Electron Microscopy Studies of Niobium Thin Films on Copper

Roy Crooks¹, Greg Thompson², Robb Morris², Michelle Adams-Hughes³, Daudi Waryoba³, and Peter Kalu³

¹ Black Laboratories, L.L.C., Newport News, Virginia

² The University of Alabama, Department of Metallurgical & Materials Engineering, Tuscaloosa, Alabama;

³ National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida

Support for R. Crooks under DOE SBIR Grant No. DE-FG02-07ER84746

TFSRF 2008
Approach:

Since bulk shows better srf behavior, study differences between thin film and bulk.

Focus on two topics:

1. **grain boundary differences** – Nb thin film grains are copied from substrate through a K-S relationship

2. **poor diffraction contrast** in thin films due to either strain or nanocrystalline structure

Methods/resolution:

- EBSD: SEM/200 nm resolution; FE SEM/20 nm resolution;
- TEM: FE TEM/0.2 nm resolution
backscattered electron imaging (BEI)

Annealed and electropolished copper

JLab ECR Nb film on Copper
BCP bulk and film EBSD patterns

BCP Bulk
Romanenko
1.5 GHz cavity
Hot Spot

Alameda CED film thin

HF etch, 30s

BCP etch, 10 s
**Significant Noise Reduction**

**OIM inverse pole figure map of niobium sheet.**

**JLab ECR film**
ECR Sample, 30 nm FE SEM

IPF Map

IQ Map

Misorientation increases > 500x faster

BCP Bulk (Romanenko, 1.5 GHz cavity) Hot Spot
EBSD from etched Nb/Cu

*Etched down to Cu*

Cu

OIM map of twin grain boundaries

(60°/<111> in copper sheet.)

What happens when you template across frequently occurring special boundaries?
Templating relationship:

Kurdjumov-Sachs fcc to bcc heteroepitaxy

(Calculations with OIM Software)

fcc

K-S

bcc

(111)[1-10] 0, 54.7, 45

(011)[1-11] 54.7, 45, 0

42.8° / [-5 -27 5] (in either reference frame)

Nb atomic diameter is ~12% > Cu
Twin Variant

$60^\circ / [-111]$

$\Sigma 3$

fcc

(111)[1-10]

0, 54.7, 45

(1-1 5)[1 -4 -1]

299, 15.7, 135

K-S

$42.8^\circ / [-5 -27 5]$

$39.3^\circ / [-14 -18 -20]$

bcc

(011)[1-11]

54.7, 45, 0

(4 -2 3)[-3 -21 -10]

329, 55 116
### Misorientations due to twin variants, after K-S

<table>
<thead>
<tr>
<th>twin axis</th>
<th>angle</th>
<th>u</th>
<th>v</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>57.3</td>
<td>21</td>
<td>-7</td>
<td>18</td>
</tr>
<tr>
<td>-111</td>
<td>39.3</td>
<td>-13</td>
<td>-18</td>
<td>20</td>
</tr>
<tr>
<td>1-11</td>
<td>50.7</td>
<td>-5</td>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>11-1</td>
<td>51.7</td>
<td>-16</td>
<td>-25</td>
<td>1</td>
</tr>
<tr>
<td>-1-11</td>
<td>38.9</td>
<td>-11</td>
<td>11</td>
<td>-10</td>
</tr>
<tr>
<td>1-1-1</td>
<td>40.2</td>
<td>-22</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>-1-1-1</td>
<td>49.9</td>
<td>19</td>
<td>6</td>
<td>-23</td>
</tr>
</tbody>
</table>
Grain Boundary Character Distribution (Misorientation Distribution Function)

- Types of grain boundaries, using angle/axis pair description
- Comparison to other niobium forms: sheet, tube, re-melted
- Boundaries in recrystallized or re-melted similar
- Alien boundaries in thin film
Grain Boundary Character Distribution: Niobium e-beam melted
DESY Niobium Tube (through-thickness)
ATI Wah Chang Niobium Sheet (through-thickness)
JLab ECR Nb thin film on Cu

Diagram showing the orientation of Nb thin film on Cu at various angles.
Some Films show no EBSD patterns

Heavily strained?

Nanocrystalline?

Covered with amorphous (slushy*) oxide?

Separation of films from Cu

concentrated nitric acid

film placed on grid and ion milled

examined in TEM at 200 kV

*Per comments by Michael Pellin
SEM image of underside of JLab ECR thin film after nitric acid digestion of Cu substrate. Nanocrystalline film, a patch of a thin, copper-like grain microstructure, EDS (energy dispersive spectroscopy) spectra showed both to be niobium.

Nitric Acid

Cu

Nb

Residual Stresses

1 mm
TEM of ion milled film JLab ECR film; nanocrystalline grain size of about 50 nm. a) bright field; b) SAD showing diffraction ring pattern which indexes as niobium.

Conclusion:
- Nano-grain Nb surface layer, grain size <50um
- Epitaxial Nb layer, grain size = ~50um
- Copper substrate, grain size = ~50um
TEM of ion milled film from a JLab ECR Single Crystal specimen; nanocrystalline grain size of about 70 nm. a) bright field; b) SAD showing diffraction ring pattern, no strong alignment
Nb film on Cu
FIB FEI SEM Secondary electron image

EBSD Patterns

Michelle Adams-Hughes
FSU/NHMFL
Nb film on Cu
FIB/FE SEM OIM
20 nm spatial resolution

Low data quality
(noise reduction used)

High data quality

Michelle Adams-Hughes
FSU/NHMFL
Bright field TEM of Nb film on Cu

Pt cap

Pt protective cap for FIB milling

Nb

Cu

100 nm

FIB cross-sectional TEM foil prepared

Nb layer measured to be ~100nm thick

Gregory Thompson & Robb Morris
University of Alabama

(FIB TEM Sample Method of IC)
Nb on Cu substrate
Bright field TEM images
Nb on Cu substrate
Bright field TEM images
Nb on Cu substrate
Electron Diffraction TEM images

Electron diffraction of Nb layer
Wide spots/rings indicate small grain size

Electron diffraction of Nb and Cu
Strong tight spots indicate diffraction of single Cu grain

Electron diffraction of Cu layer
Conclusions

GBCD of films shows “alien” boundaries generated by templating across twins. These niobium boundaries should be higher energy than “native” boundaries, and more likely to contain impurities.

Better results with single crystal substrate and epitaxy?

Weak EBSD patterns generated from large grain thin films with severe strain and from nanocrystalline films.

With lattice misfit (~12%) and thermal expansion differences (Nb 7.3 x 10^-6 K^-1 and Cu 16.5 x 10^-6 K^-1) can this be avoided?

It would be worthwhile to look at strain levels in FIB sectioned thin films as a function of distance from Cu to quantify the “decay of defect density” (L. Phillips).