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Electrodeposition of Chromium Film Using Cr^{3+} Solution

Fundamental Study of Crack Formation

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Introduction

What is the purpose of this study?

Understand issues with electrodeposition (ELD) of chromium (Cr) film from Cr^{3+} solution and then suggest an approach to address them.

What is ELD?

In ELD process by applying current metallic ions in solution reduce and form a metallic coating on the surface of an electrode.

Why Cr?

Cr has attractive appearance → decorative application

Cr is hard and anti-corrosion → engineering application

General approaches for ELD of Cr?

Cr(IV) ions → + high quality films

- highly carcinogenic ☹

Cr(III) ions → + environmentally friendly

- issues with quality due to **crack formation**

What have we done so far?

We fundamentally study the origin of cracks in the films.

We propose a promising approach to reduce the cracking.

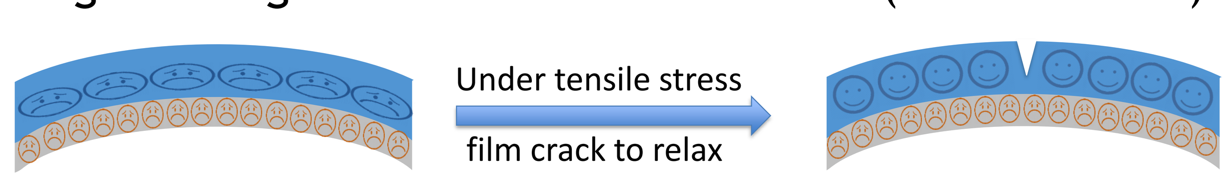
Background

Why do films crack?

1. low fracture toughness (Γ_f)

Critical thickness for fracture : $(h_f)_c \propto \Gamma_f$

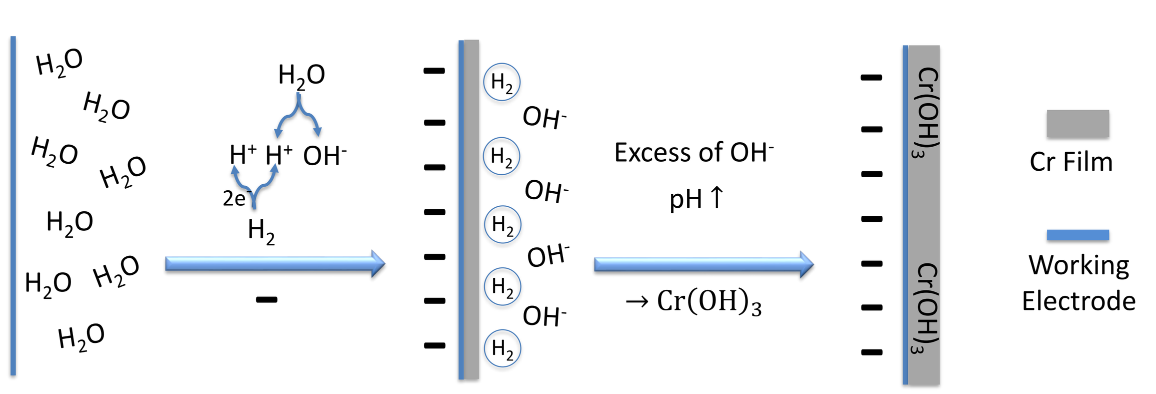
1. high driving force for crack formation (tensile stress)



Fracture Toughness in Cr(III) film?

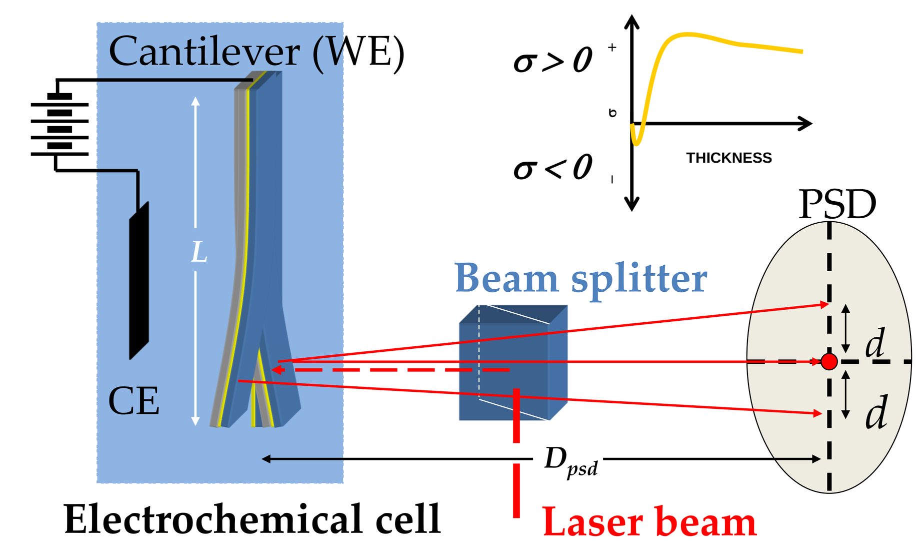
Cr(III) due to stability in aqueous solutions needs high overpotential to deposit. This causes electro-reduction of water. $H_2O \rightarrow H^+ + OH^-$

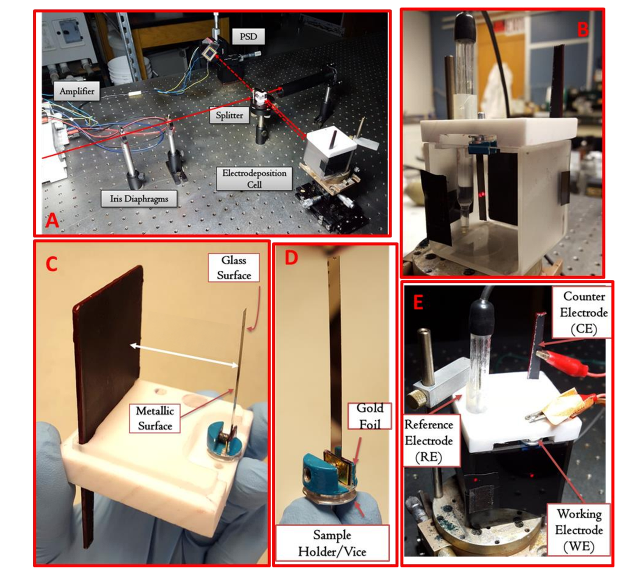
The resulted H^+ are consuming in the negative electrode surface which leads to high pH in the interface → in favor of $Cr(OH)_3$ formation in film which reduce fracture toughness



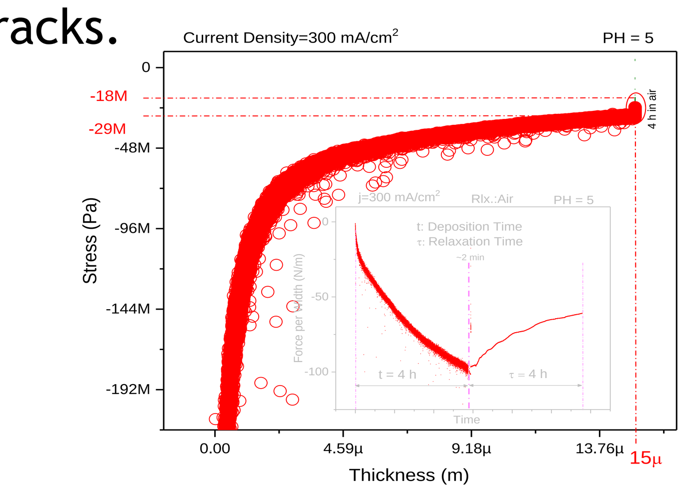
Experimental Stress data

Understanding stress-evolution during growth and relaxation of the film is the key to find the origin of cracks.





With our in-situ stress measurement set-up we observed value and nature of the stress during the growth and relaxation.

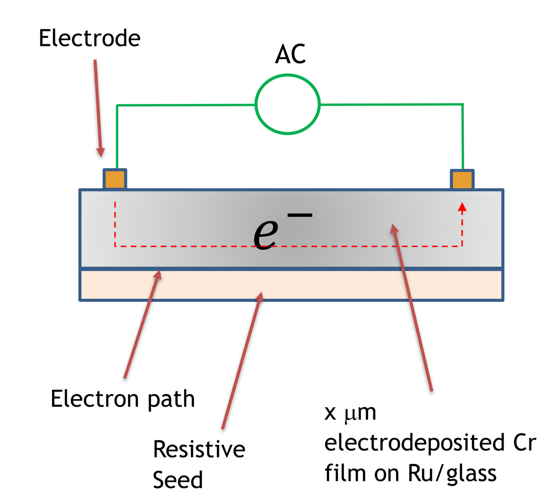


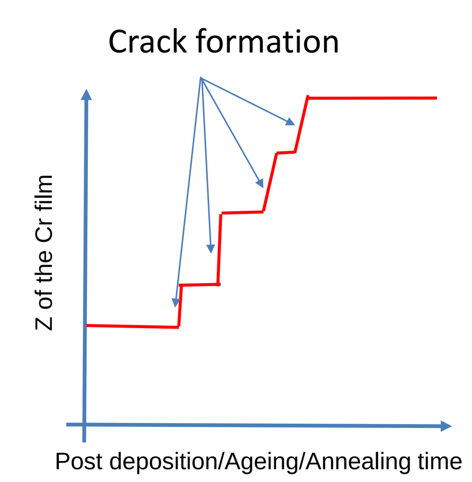
During the film growth: compressive stress → no crack formation

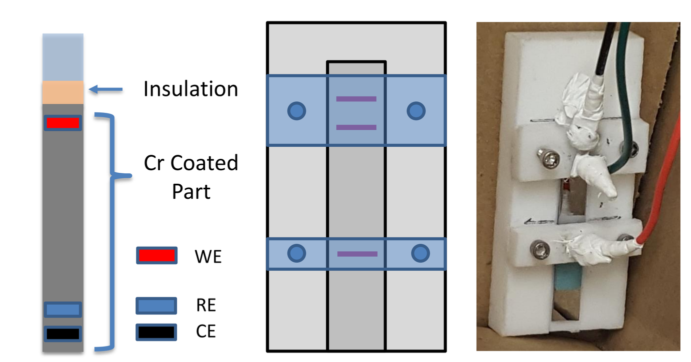
After the deposition: tensile stress relaxation → film cracking

Experimental Impedance data

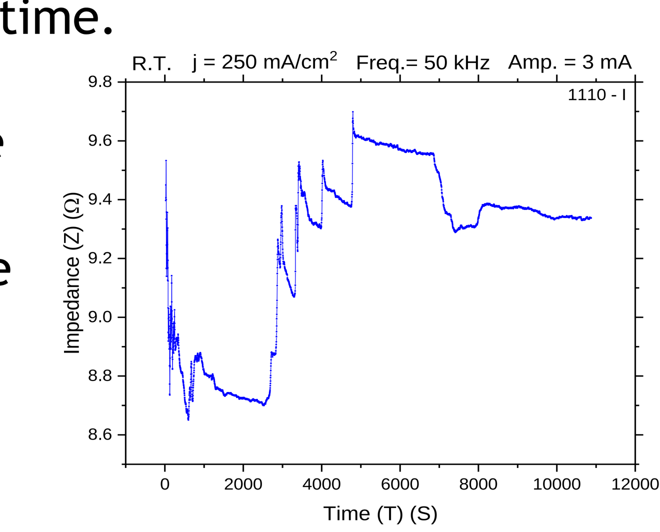
To further investigate the film post-deposition evolution we observed impedance transient of the film over time.







With our set-up we were able to see changes in impedance transient of the film after the deposition, which were indication of film evolution.

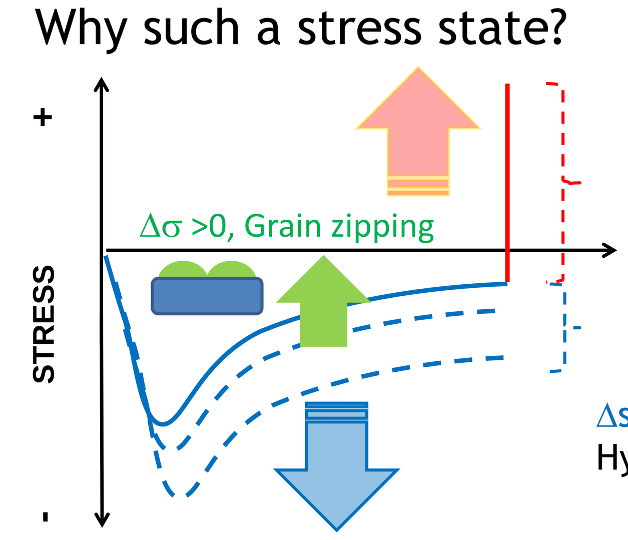


Overall increase in impedance transient→ crack formation

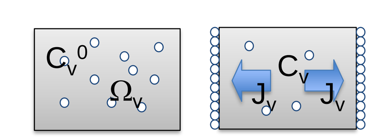
Inconsistency in the transient → decomposition and formation of scattering phases

Analysis

Why such a stress state?



Δs >0 ; f(t, T, s_R)
Ageing /annealing stress



σ_R =f(t,φ, (1- φ))
Steady state stress depend on balance between growth rate and hydrogen formation rate.

Δs <0; H_2(gas) → H_2(solid solution, or MH_x)
Hydrogen incorporation process

Why such a impedance state?

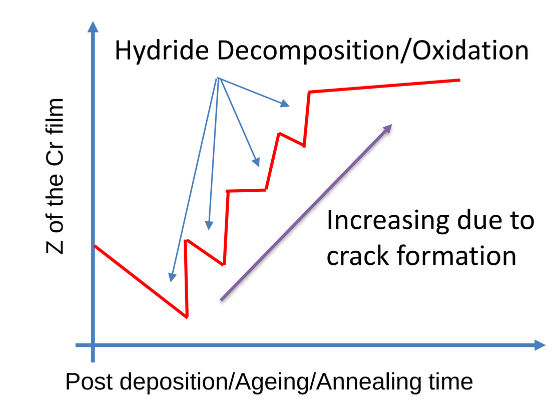
Postdeposition Steps:

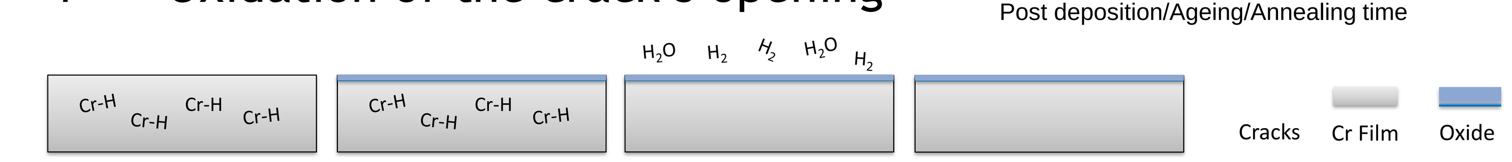
1st - Surface passivation

2nd - Cr-Hydrides decomposition

3rd - Crack formation.

4th - Oxidation of the crack's opening

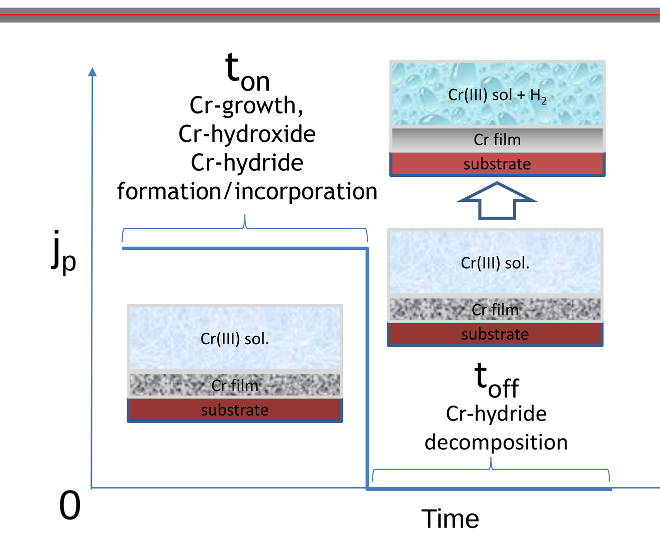


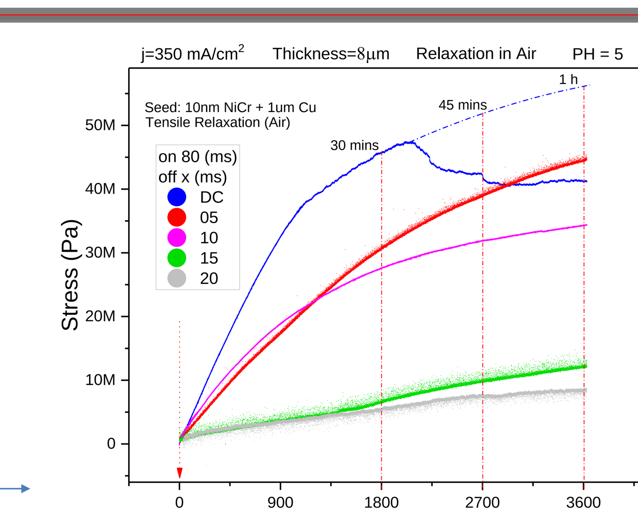


Solution

The root of crack is decomposition of hydride, what if we design process that generate less hydride at the first place?

With pulse deposition method, we introduce cycles of current on/off time where off-times allow decomposition of Cr-hydride formed during the "on" step of deposition.





Less tensile relaxation by increasing the t_{off} indirectly suggests that we had less compressive stress during the deposition

→ less Cr-hydride formation

→ Less crack formation

Conc.

1. Cr-deposition film using Cr^{3+} is favorable due to environmental aspects. This film forms cracks.
2. Hydrogen evolution during the deposition makes pH of interface high. This causes incorporation of Cr-H and $Cr(OH)_X$ in the film.
3. Second phase incorporation cause the film to undergo compressive stress during the deposition
4. Cracks form after the deposition during tensile relaxation when Cr-H phase start to decompose.
5. Preliminary data for pulse deposition has shown to be promising.

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