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Origins of Stress During Electrodeposition

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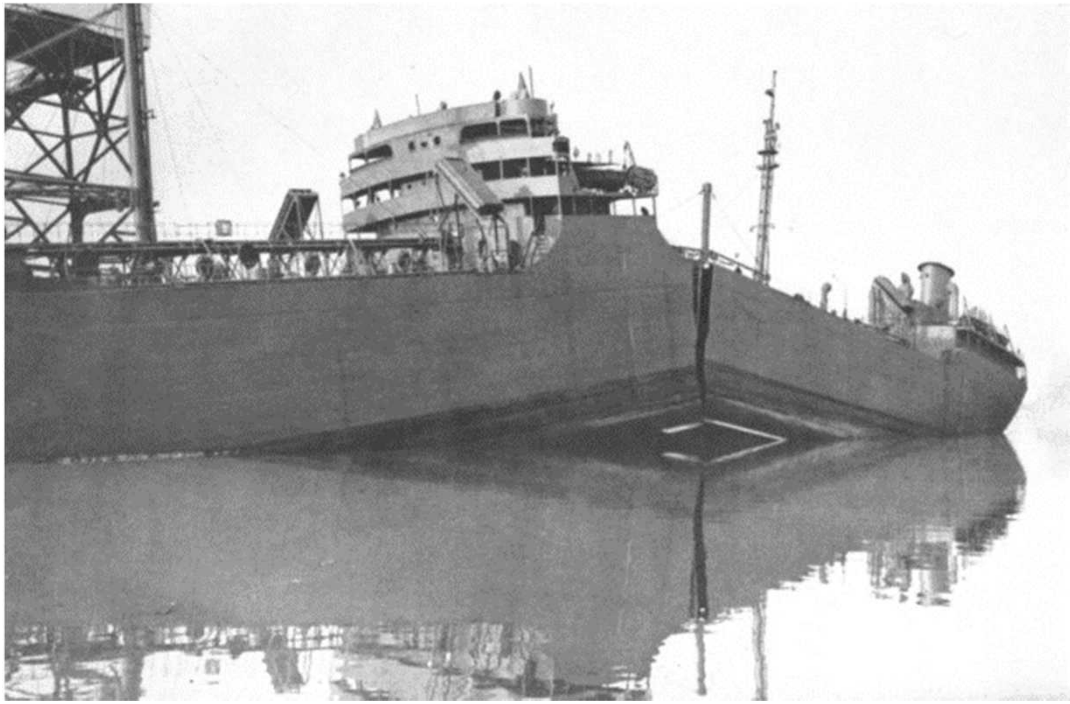
Stress can be bad!

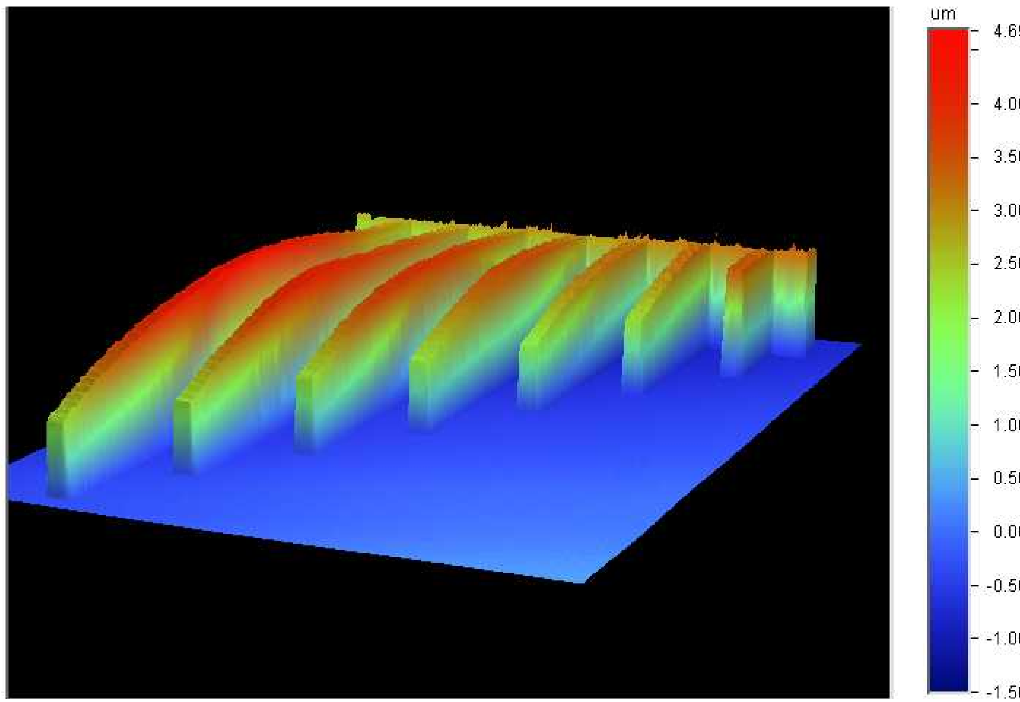


- Likely the most famous intrinsic stress induced failure.
- Stress is the result of changes in density.

Thin Film Stress

- **Stress is a main factor that limits the structures that can be fabricated.**

Interference micrograph of electroplated Ni cantilevers



- **Electrodeposited Ni typically has a gradient in the stress.**
- **This induces a curvature in free-standing parts.**

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Intrinsic stresses

Growth flux driven

- Island coalescence
- Lattice mismatch
- Capillarity
- Interstitial incorporation

Accepted mechanisms

- Adatom strain fields
- Chemical potential driven adatom insertion
- Dislocation
- Excess vacancy (or interstitial) reduction

Debated mechanisms

Microstructural reorganization

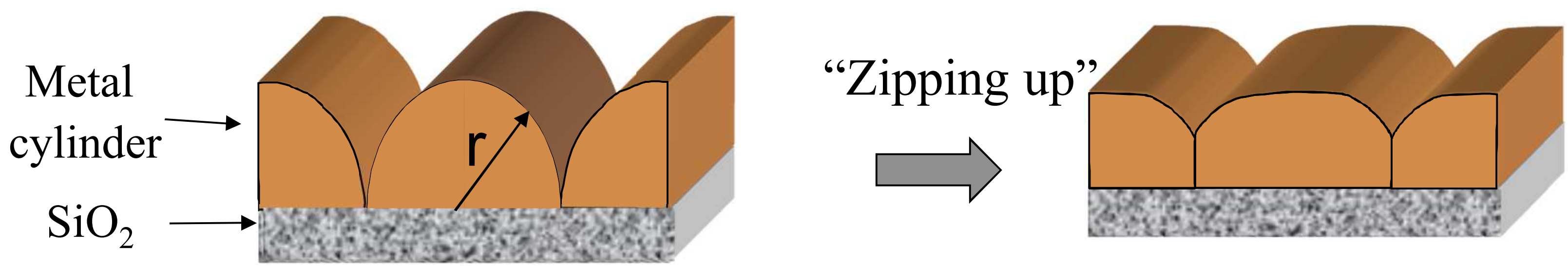
- Grain Growth
- Phase changes
- Alloying
- Thermal Stress

Accepted mechanisms

- Island coalescence
- Lattice mismatch
- Capillarity
- Interstitial incorporation

Island coalescence – Tensile stress

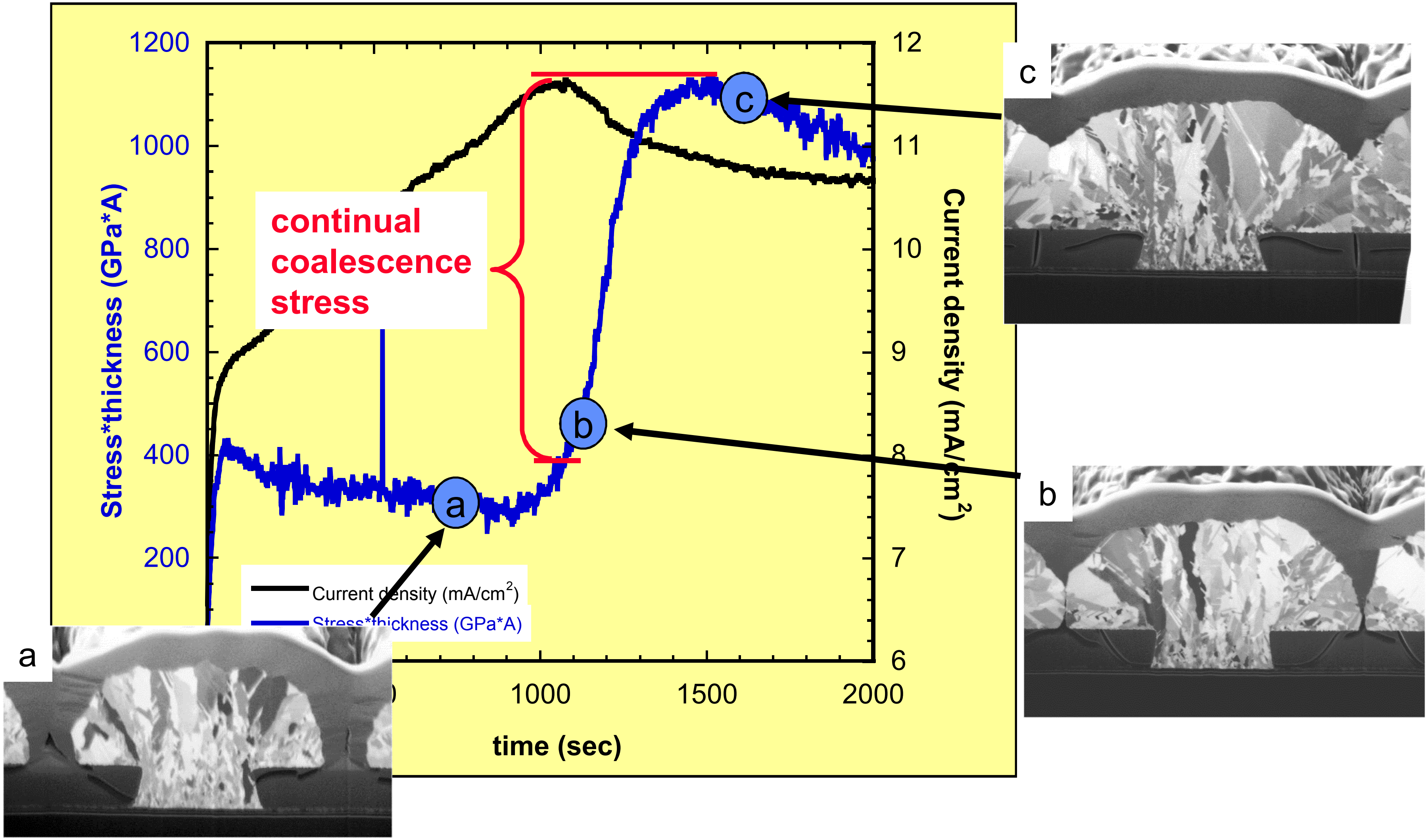
There are a number of models for the stress creation during island coalescence. However, they are all based on the minimization of surface area.



- **Hoffman**[1] – estimated critical gap size needed for surface to snap together forming a grain boundary.
- **Nix**[2] – Model based on crack closure in 2-D cylinders – over estimates stress by 20x due to averaging of stress.
- **Seel**[3] - FEM of 2-D cylinders coalescing – predicts stress similar to those observed.
- **Freund**[4] – Analytical model based on Hertzian contact.

1 – Doljack and Hoffman, *Thin Solid Films* **12**, 71 (1972).
2 – Nix and Clemens, J. Mater. Res. **14**, 3467 (1999).
3 – S. C. Seel, et. al. JAP **88**, 7079 (2000).
4 – L.B. Freund, E. Chason, JAP **89**, 4866 (2001).

It is not the initial contact that matters.



As growth continues after coalescence the contact angle between islands increases.

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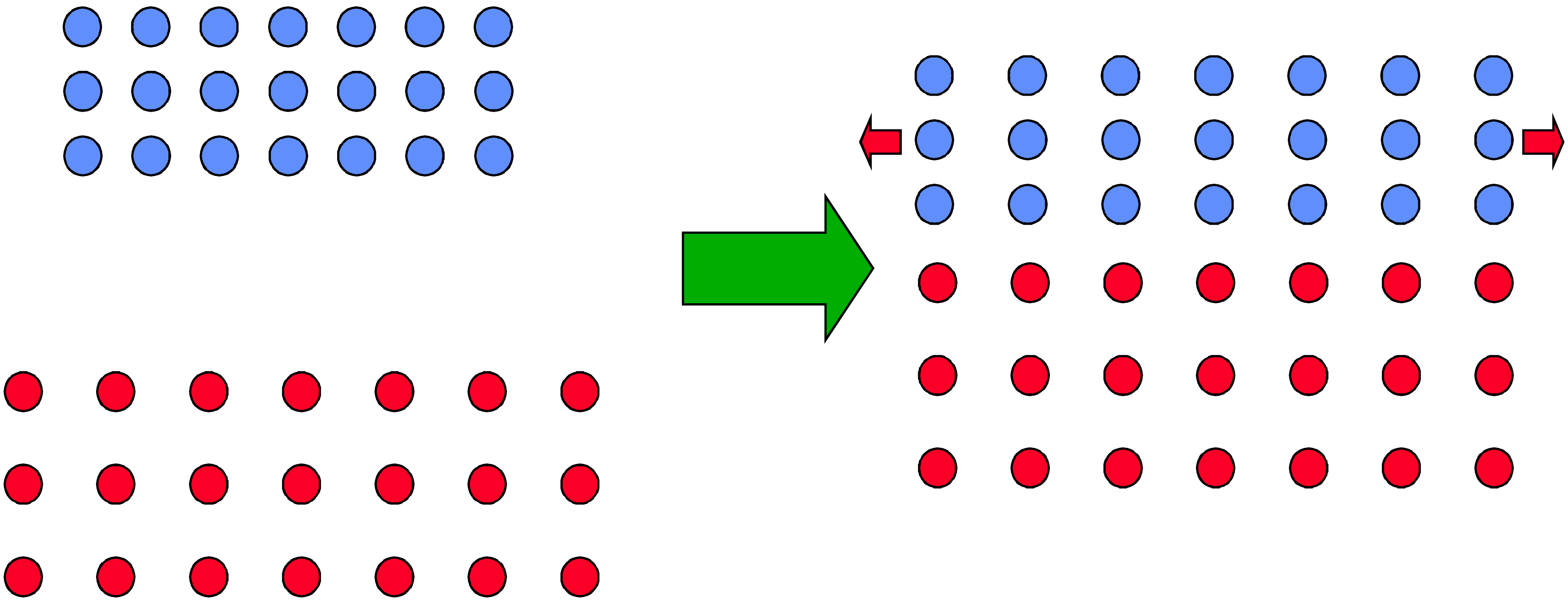
Lattice mismatch – Tensile / Compressive

Stress is induced by a difference in the lattice parameter between the film and the substrate

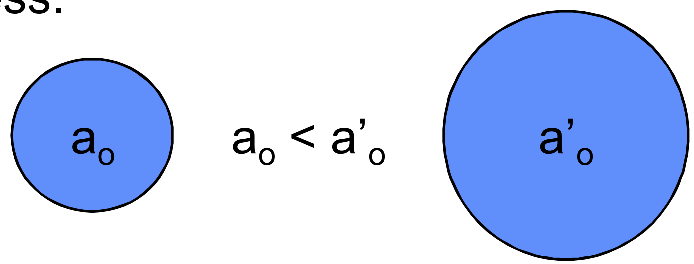


If the strain is large (greater than a few percent) the film my re-orient to grow with a different texture, which could potentially change the sign of the stress.

Capillarity Stress - Compression

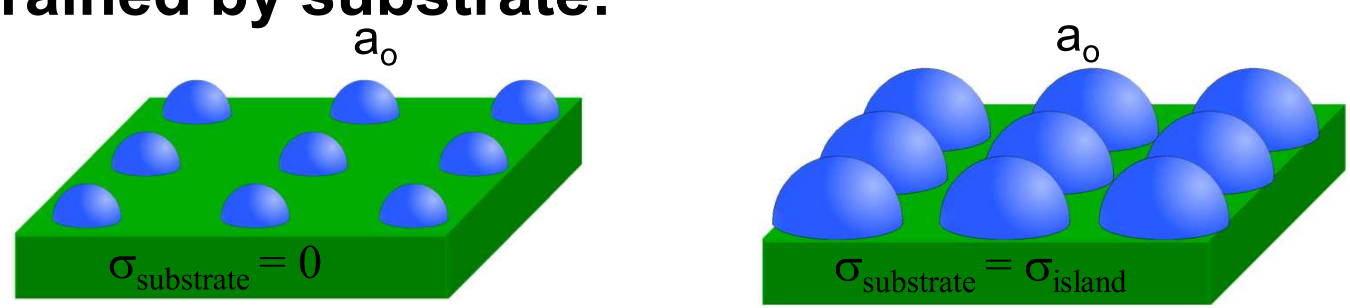
Free space:

A tensile surface stress causes the lattice parameter inside of a small sphere to be smaller then bulk, i.e. it is being squeezed by the surface stress.



The larger the sphere gets the less effect the surface has on it resulting in a larger lattice parameter in the sphere (that asymptotically approaches the bulk value).

Constrained by substrate:



Initially, the lattice parameter is smaller then bulk because of the surface stress. However, if it is attached to a substrate, the lattice parameter can not increase as the effect of the surface stress decreases.

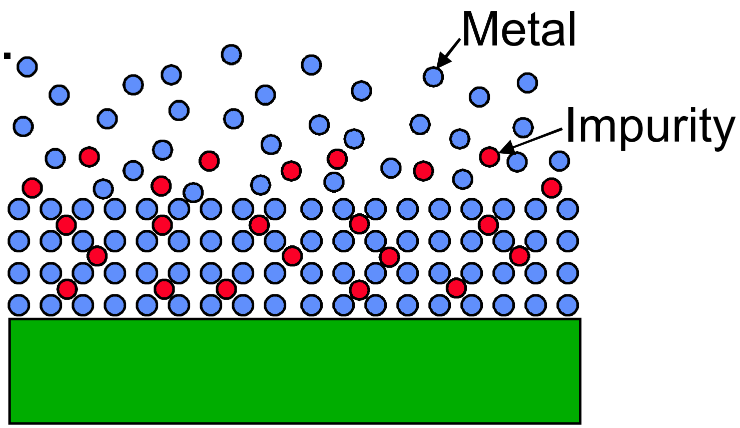
Robert C. Cammarata, Prog. Surf. Sci. **46**, 1 (1994).

Interstitial Incorporation - Compression

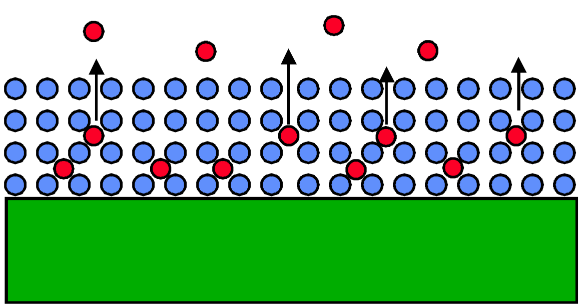
Following the argument of Armyanov, et al.[1] for hydrogen incorporation in Ni.

1. During plating the impurity will become trapped in the deposit creating a compressive stress.
2. When plating is stopped, mobile impurities, e.g. hydrogen, can will diffuse out of the film inducing a tensile stress.

1.



2.



1 – S. Armyanov and G. Sotirova-Chakarova, J. Electrochem. So **139**, 3454 (1992).

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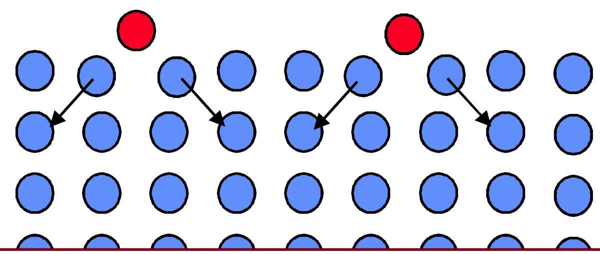
Debated Mechanisms

- Adatom strain fields
- Chemical potential driven adatom insertion
- Dislocation
- Excess vacancy (or interstitial) reduction

Adatom Strain Field - Compressive

Adatoms: Adatoms cause a distortion of the lattice that can induce a compressive stress if the distortion is locked into the lattice.

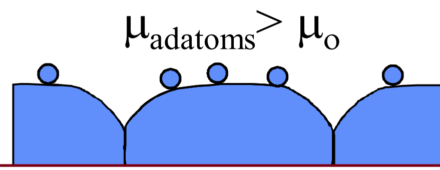


- Magnitude is too small to account for full compressive stress.
- Questionable if stress can be "locked in."

* C. Friesen and C.V. Thompson, Phys. Rev. Lett. **89**, 126103-1 (2002).

Adatom Insertion

Deposition of atoms results in an increased chemical potential on the surface of the grain due to a super-saturation of atoms on the surface.

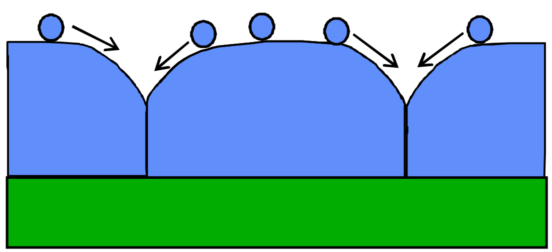


μ_o = chemical potential of free

Only indirect evidence of mechanism

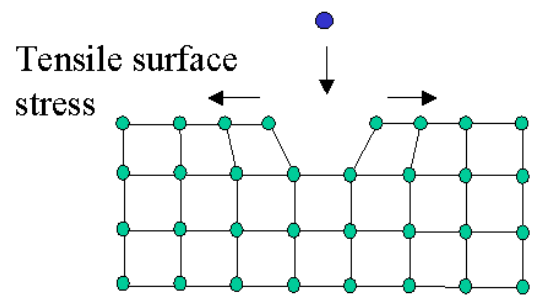
Likely low coordination trapping sites.

Grain-boundaries



*Chason, et al. Phys. Rev. Lett. **88**,156103 (2002).

Coalescing steps



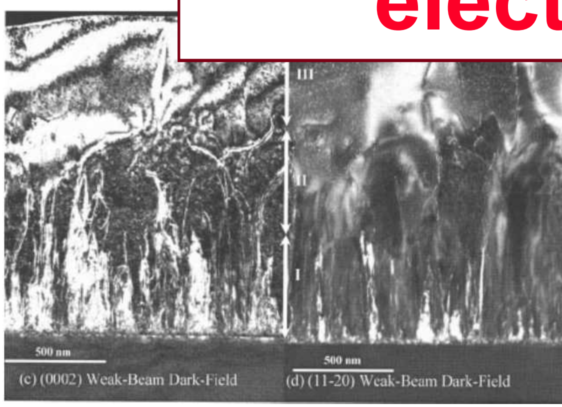
*W. D. Nix and B. M. Clemens, J. Materials Research **14**, 3467 (1999).

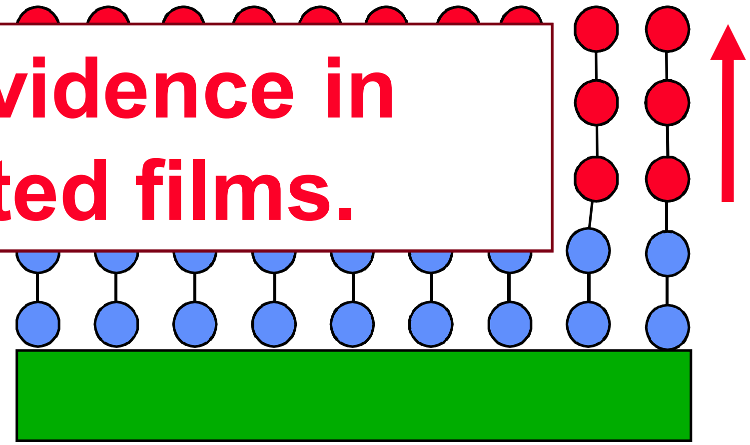
Dislocations – tensile or compressive

- **Dislocations are typically though of as stress reducing mechanisms.**
- **However, depending on the type and location of a dislocation it can create tensile or compressive stress.**
  - **The addition of an edge dislocation can induce t... stress depe... vector.**

After the insertion of an edge dislocation the film will be under compression.

No direct evidence in electroplated films.





- The elimination of threading dislocations in GaN has been linked to creation of tensile stress. (S. Raghavan, et. al. APL **88**, 041904 (2006)).
- Has not been proven as active mechanism in electrodeposited films (J. Dini, *Electrodeposition: The Materials Science of Coating and Substrates*, p299-300, 1993).

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Excess vacancy reduction – Tensile stress

- **During growth vacancies[1] and / or interstitial[2] atoms can be created.**
- **Since mobility of holes and interstitials is high they can diffuse to the grain-boundaries where they will either create tensile stress (vacancies) or compressive stress (interstitials).**

(1) L.B. Freund and S. Suresh, *Thin Film Materials – Stress, Defect Formation, and Surface Evolution,* p. 79-80 (2003).

(2) J. Rottler, D. Srolovitz, R. Car. Phys. Rev. B, **71**, 064109 (2005).

Diffusion process has been observed, but never proven to be a significant source of stress.

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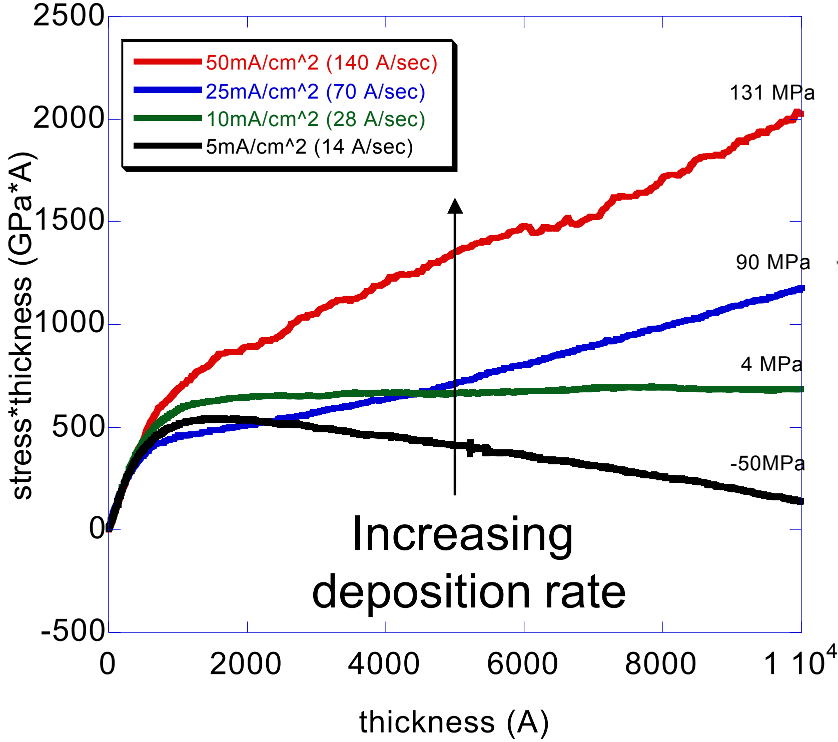
Electroplating Knobs to Vary Stress

- Deposition rate
- Bath Temperature
- Chemistry
  - Anion – unknown mechanism
  - Additives – various mechanisms
  - Co-deposition – various mechanisms

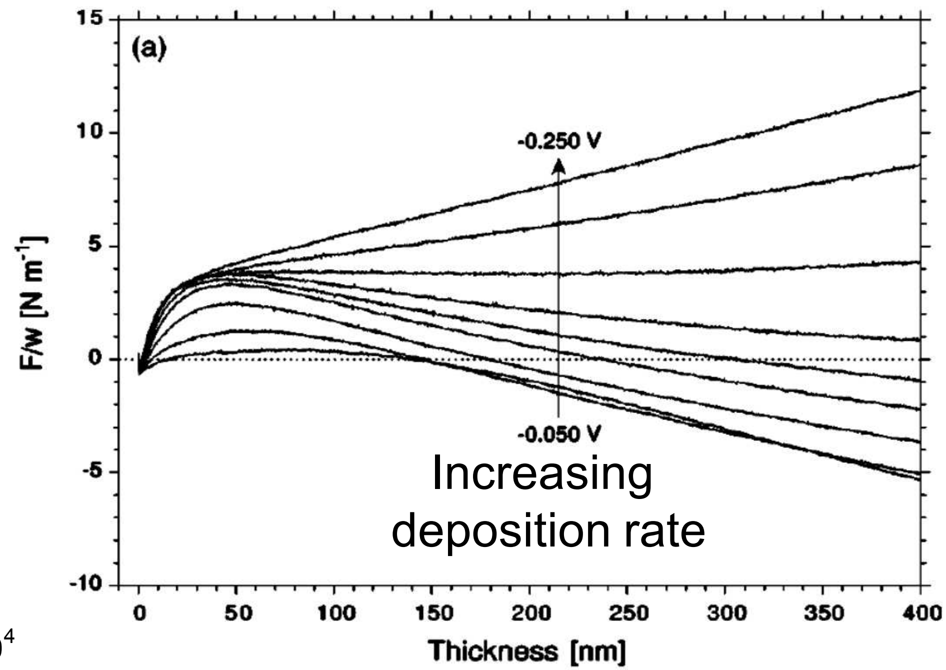
Deposition Rate effects on Stress

Electrodeposited Ni on Au



Sean J. Hearne and Jerry A. Floro
J. Appl. Phys. **97**, 014901 (2005)

Electrodeposited Cu on Au



O. E. Kongstein, U. Bertocci, and G. R. Stafford,
J. of the Electrochemical Society, 152, p. C116-C123 (2005)

Increased deposition rate yields more tensile stress

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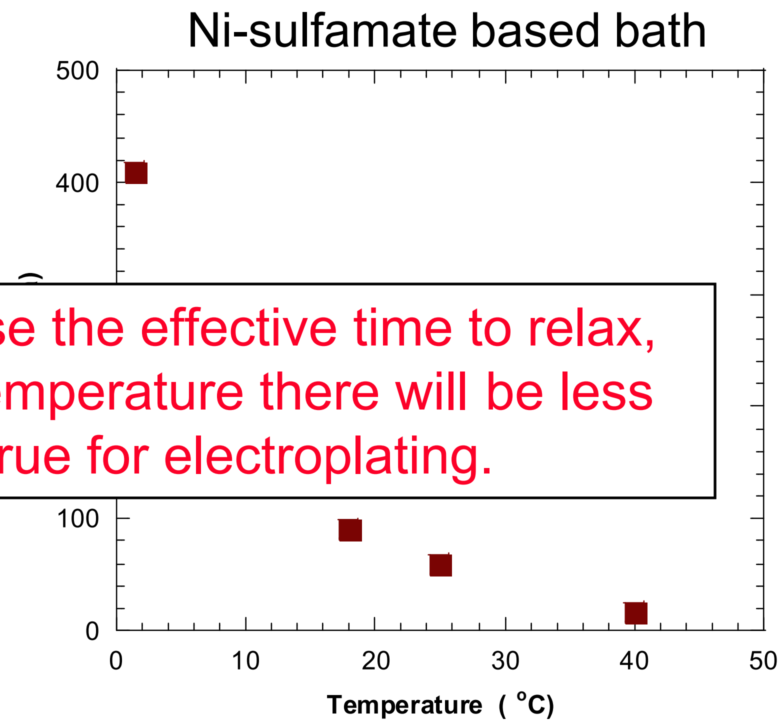
Bath temperature

- Increased temperature typically results in reduced stress.

- Pr in results in larger diffusion distances allowing for a lower energy state to be found by the adatom.

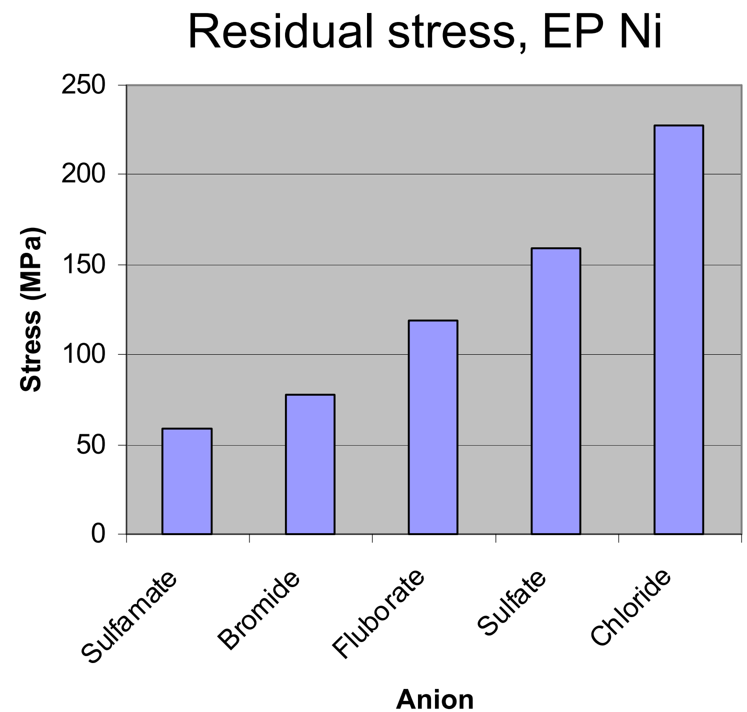
Take home point: If you increase the effective time to relax, either by lower rates or higher temperature there will be less stress. – true for vacuum world true for electroplating.



J.B. Kushner, *Metal Finishing* **58**, p 81 (1958).

Chemistry - Anion

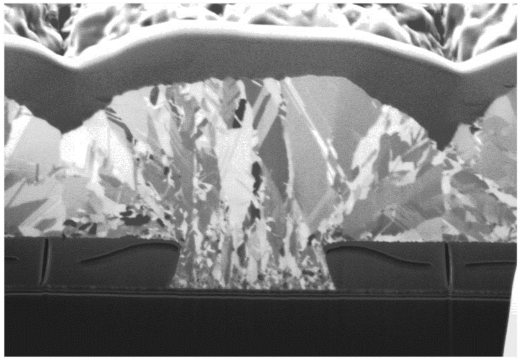
- **Varying the anion has been observed to have a strong affect on the intrinsic stress.**
- **The mechanism has not been identified.**

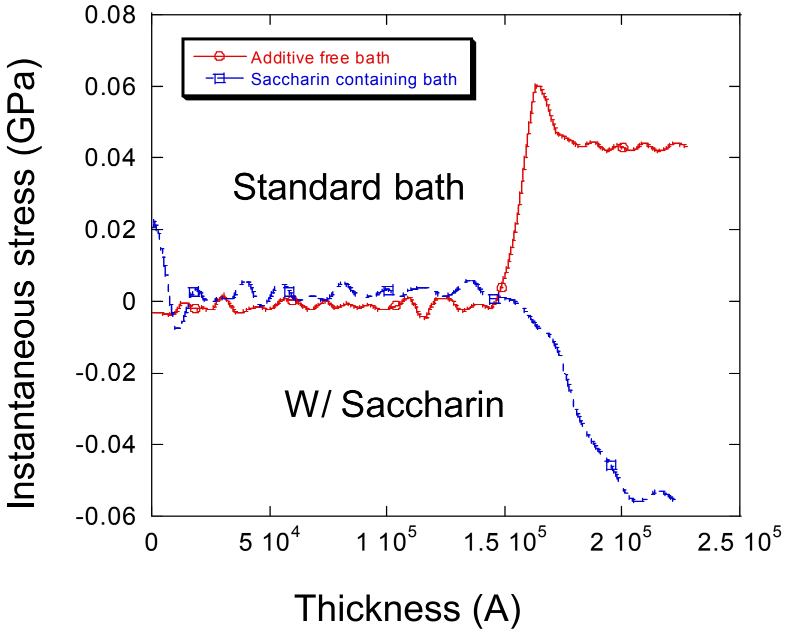


JB Kushner, Metal Progress, **81**, 81 (1962)

Chemistry - Additives

The addition of Saccharin in Ni eliminates the tensile rise caused by coalescence.

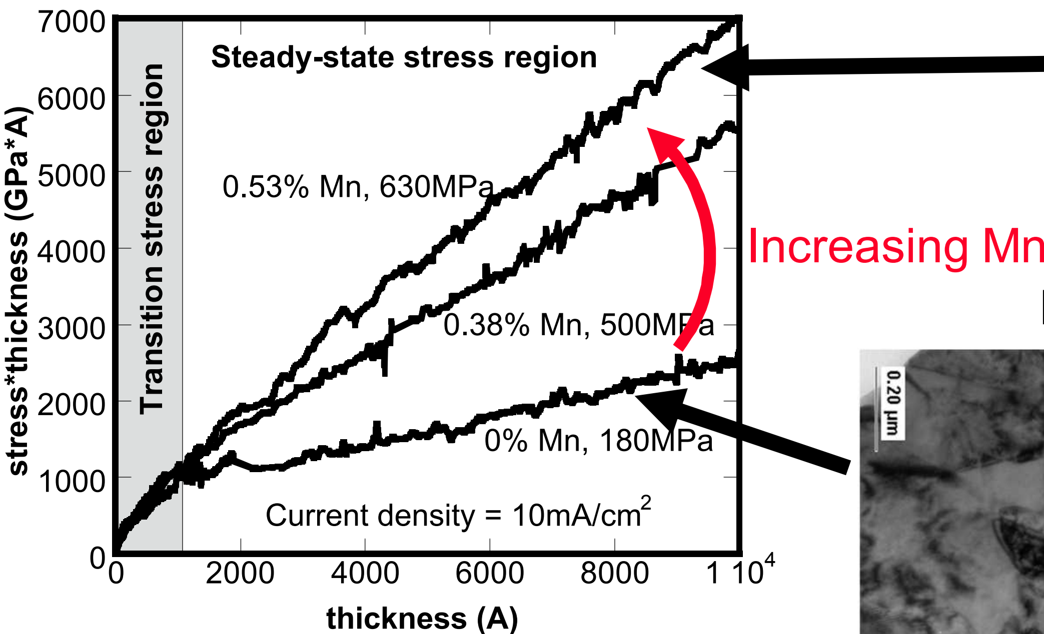




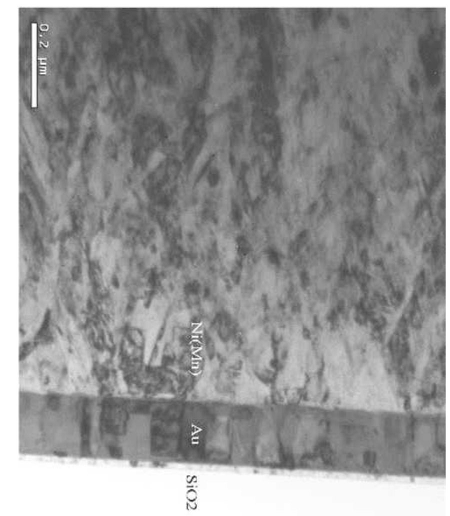
Chemistry – Co-deposition

Can result in tensile stress or compressive stress

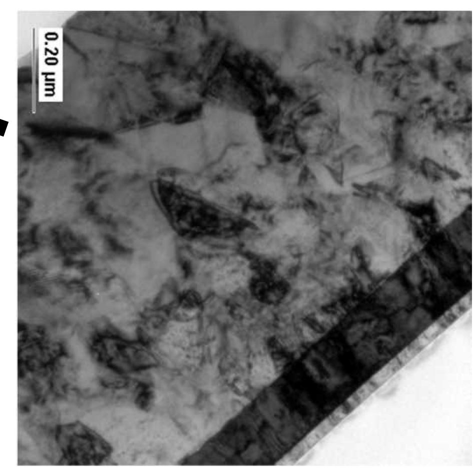
- **Alloying Ni with Mn results in tensile stress.**
- **This is likely the result of smaller grain inducing more coalescence stress or local lattice distortions.**



NiMn



Ni



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Take home points

- Multiple possible mechanisms for creating either tensile or compressive stress during electro-deposition.
- Accepted mechanisms
  - Island coalescence
  - Lattice mismatch
  - Capillarity
  - Interstitial incorporation
- Debated
  - Adatom strain fields
  - Chemical potential driven adatom insertion
  - Dislocation
  - Excess vacancy (or interstitial) reduction
- Stress can be varied greatly by varying the plating conditions.
- No one answer fills all.

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