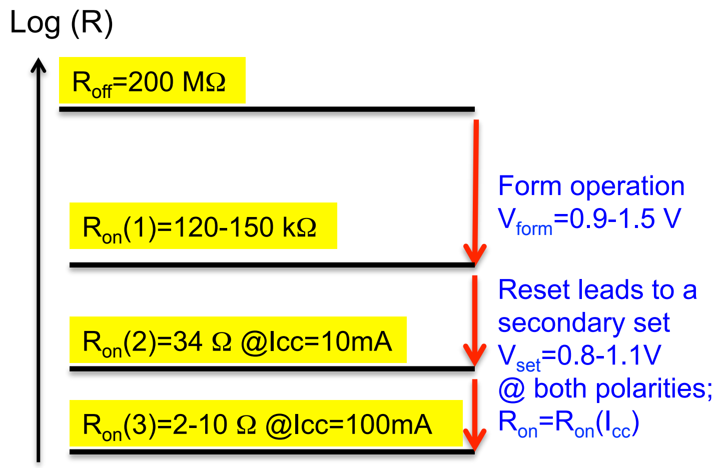
Comparison of low-k dielectrics: SiOC:H, SiC:H, and SiCN:H



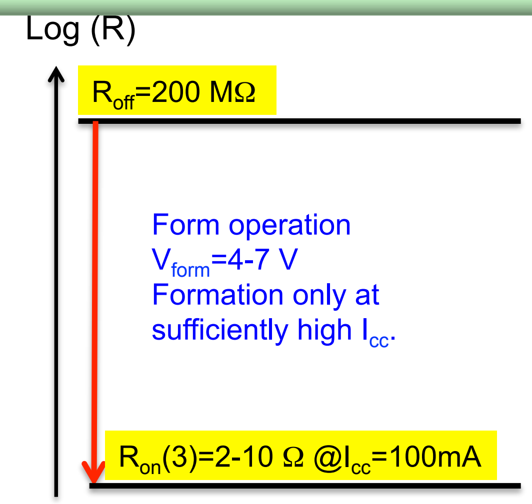
Dielectric material	Dielectric constant k	Density (g/cm3)	Cu^+ diffusivity	V_{form} (V)	Source of Cu^+
SiOC:H	3.2	1.5	fast	0.9-1.45	$CuO+H_20 \rightarrow Cu^+ + 2OH^-$
SiC:H	5.0	1.8	slow	4-5	Cu^+ moisture?
SiCN:H	5.85	2.25	very slow	5-7	Cu^+ moisture?

- Parameters dielectric constant and density scale with Cu diffusivity and V_{form}
- Cu diffusion competes with bulk conduction mechanisms.
- In case of SiOC:H the bulk dielectric conduction is screened by the fast Cu filament formation.
- SiC:H and SiCN:H need sufficiently high current to form Cu filament.

Comparison: of low dielectrics SiOC:H vs SiC:H and SiCN:H



SiOC:H

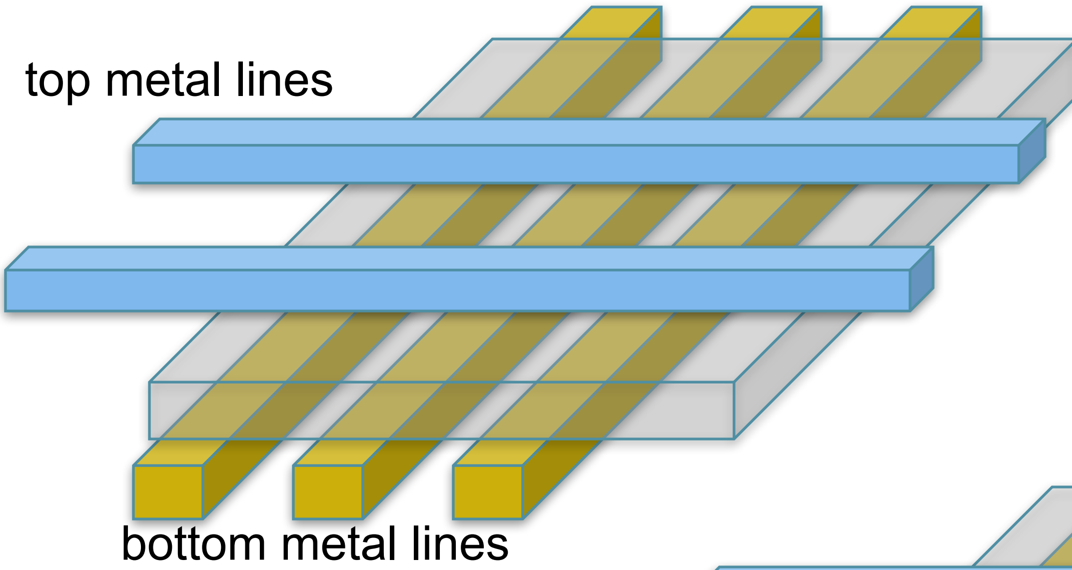


SiOC:H, SiC:H and SiCN:H

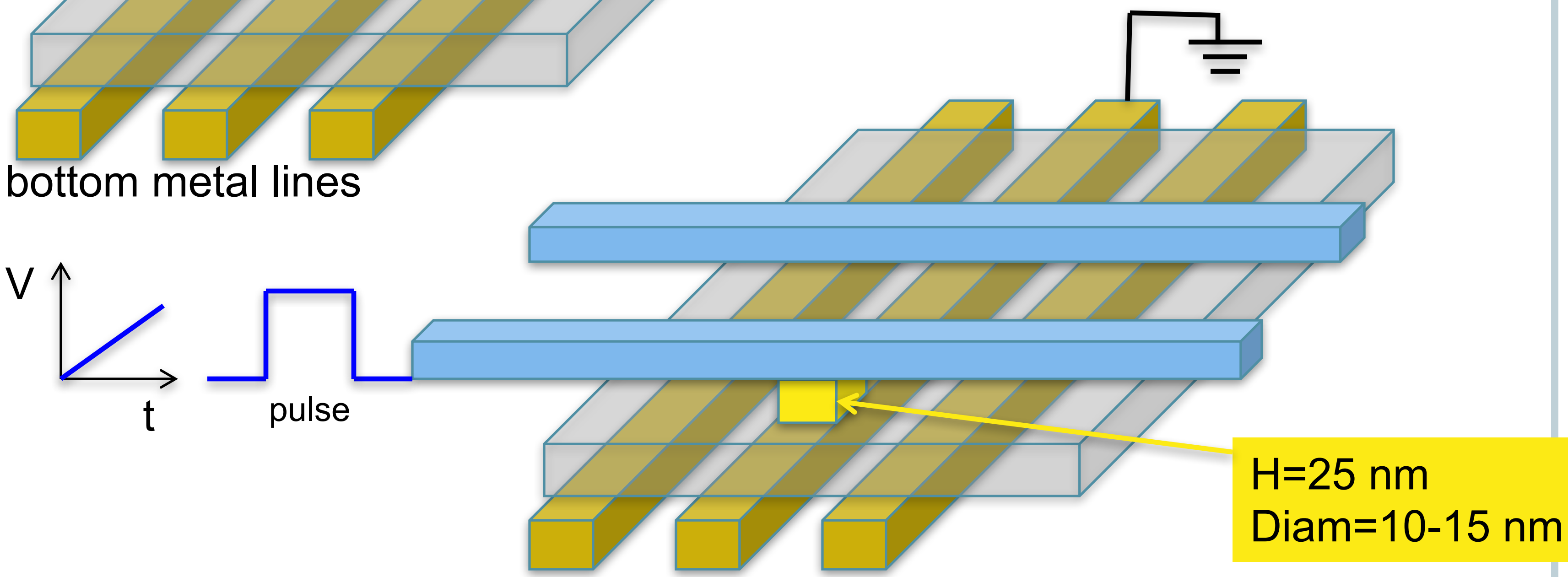
Because of low density Cu can diffuse through SiOC:H readily.
But the low density of SiOC:H cannot support high density Cu filament. The resulting CF is highly resistive and conduction based on electron tunneling from Cu atom to Cu atom. At high currents Cu electrode at the contact is heated up providing a large number of Cu atoms beyond the electrochemical reaction Cu → $Cu^{+}+e^{-}$. The Cu atom diffusion enables high density Cu CF.

In case of SiC:H and SiCN:H strong fields are needed to break the bonds of the matrix. Cu can move only when some sort of vacancy or defect has been created by high electric fields.

Possibiliy of “Electric Definition” of a Via



SiOC, SiC, SiCN are used us Cu barrier diffusion and etch stop layers and are sandwiching low-k ILD. Thus they are the critical layers to enable a Cu via filament.



Such electrically defined vias by application of a voltage pulse or voltage ramp to one of the lines while the other is grounded could have much better electromigration properties because it is anchored in the dielectric matrix and Cu ions do not move readily. The dimension of via: diameter 10 -15 nm, height = thickness of dielectric layer typically 25 nm.

Summary

Device	V_{form} (V)	Nonvolatile Cu filament	R_{on} (Ω)	Reset (V)	Cu^+ Generation
SiOC:H	0.9-1.45	I_{cc} >1μA	2-150k	no secondary set	Strong Intrinsic, extrinsic H,O
SiC:H	3.5-4.0	I_{cc} >0.1mA	2-30	no	weak (extrinsic O)
SiCN:H	5-7	I_{cc} > 0.5mA	2-15	no	very weak (none)

SiC & SiCN inefficient in ionization of Cu.

Source of Cu^+ ions

Intrinsic

2CuO + 2H → 2Cu(OH)→2Cu^+ + 2OH-   only SiOC
Cu → Cu^+ +e^- SiOC, SiC, SiCN

extrinsic

moisture (H_2O) diffusion
SiOC –high, SiC- low, SiCN-none

S. King et al ECS J. Sol. Stat. Sci.Tech. 1(6) N115 (2012)

- **Hydrogen (esp in presence of oxygen) prone to ionize Cu**
- **Source of Cu^+ ions vs Cu^+ diffusivity issue**
- **Density g=2.1g/cm3 critical for H_2O diffusion**

Virginia Tech

Summary

- When Cu electrode is powered a permanent Cu filament can be formed.
- Cu filament cannot be ruptured due to cylindrical form caused by Ti counter electrode.
- Cu filament formation in SiC:H and SiCN:H possible for a minimum compliance current.
- At high I_{cc} the ON-Resistance is very low ~ 5Ω.
- In case of SiOC:H a two stage transition from 200 MΩ to 150 kΩ and then from 150 kΩ to 10 Ω (ratios 10^3 and 10^4, respectively). The ratios can be tuned by choice of I_{cc} level.
- Low density of SiOC:H cannot support initially high density Cu filament. Only local heating of the Cu electrode provides a source of Cu atoms to densify Cu filament.
- The formation mechanism can be used to realize a PROM memory or FPGA capability.
- A special application could be self-aligned formation of electric vias by voltage pulses or voltage ramps.
- A good Cu diffusion barrier may mean not only low Cu+ mobility but also low Cu ionization potential

Virginia Tech