Low-temperature electroplating of zirconium: Ionic mixture methods

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1.0 Results

- Zr films up to 6 microns thick have been deposited on Mo substrates
- Contamination levels low
- Surface coverage is high
- Film quality higher & cost lower than other plating methods
2.0 Background & Motivation

• Zirconium is a refractory metal
  ▪ Useful for solar panels, electronics, furnaces, catalysis, etc.
  ▪ Reduction potential past splitting point of water
• Current methods of plating Zr; all have issues
  ▪ Co-rolling/co-extrusion
  ▪ Applied coatings (plasma spray, sputter coating)
  ▪ Molten salt electroplating
  ▪ Ionic liquid (IL) electroplating
• Ionic mixtures
  ▪ Deep eutectic solvents (DES)
  ▪ DES/IL mixtures
  ▪ Room temperature to 125 °C
3.0 System Set-Up

- Gamry’s Dr. Bob’s Cell
  - Non-aqueous silver references
  - Glassy carbon electrode
  - ¼” wide Mo foils
- Deep Eutectic Solvent
  - Ethaline (1:2 choline chloride: ethylene glycol)
  - Ar cleaned under vacuum at 150 °C for 24 hours
  - +0.25 M ZrF₄ and LiF
- Electroplating
  - DC and AC both trialed
  - Pulse plating most successful
    - 100 ms plate, 10 ms rest
  - Stirred
  - Ar bubble and blanket
- Cyclic voltammetry study
4.0 Cyclic Voltammetry

![Graph showing cyclic voltammetry results with ZrCl₂ Deposition between -0.6 to -0.5 V and Zr Deposition between -1.81 to -1.85 V (concurrent with IL range).]
5.0 SEM Imaging, DC Plating

- Metal deposition
  - Coverage > 99.9±0.4%
- Isolated salts
- Porosity 0.01-0.1%
- Grains 30-50 nm
6.0 Literature vs. DC Plating Results

veprints.unica.it/1081/1/PhD_Thesis_LauraMais.pdf
7.0 Film Morphology

- AC plating produces a smoother film than DC plating
- Addition of IL
  - Inhibits plating
  - Smooths roughness
  - Nanotextured Zr
8.0 How do we know we have a metallic coating?

RF, XPS & XRD Help Confirm Metallic Zr

- **XRF**
  - Zr signal occludes Mo signal
    - Mo diminishes & Zr stable
  - S from 0.1 – 2%
  - Intermittent Cl from 0.1 – 0.3%

- **XPS**
  - ZrO (surface oxide) seen

- **XRD**
  - Metallic signature for Zr & Mo
  - No bulk oxides
  - No bulk sulfides
  - Some LiCl and ZrCl
Time-Temperature Effects

![Graph showing Time-Temperature Effects](image)

Ionic Liquid Options

- Other cations
  - BMP short supply
  - Polarity & viscosity
  - BMP BTS (Best Prior)
  - DMA BTS (Polar, ↓µ)
  - MTA BTS (Non Polar, ↑µ)
  - TES BTS (Non Polar, ↓µ)
- Sulfur contamination
  - 2, 31, 12, 13%
  - S-Mo interference
- BMP BTS most reliable IL
  - Can be difficult to acquire
  - MTA BTS & TES BTS possible alternates
  - Smooth film deposition

How do we know we have a metallic coating?
 Ionic Liquid Options

**BMP BTS** = 1-Butyl-3-Methyl-Pyrrolidium Bis (Trifluoromethylsulfonyl)imide

**DMA BTS** = Diethylmethyl (2-Methoxyethyl)Ammonium Bis (Trifluoromethylsulfonyl)imide

**MTA BTS** = Methyl-Triocylammonium Bis (Trifluoromethylsulfonyl)imide

**TES BTS** = Triethylsulfonium Bis (Trifluoromethylsulfonyl)imide
9.0 Conclusion

- Demonstrated conformal Zr platings at low temperatures
- Deposition of metallic Zr film from DES
  - DC plating: 100s of nm thick
  - AC plating: 6 microns, smoother, cleaner
- ILs can be used as a growth inhibitor
- ZrF$_4$ is more soluble in DES than IL
  - Greatly improves deposition
- Deposition is diffusion limited
  - Pulse plating improves deposition
- Moving on to other metals of interest