Energetics of Recrystallization in Electroplated Copper Thin Films and Effects of Texture

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  - **Co-authors*

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  - Michael Rizzolo
  - Eric Eisenbraun
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  - Seung-Yub Lee
  - Hande Ozturk
  - Adrian Chitu

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Outline

- **I. Introduction**
  - a) Instruments and Methodologies
  - b) High Resolution XRD Method
- **II. Modulators of Recrystallization Time**
- **III. Energetics**
- **IV. Location of initial nucleation and growth**
- **V. Conclusions**

Introduction

References:

Prediction of recrystallization times in electroplated copper thin films; Mikhail Treger, Christian Witt, Cyril Cabral Jr., Conal Murray, Jean Jordan-Sweet, Robert Rosenberg, Eric Eisenbraun, I.C. Noyan, Thin Solid Films (2016) **doi:10.1016/j.tsf.2016.06.056** (**http://www.sciencedirect.com/science/article/pii/S0040609016303005**)

Characterization of room temperature recrystallization kinetics in electroplated copper thin films with concurrent x-ray diffraction and electrical resistivity measurements; Mikhail Treger, Christian Witt, Cyril Cabral Jr., Conal Murray, Jean Jordan-Sweet, Robert Rosenberg, Eric Eisenbraun, I.C. Noyan, J. Appl. Phys. 113, 214904 (2013); http://dx.doi.org/10.1063/1.4807899

Evolution of strain energy during recrystallization of plated Cu films; Conal E. Murray, R. Rosenberg, C. Witt, M. Treger and I. C. Noyan, J. Appl. Phys. 113, 203515 (2013); http://dx.doi.org/10.1063/1.4807409

Motivation

For the last 10-15 years copper has been the interconnect material of choice:

I. Performance & Reliability
   1. Low resistivity
   2. High resistance to electromigration
   3. Inexpensive

II. Challenges with Copper
   1. Difficult to pattern using conventional etching techniques
   2. Quickly diffuses into silicon devices
   3. Undergoes room temperature recrystallization

What is the source of this phenomenon and how might we control it?

Motivation

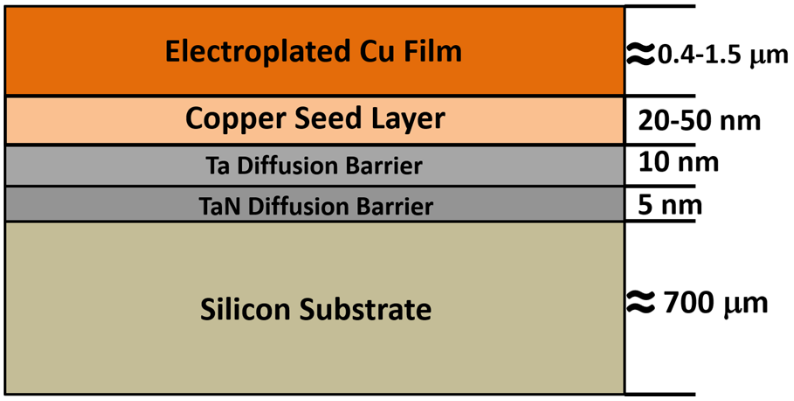
For the last 10-15 years copper has been the interconnect material of choice:

I. Performance & Reliability
   1. Copper has very low resistivity
   2. Copper has a high resistance to electromigration

II. Room Temperature Recrystallization
   1. Very small 20-50 nm crystals grow to be 1-2 μm in size
   2. Recrystallization typically occurs at $T/T_m=T_h>0.4$; T_m of Cu = 1082 ^{0}C
   3. RT recrystallization occurs at $T_h \approx 0.2$!

What is the source of this phenomenon and how might we control it?

Samples



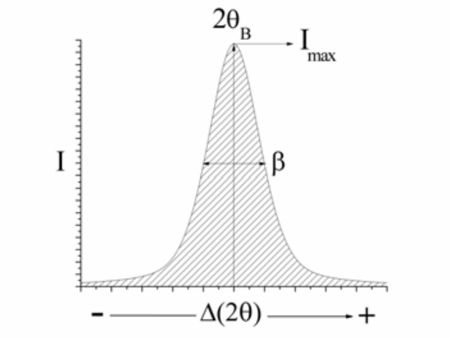
Parameters Studied

1. Plating Parameters
   - Additive/Impurity Conc.
   - Thickness of Film
   - Texture of Film
2. Seed Layer Parameters
   - Texture
   - Thickness of Seed
   - Metallurgies
3. Diffusion Barriers
   - α-Ta/TaN
   - β-Ta
4. Storage Temp.
5. Interfacial Roughness

Methodologies

- TEM
  - Direct microstructural info.
  - High resolution but very local
  - Destructive
  - Time consuming sample prep.
- FIB/EBSD/SEM/SIMS
  - Direct microstructural info.
  - Flexible length scales
  - Destructive if combined with FIB
  - Surface sensitive
- Electrical Resistivity
  - Non-destructive and real-time
  - Requires a priori model to obtain microstructural info.
- Lab XRD
  - Volume averaged
  - Non-destructive
  - Limited energy selectivity, resolution and flux
- **Synchrotron XRD**
  - Volume averaged microstructural
  - Non-destructive
  - High resolution needed for this length scale
  - High flux allows for real-time kinetics studies
- **Goals:**
  - Effects on recrystallization time
  - Effects on microstructural parameters, i.e. grain size

XRD Characterization



$$\lambda = 2d\sin(2\theta/2)$$

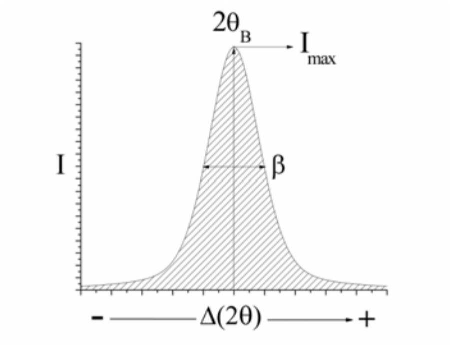
$$\varepsilon_z = \frac{d_{hkl} - d_0}{d_0}$$

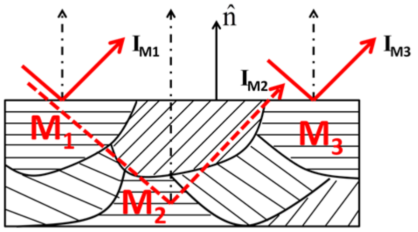
$$D_{hkl} = t = \frac{C\lambda}{\beta\cos(\theta_B)}$$

Diffraction Peak Parameters → Direct Microstructural Information:

1. Bragg Angle shifts are proportional to strain
2. Integrated Intensity is proportional to scattering volume
3. Full Width at Half Max (β) is inversely proportional to thickness perpendicular to the film surface.
4. **Thus we can monitor the out-of-plane strain, out-of-plane grain size and volume fraction of any grain population with time.**

XRD Characterization





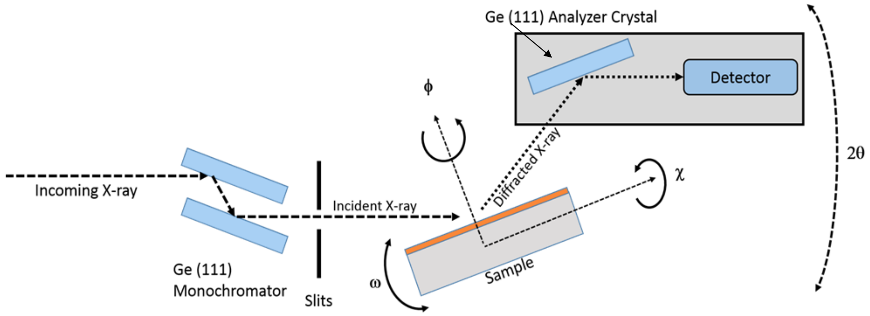
$$\bar{I}_{hkl} = \int I(2\theta)\,d(2\theta) \propto V_{hkl}$$

Diffraction Peak Parameters → Direct Microstructural Information:

1. Bragg Angle shifts are proportional to strain
2. Integrated Intensity is proportional to scattering volume
3. Full Width at Half Max (β) is inversely proportional to thickness perpendicular to the film surface.

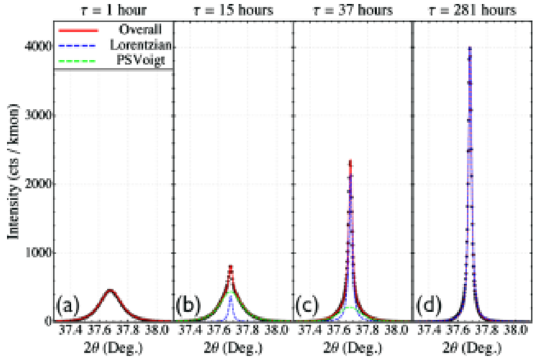
The out-of-plane strain, out-of-plane grain size and volume fraction are orientation specific.

X-ray Setup



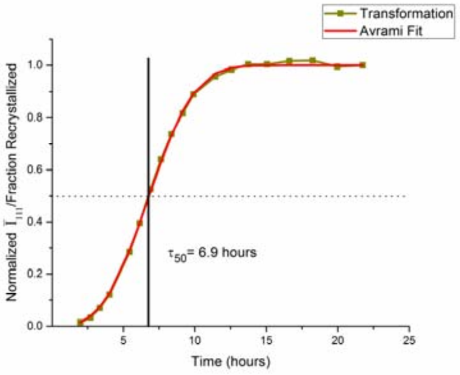
- Schematic view of X20a beamline at NSLS-I in the high resolution setup
- Analyzer crystal acceptance (≈.002^0)
- Incident flux ≈10^{10} photons/sec. Approximately 10^4 times that of a lab source

Synchrotron XRD vs. Time



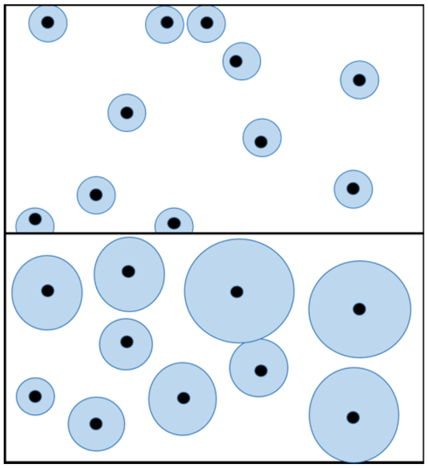
1. We monitor **β, θ_B,** and **Integrated Intensity** of the as-plated and transforming grains as a function of time.
2. Instrument resolution is very high (β = .0089 deg.). Can resolve up to 1μm size particles.
3. **As-plated grains** are modeled with a **Pseudo-Voigt** (Green).
4. **Recrystallized grains** are modeled with a **Lorentzian** (Blue).
5. As recrystallization progresses **the Lorentzian grows while the PSV decreases**.

Johnson-Mehl-Avrami-Kolmogorov (JMAK) Model



- **f_{trans}= 1-exp[-Kt^n]**
- **τ_{50}= [ln[0.5]/[-K]]$^{1/n}$**
- ***f_{trans}***= *Fraction Recrystallized*
- τ_{50}= 50% recrystallization point
- ***K***= *constant encompassing nucleation and growth rate*
- ***n***= *"order" of growth constant*
  - *3D Growth: n=3-4*
  - *2D Growth: n=2-3*
  - *1D Growth: n=1-2*

Johnson-Mehl-Avrami-Kolmogorov (JMAK) Model



- ➢ $f_{trans} = 1-\exp[-Kt^{n}]$
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- ➢ f_{trans}= *Fraction Recrystallized*
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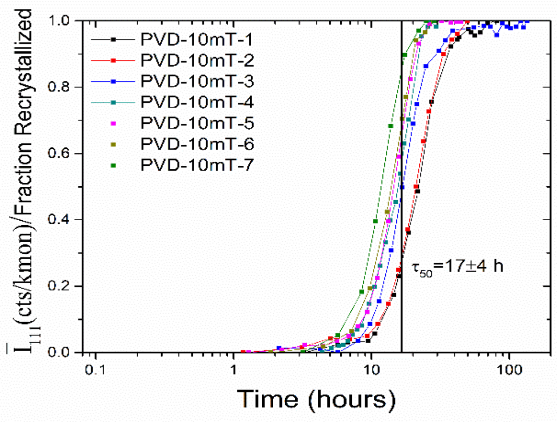
  - •*3D Growth: n=3-4*
  - •*2D Growth: n=2-3*
  - •*1D Growth: n=1-2*

Modulators of Recrystallization Time

Submitted: Thin Solid Films (under second review)

Repeatability

- Seven coupons,
- All from the same wafer,
- Identical chemistry and plating parameters.

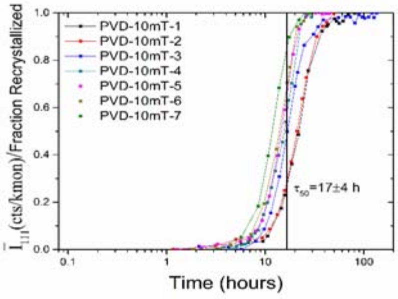


Repeatability

- **Seven coupons,**
- **All from the same wafer,**
- **Identical chemistry and plating parameters.**

$R_{Tx}= \bar{I}_{111}/\bar{I}_{200}\Big|_{\tau=\tau_0}$

Coupon ID	τ_{50} (hours)	K(x 10^{-4})	m	$R_{Tx}= \bar{I}_{111} /\bar{I}_{200}\Big|_{\tau=\tau_0}$
PVD-10mT-1	21±2	0.54±0.38	3.09±0.23	145±11
PVD-10mT-2	21 ±2	1.1±0.73	2.86±0.21	139±10
PVD-10mT-3	17±2	0.67±0.86	3.24±0.44	107±7
PVD-10mT-4	15±2	0.93±0.5	3.28±0.20	99±5
PVD-10mT-5	15±2	0.69±.76	3.44±0.41	95±6
PVD-10mT-6	14±2	0.97±0.84	3.38±0.32	95±6
PVD-10mT-7	12±2	4.1±2.6	3.03±0.26	77±5
Average	17±4	1.28±1.25	3.2±0.2	109±25



Repeatability

- Seven coupons,
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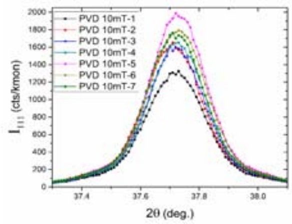
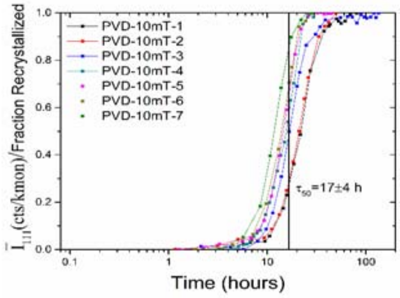


111 Cu reflections from Cu seed 10mT Ar pp.



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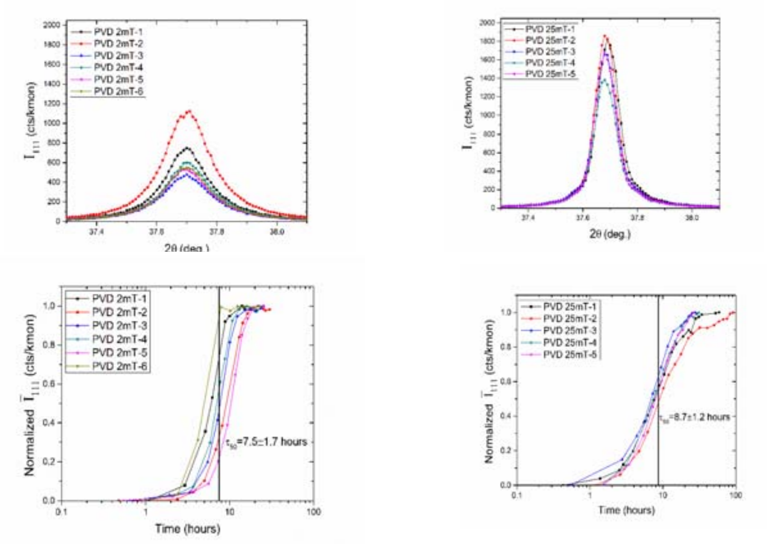
Seed Layer Texture-1



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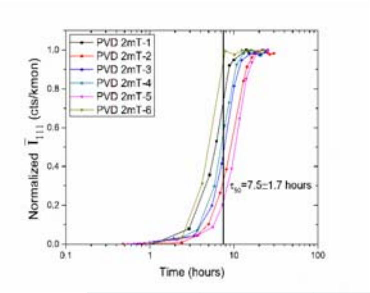
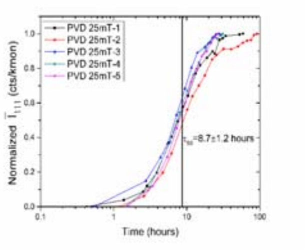
PVD seed, 50 nm,@ 2mTorr and 25mTorr Ar pp.

Seed Layer Texture-1





Sample ID	Argon PP (mTorr)	τ_{50} (hours)	R_{Tx}	K(x 10^{-4})	m
PVD-2mT	2	7.6±2.0	27±14	14±9	3.3±0.4
PVD-25mT	25	8.7±1.2	44±9	236±101	1.6±0.3

$$R_{Tx}=\bar{I}_{111}/\bar{I}_{200}\Big|_{\tau=\tau_0}$$

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PVD seed, 50 nm,@ 2mTorr and 25mTorr Ar pp.

Film Thickness-1

Sample ID	Film Thickness (µm)	R_{Tx}	τ_{50} (hr)	K(x 10^{-4})	m
PVD-20	0.4±0.06	1736±376	--	--	--
PVD-30	0.55±0.07	1476±302	--	--	--
PVD-40	0.7±0.01	854±87	150±10	2.9±0.3	1.56±.02
PVD-60	0.8±0.03	534±77	59±6	3.2±0.4	1.89±.03
PVD-80	1.0±0.06	267±32	40±10	10±0.4	1.80±.01

$$R_{Tx}=\bar{I}_{111}/\bar{I}_{200}\Big|_{\tau=\tau_0}$$

50 nm PVD seed layer deposition at 10 mTorr Ar partial pressure,.
Identical electroplating process for all coupons.
Gradually longer plating times.

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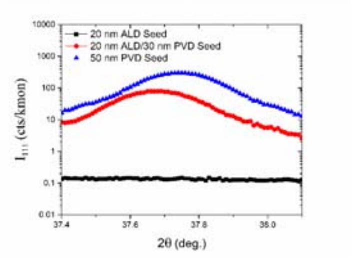
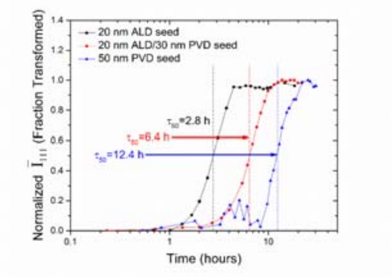
Seed Layer Texture-2





	Seed Layer Stack	τ_{50} (hours)	R_{Tx}	Seed $\bar{I}_{111}$	Electroplated Film Thickness (µm)
ALD	20 nm ALD	2.8±0.3	6±1	3E-4±7E-5	1.35±0.12
PVD-ALD	20 nm ALD on 30 nm PVD	6.4±0.4	19±1	0.37±8E-3	1.39±0.09
PVD	50 nm PVD	12.4±0.8	112±10	1.36±0.16	1.37±0.10

$$R_{Tx} = \bar{I}_{111}/\bar{I}_{200}\Big|_{\tau=\tau_0}$$

Film Thickness-2

Sample ID	Film Thickness (µm)	R_{Tx}	τ_{50} (hours)
ALD-20	0.33±0.06	4.0±0.2	48±5
ALD-40	0.64±0.05	5.1±0.2	12.0±1.2
ALD-60	0.85±0.08	5.9±0.1	8.2±0.8
ALD-80	1.00±0.11	6.4±0.1	7.4±0.5

$$R_{Tx} = \bar{I}_{111}/\bar{I}_{200}\Big|_{\tau=\tau_0}$$

Dependence of the 50% recrystallization time, and the time-zero texture ratio, R_Tx with electroplated film thickness when an **ALD Cu seed layer is used**.

Other Metallurgies

Sample ID	Diffusion Barrier	Seed Layer Stack	τ_{50} (hours)	R_{Tx}	Seed $\bar{I}_{111}$	Electroplated Film Thickness (μm)
PVD-Co	10 nm α-Ta on 5 nm TaN	20 nm Evap Co on 30 nm PVD Cu	8.4±0.9	31±2	0.35±.01	1.49±0.16
PVD-Evap-Cu	10 nm α-Ta on 5 nm TaN	20 nm Evap Cu on 30 nm PVD Cu	7.6±0.7	25±4	0.43±.01	1.73±0.29
PVD-β-Ta	10 nm β-Ta	50 nm PVD	9.1±0.2	55±4	4.0±0.25	1.34±0.16

$$R_{Tx}= \bar{I}_{111}/\bar{I}_{200}\Big|_{\tau=\tau_0}$$

Recrystallization responses for Cu films electroplated on evaporated Co and Cu seed layers (first two rows) and on a PVD Cu layer deposited on a single 10 nm thick layer of β-Ta.

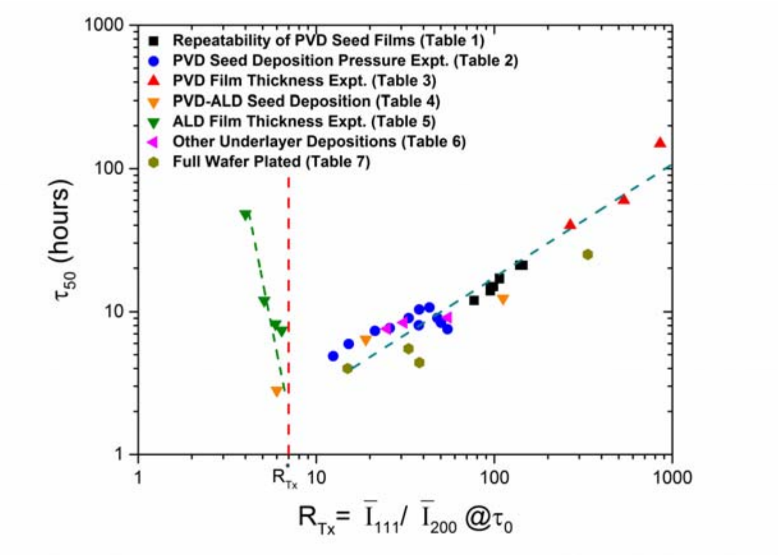
Manual vs. Industrial Plating

Sample ID	Film Thickness	τ_{50} (hours)	R_{Tx}
I-PVD-400	0.55±0.03 μm	25±1	335.±19
I-PVD-600	0.85±0.05 μm	4.4±0.1	38±9.
I-PVD-800	1.14±0.07 μm	5.5±0.2	33.±8
I-PVD-1000	1.48±0.02 μm	4.0±0.1	15±0.3

$$R_{Tx}= \bar{I}_{111}/\bar{I}_{200}\Big|_{\tau=\tau_0}$$

Recrystallization time of films electroplated on 50 nm PVD seeds by industrial full wafer plating.

Summary-I



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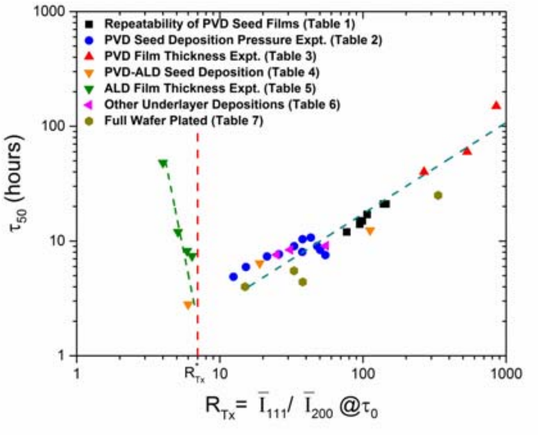
Summary-I

Control of chemistry and plating parameters are insufficient to control plated film recrystallization.

Processes that do not change the *texture ratio at time zero*, R_{Tx}, do not change recrystallization time.

Plastic flow due to thermal contraction is an example:



Immediately after plating coupons were stored in:

Ice-water (O °C)
Dry ice (−78.5 °C)
Liquid nitrogen (−195.8°C)

τ_{50} did not change within error.

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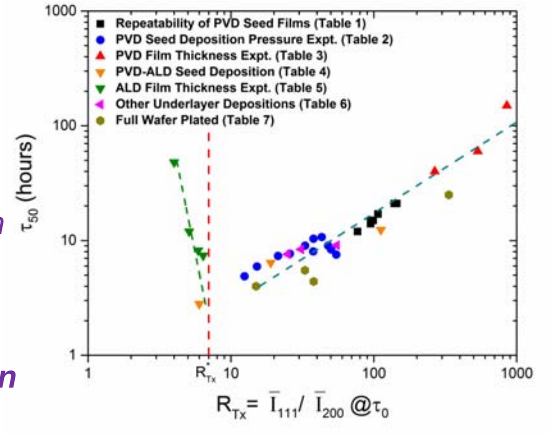
Summary-I

Seed layer texture is the biggest driver of R_{Tx},

Characterizing:
1-Thickness and texture of seed layer
2- R_{Tx} ratio of the plated film
over the wafer surface will yield uniform τ_{50} values.



- ✓ ***Recrystallization rate in the trenches is controlled by local texture. [Prof. Dunn & co-workers; Prof. Ho +]***
- ✓ ***Techniques for controlling local texture in the trenches is needed.***

Energetics-I

There is a critical R^*_{Tx} value below which even very thin films recrystallize!

$R^*_x < 7$, 300 nm thick plated Cu films recrystallize @ T_R.

$R^*_x >> 7$, 400 nm thick plated Cu films do not recrystallize @ T_R.

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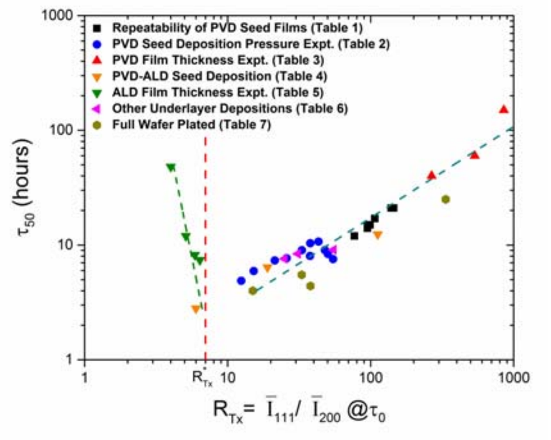

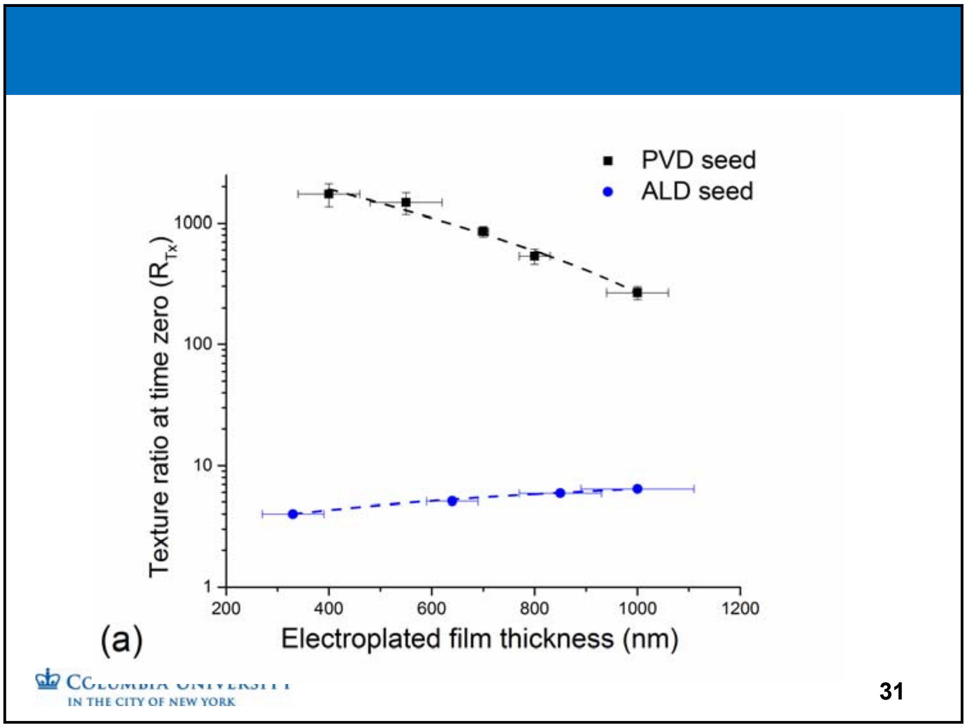
PVD seed
ALD seed
Texture ratio at time zero (R_{Tx})
1000
100
10
1
200
400
600
800
1000
1200
(a)
Electroplated film thickness (nm)
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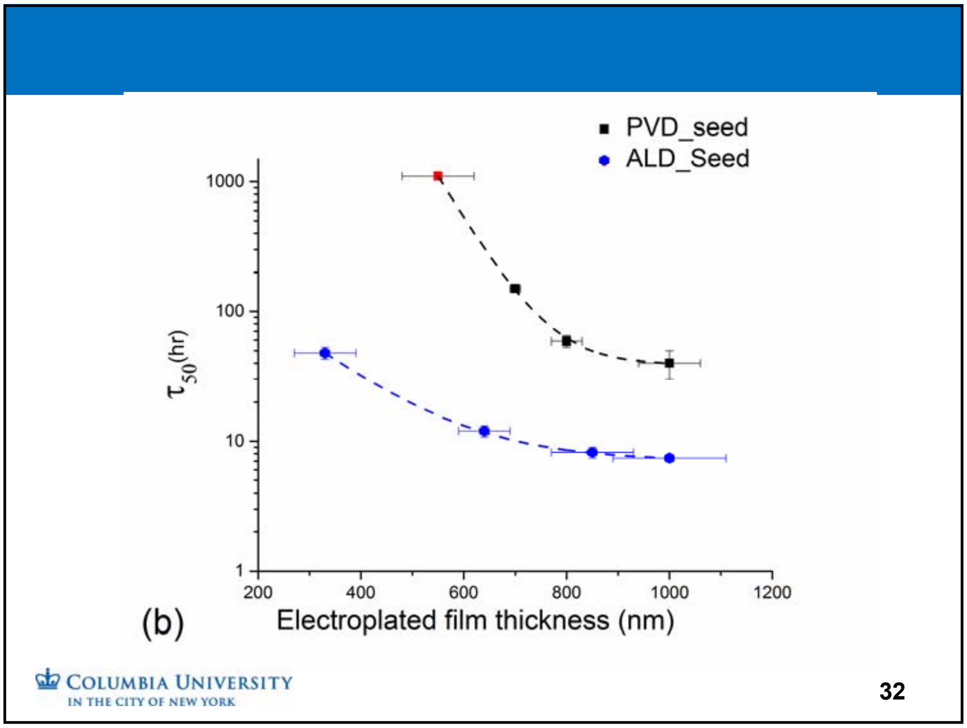
PVD_seed
ALD_Seed
τ_{50}(hr)
1000
100
10
1
200
400
600
800
1000
1200
(b)
Electroplated film thickness (nm)
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Energy Sources for Recrystallization

1. **Film Densification/Surface Energy Minimization**
   - **Elimination of grain boundaries**
   - **Curvature driven surface energy minimization of grain size**
   - **Theoretically insufficient energy**
2. **Stacking Faults and Dislocations (Defects)**
   - **Not observed**
     - J.M.E. Harper, C. Cabral, P. C. Andricacos, L. Gignac, I. C. Noyan, K. P. Rodbell, and C. K. Hu, Journal of Applied Physics 86, 2516 (1999).
3. **Impurities**
   - **Not supported by recent observations**
     - M. Rizzolo, S. Novak, E. Lifshin, and K. A. Dunn, Applied Physics Letters 101, 101901 (2012).
   - As yet there has been no demonstrated connection:
     - Between Impurities and Texture
     - Impurity type and Texture
4. **Residual plating stress energy is unevaluated!**
   - **Dismissed in literature as likely too small, but never quantified**
   - In 2013 we showed there exists a threshold for in-plane biaxial stress below which recrystallization does not occur (this is 0.1 J/m^2 at a ε=0.1%)

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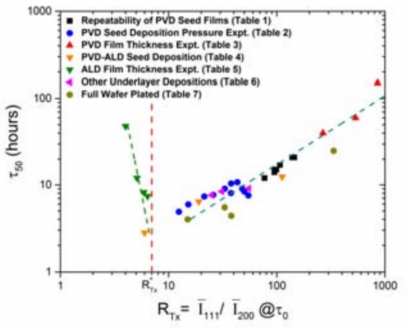
MODEL?

Room temperature recrystallization depends on the interplay between plating strain and surface energy minimization processes for a given texture!

Our data is insufficient to develop and test a full predictive model.

This is primarily due to the variability of our samples.



- **Needed**: plated films with:
  - Uniform thickness,
  - Uniform specified texture,
  - Frozen immediately after plating
  - With before/after curvature measurements.

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In Closing

We have also performed:

- *More EBSD vs. X-ray measurements,*
- *Resistivity vs. X-ray measurements,*
- *Activation energy determination,*
- *Effect of bending stress, etc.*

We hope to publish these results shortly.

Thank you for your attention