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|            | Low-temperature<br>electroplating of<br>zirconium: lonic mixture<br>methods  |
|            | March 2022   |
|            | Christina Arendt<br>Lance Hubbard  |
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|            | U.S. DEPARTMENT OF<br><b>ENERGY</b> Prepared for the U.S. Department of Energy<br>under Contract DE-AC05-76RL01830 |

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# Low-temperature electroplating of zirconium: lonic mixture methods

March 2022

Christina Arendt Lance Hubbard

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory Richland, Washington 99354

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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 ZrF<sub>4</sub> 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



# 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



Ionic Mixture & AC



Ionic Mixture & AC



IL & AC Plating



- AC plating produces a smoother film than DC plating
- Addition of IL
  - Inhibits plating
  - Smooths roughness

8

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 CI 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**



#### **Ionic Liquid Options**

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



#### **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-Trioctylammonium 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<sub>4</sub> 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

# Pacific Northwest National Laboratory

902 Battelle Boulevard P.O. Box 999 Richland, WA 99354

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